Thermomechanical Properties of Elastomeric-Filled Composites

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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27th of July, 2009
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Publications

Refereed conference papers


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<td>EPDM</td>
<td>Ethylene-propylene-diene monomer</td>
</tr>
<tr>
<td>EMA</td>
<td>poly(ethylene-co-methyl acrylate)</td>
</tr>
<tr>
<td>TPE</td>
<td>Thermoplastic elastomer</td>
</tr>
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<td>TPU</td>
<td>Thermoplastic polyurethane</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental scanning electron microscope</td>
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<tr>
<td>TG</td>
<td>Thermogravimetry</td>
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<td>TGA</td>
<td>Thermogravimetric analyser</td>
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<tr>
<td>( T_{0.5} )</td>
<td>Decomposition temperature, temperature at which 50 ( %.w/w ) mass loss occurs</td>
</tr>
</tbody>
</table>
Regarding modulated force thermomechanometry (mf-TM):

- $E^*$: Complex modulus
- $E'$: Storage, elastic modulus
- $E''$: Loss, viscoelastic modulus
- $\tan \delta$: Loss tangent, damping

Regarding Williams-Landel-Ferry model (WLF model):

- $C_1$ and $C_2$: Material dependent numerical constants relating to free volume expansion
- $a_T$: Time temperature superposition shift factor

Regarding Vogel Fulcher Tammann Hesse equation (VFTH model):

- $\tau(T)$: Relaxation time as a function of temperature
- $\tau_0$: Pre-exponential factor
- $B$ and $T_0$: Material dependent numerical constants

Regarding Expanded V’ant Hoff equation:

- $A$ and $C$: Material dependent numerical constants
- $T_0$: Reference temperature

Regarding Burgers / Maxwell-Voigt / 4 Element model:

- $\varepsilon$: Strain
- $\sigma$: Stress
- $E_1$: Elastic modulus of resistance to elastic deformation
- $\tau$: Retardation time equal to $\eta_2/E_2$
- $E_2$ and $\eta_2$: Elastic and viscous contributions to resistance to viscoelastic deformation
- $t$: Time
- $\eta_3$: Viscosity
List of symbols and abbreviations

Regarding Kohlrausch-Williams-Watts function (KWW):

- $\phi(t)$: Physical relaxation as a function of time
- $A$: Pre-exponential factor
- $t$: Time
- $\tau$: Characteristic relaxation time
- $\beta$: Stretched exponential factor

Regarding Debye relaxation model (D):

- $D$: Debye relaxation model
- $E^*$: Complex modulus (written as $\varepsilon^*$ if referring to the complex dielectric constant)
- $E_0$: Zero, Terminal modulus (written as $\varepsilon_0$ if referring to the dielectric constant value at low frequencies)
- $E_\infty$: Infinite, Plateau modulus (written as $\varepsilon_\infty$ if referring to the dielectric constant value at high frequencies)
- $\omega$: Angular frequency (where frequency is $\omega = 2\pi f$)
- $i$: $\sqrt{-1}$
- $\tau$: Relaxation time
List of symbols and abbreviations

**Regarding Cole-Cole relaxation model (CC):**

CC     Cole-Cole relaxation model

E*     Complex modulus (written as \( \varepsilon^* \) if referring to the complex dielectric constant)

E_0     Zero, Terminal modulus (written as \( \varepsilon_0 \) if referring to the dielectric constant value at low frequencies)

E_\infty     Infinite, Plateau modulus (written as \( \varepsilon_\infty \) if referring to the dielectric constant value at high frequencies)

\( \omega \)     Angular frequency (where frequency is \( \omega = 2\pi f \))

\( i \)     \( \sqrt{-1} \)

\( \tau \)     Relaxation time

\( \alpha \)     Shape parameter relating to symmetry of analysis data

**Regarding Cole-Davidson relaxation model (CD):**

CD     Cole-Davidson relaxation model

E*     Complex modulus (written as \( \varepsilon^* \) if referring to the complex dielectric constant)

E_0     Zero, Terminal modulus (written as \( \varepsilon_0 \) if referring to the dielectric constant value at low frequencies)

E_\infty     Infinite, Plateau modulus (written as \( \varepsilon_\infty \) if referring to the dielectric constant value at high frequencies)

\( \omega \)     Angular frequency (where frequency is \( \omega = 2\pi f \))

\( i \)     \( \sqrt{-1} \)

\( \tau \)     Relaxation time

\( \beta \)     Shape parameter relating to skewness of analysis data
### Regarding Havriliak-Negami relaxation model (HN):

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>HN</td>
<td>Havriliak-Negami relaxation model</td>
</tr>
<tr>
<td>$E^*$</td>
<td>Complex modulus (written as $\varepsilon^*$ if referring to the complex dielectric constant)</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Zero, Terminal modulus (written as $\varepsilon_0$ if referring to the dielectric constant value at low frequencies)</td>
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<tr>
<td>$E_\infty$</td>
<td>Infinite, Plateau modulus (written as $\varepsilon_\infty$ if referring to the dielectric constant value at high frequencies)</td>
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<tr>
<td>$\omega$</td>
<td>Angular frequency (where frequency is $\omega = 2\pi f$)</td>
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<tr>
<td>$i$</td>
<td>$\sqrt{-1}$</td>
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<tr>
<td>$\tau$</td>
<td>Relaxation time</td>
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<tr>
<td>$\alpha$</td>
<td>Shape parameter relating to symmetry of analysis data</td>
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<tr>
<td>$\beta$</td>
<td>Shape parameter relating to skewness of analysis data</td>
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### Regarding mastercurves:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$a_T$</td>
<td>Frequency-based shift factors</td>
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<tr>
<td>$a_V$</td>
<td>Modulus-based shift factors</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Relaxation time</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>Relaxation time at reference temperature</td>
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Abstract

The aim of this research project was to modify the matrix polymer’s relaxation processes by the inclusion of filler and to characterise the interfacial interaction in between matrix polymer and filler. Three types of elastomers were selected for this research: a purely amorphous elastomer (poly(ethylene-co-propylene) diene monomer) (EPDM), a semi-crystalline elastomer (poly(ethylene-co-methyl acrylate)) (EMA) and a thermoplastic elastomer (thermoplastic polyurethane) (TPU). These elastomers possessed reinforcement via chemical crosslinking, crystalline molecular segments and hydrogen bonding. Fillers in the form of aluminas (with EPDM) and fumed silicas (with EMAs and TPUs) were added to the elastomers to form composites.

Materials were prepared via a solvent casting method. Elastomers were dissolved in an appropriate solvent and fillers were added. A crosslinking agent was also added to the dissolved EPDM. Fillers were dispersed with ultrasonication after which dissolved elastomer-filler compositions were dried then pressed into films. EPDM composites underwent thermally-induced crosslinking.

Characterizing techniques including environmental scanning electron microscopy (ESEM), thermogravimetry and analytical techniques including dynamic force thermomechanometry (df-TM), static force thermomechanometry (sf-TM) and modulated force thermomechanometry (mf-TM) were used to examine the interaction between filler and elastomer. Analysis was performed on data from sf-TM (4-element model for creep analysis data, Kohlrausch-Williams-Watts model for recovery analysis data) and mf-TM (Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami relaxation equations). Mastercurves were created from multi-frequency mf-TM data. Sinusoidal frequency mode was determined to be the best method for obtaining multi-frequency data and the HN-based mastercurve method was the best method for constructing mastercurves. The accuracy of three different shift factor models (Williams-Landel-Ferry, Vogel-Fulcher-Tammann-Hesse and arctan based V’ant model) was compared. Super-mastercurves were constructed from mastercurves.

ESEM micrographs of EPDM materials revealed that greater compatibility between elastomer and filler resulted in better dispersion of filler. All elastomers were observed to have thermal reinforcement provided by the presence of fillers. Greater compatibility between elastomer and filler resulted in increased thermal stability, as seen in EPDM composites. Thermal reinforcement was observed to increase with increasing silica volume fraction with the
Abstract

temperature of 50 % w/w loss increasing by approximately 20 °C for the EMA-based materials and by 70 °C for the TPU-based materials at the highest filler volume fraction.

Stress-strain analysis data indicated that composites were tougher with greater compatibility between filler and elastomer matrix. The Young’s moduli and strength of all elastomer based systems were observed to increase, but toughness decreased with increasing filler volume fraction.

Creep and recovery analysis showed that greater compatibility between filler and elastomer, and increased filler volume fraction resulted in more resistance to elastic and viscoelastic deformation, and viscous flow. Modelling of creep analysis data revealed that the presence of any filler resulted in increased resistance to instantaneous and time dependant uncoiling and extension of molecules. Increasing filler volume fraction resulted in greater resistance to instantaneous and time dependant uncoiling of molecules, and irreversible flow. Materials analysed with a reduced force had greater resistance to all modes of deformation as indicated by their parameter values being greater than those obtained at a higher force. Modelling of recovery analysis data revealed greater compatibility between filler and elastomer resulted in less resistance to recovery and less constraints to the operation of relaxation modes. Resistance to recovery decreased with increasing filler volume fraction. Relaxation times decreased with increasing filler volume fraction. Parameter values obtained from analyses conducted with reduced analysis force indicated that a lower analysis force resulted in less resistance to viscoelastic recovery, longer relaxation times and fewer constraints to the operation of relaxation modes.

Modulated force thermomechanometry characterised the elasticity and damping properties of materials. The storage modulus was observed to increase with increasing filler volume fraction; however increased compatibility between filler and elastomer resulted in reduced E’ values. The temperature of failure increased with compatibility and increasing filler volume fraction. The loss modulus was observed to increase with increasing filler volume fraction; however increased compatibility between filler and elastomer resulted in lower loss of energy. The tan δ values decreased with the addition of any filler and increasing filler volume fraction; however increased compatibility between filler and elastomer reduced the tan δ by a lesser amount.

Mastercurves were constructed from the isothermal multi-frequency mf-TM data for the EMA and TPU series of materials. They possessed frequency ranges of approximately $10^9 – 10^{17}$ Hz. The storage modulus mastercurve data values were observed to increase with increasing filler volume fraction for all materials. The storage modulus values plateaued at
10 % v/v filler. The loss modulus mastercurves of both EMA and TPU-based materials possessed a peak in the loss modulus data corresponding to \( T_g \). The materials plateaued at approximately the same modulus values at the highest transposed frequencies. The modulus data obtained at the highest analysis frequencies exhibited constructive interference with the effects most pronounced in the highest filled composites. The WLF model most accurately modelled shift factor values with respect to temperature. The Wicket error function was used to determine the accuracy of modelling with the relaxation equations. The HN equation modelled the mastercurve data most accurately. The zero and infinite modulus HN parameter values increased with increasing silica volume fraction. The infinite modulus values plateaued at 10 % v/v filler at the highest transposed frequencies. The relaxation time parameter values increased with increasing filler volume fraction while the \( \alpha \) and \( \beta \) shape parameters were observed to overall decrease.

Mastercurves could not be constructed for EPDM-based materials as they could not be analysed at sufficiently high frequencies, so single frequency mf-TM data was used with the HN relaxation equation. The addition of compatibilized filler resulted in an increase in \( E_\infty \) modulus values while the uncompatabilized filler caused a reduction. The \( \alpha \) shape parameter was observed to decrease with the addition of all fillers with the untreated filler resulting in the greatest reduction. The \( \beta \) shape parameter was observed to slightly decrease with the addition of the compatibilized fillers but increase with the addition of the uncompatabilized filler. The calculated relaxation times were observed to decrease with decreasing compatibility between filler and elastomer.
Chapter 1 Introduction

Overview

Elastomers are a flexible class of materials; however they usually are observed to permanently deform under applied stresses with little inherent resistance. Therefore some form of reinforcement is required to bestow a level of reversibility to the elastomer. Reinforcement can be achieved by altering the chemical molecular composition of the elastomer (chemical crosslinking) or by the addition another material (physical crosslinking). Chemical crosslinking can be achieved by forming chemical bonds between segments of the elastomer. Physical crosslinking can be achieved by the addition of inorganic particles (referred to as filler) or other materials such as polymers.

Three types of elastomers were selected for this research: a purely amorphous elastomer (poly(ethylene-co-propylene) diene monomer) (EPDM), a semi crystalline elastomer (poly(ethylene-co-methyl acrylate)) and thermoplastic elastomers (thermoplastic polyurethane). These elastomers were used in a number of elastomer-filler compositions. Chemical crosslinking (radical initiated via dicumyl peroxide) and a filler (alumina) were used to synthesise the EPDM materials. The EMA materials possessed inherent reinforcement provided by crystalline segments of polyethylene and further reinforcement provided by silica nanoparticles. The TPU materials possessed inherent reinforcement provided by hydrogen bonding mainly between hard phase separated urethane segments and further reinforcement provided by silica nanoparticles.

Thermomechanical analysis has been typically used to analyse the materials response to an applied force; however thermomechanometry is able to characterise other material properties including material transitions and polymer-filler interactions. Three forms of thermomechanometry: dynamic-force, static-force and modulated-force were employed to characterise contributions of various components of the materials (fillers, chemical crosslinks, crystallinity, H-bonding, molecular components) to material response and transitions.

Analysis data obtained from thermomechanometry can be modelled with various equations. The equations used for static force thermomechanometry were the 4-element model (creep analysis) and KWW (recovery analysis). These models each give parameter values which can be used to describe various material properties. The models used for modelling modulated-force thermomechanical analysis data investigated in this research were based upon the Debye relaxation model[1]. These models; The Cole-Cole, Cole-Davidson and Havriliak-
Negami models are all still widely used in research; however they are almost always used with dielectric analysis data[2-6]. It has been stated that relaxation models classically used for dielectric analysis can be used for thermomechanometry data[7]. This research will investigate which relaxation equations are best suited for modelling the data.

**Aim**

The aim is to modify the matrix polymer’s relaxation processes by the inclusion of filler, to characterise the interfacial interaction in between matrix polymer and filler and create mastercurves based upon mechanical data and relaxation times.

**Objectives**

- To prepare graded seal compounds comprising of aluminium oxide coated in a styrene-based polymer in an EPDM polymeric matrix
- To prepare polar polyethylene-silica nanocomposites using ultrasonic dispersion
- To prepare thermoplastic polyurethane-silica nanocomposites using ultrasonic dispersion
- Characterise dynamic, static and modulated-force thermomechanical properties of all materials
- To model the static analysis data of all materials
- To construct time temperature superposition mastercurves based on modulated-force thermomechanometry data
- To compare mastercurves created from sinusoidal and synthetic frequency modulated-force thermomechanometry data
- To compare the accuracy of various shift-factor models in modelling shift factor data
- To model modulated-force relaxation models and apply them to the formation of mastercurves
- To construct mastercurves with a modulated-force relaxation model
- To construct super-mastercurves from mastercurve data
Questions

How can the coated filler particles be dispersed adequately in the desired polymeric matrix?

What effects will the graded seal system have on the mechanical properties of EPDM?

Is the graded seal system an effective method of inserting new fillers into elastomers?

Which relaxation equation is best used to model modulated-force thermomechanical data?

Can molecular relaxation time models be used to construct mastercurves?

Structure of thesis

The following research was conducted to determine the effect of filler on various polymeric matrices. The properties that were investigated via mechanical analysis including dynamic-force, static-force and modulated-force thermomechanometry.

The research will be presented in eight chapters. Chapter 1 presents an introduction to research that has been conducted. The research aim and objects, and the outline of this thesis have been summarised.

Chapter 2 presents a literature review of elastomers and their various properties, fillers, thermomechanical analysis and data analysis models.

Chapter 3 presents a description of the materials and experimental techniques employed in this research. The methodologies used for the synthesis of materials, material analysis and data analysis are described.

Chapter 4 investigates the effect of alumina with varying surface chemistry on EPDM-alumina composites through thermomechanical analysis, and subsequent analysis of thermomechanical data demonstrating how single frequency mf-TM data can be used to calculate relaxation times.

Chapter 5 presents research conducted into the effect of silica nanoparticles and differing methyl acrylate weight fractions on the thermomechanical properties of EMA elastomers. Four types of modulated-force relaxation equations were used to model mastercurve data and the results were compared. Two mastercurve construction techniques were compared and subsequently super-mastercurves were created.

Chapter 6 investigates the effect of silica nanoparticles and differing molecular components on the thermomechanical properties of TPU elastomers. Mastercurves were created via the HN equation method and three shift factor models were compared. The HN parameters used
Chapter 1 Introduction

to create the mastercurves and those calculated from a subsequent modelling of transposed mastercurve data with the HN equation were compared. Super-mastercurves were created.

Chapter 7 compares the analysis results of the three classes of elasmoters obtained under similar instrumental settings.

Chapter 8 provides the overall conclusions and suggestions for further research.
Chapter 2 Literature Review:

Introduction

The focus of this thesis is on the thermomechanical properties of elastomeric-based materials. This chapter presents a broad review of concepts relating to elastomer technology, thermomechanical analysis and data analysis. The review will discuss the types of elastomer and fillers used, various instrumental techniques applied and equations used for modelling of instrumental output data.

Properties governing physical characteristics of polymers

Polymers are a class of material comprised of long chain molecules. They are complex systems with a range of inherent properties, which govern their physical properties. The chains lengths in segments of a polymer will relate to its molecular weight and monomer composition. Aspect ratio, $r$ of polymers is defined as the ratio of length, $L$ of the symmetry axis to the diameter, $d$ of the circular transverse cross-section of the polymer molecule. This relation can be represented by the equation $r = L / d$.

Conformation is the different spatial arrangements of molecules that are altered by rotation about single bonds and do not involve any bonds breaking to change them. There is a myriad of conformations available for polymers; however there is an associated energy with each. Usually a polymer will take on the conformation of least energy. However not all conformations are equally probable. This is due to intramolecular properties hindering molecular rotation. Such properties include hydrogen bonding (H-bonding), polar interactions and steric hindrance. H-bonding is an electrostatic bond between a positive-charged hydrogen atom and a negatively charged atom (usually oxygen, nitrogen or fluorine atoms). Steric hindrance occurs when bulky, side groups are present. Rotations are prevented by the spatial exclusion exerted between these groups.

A single polymer chain will adopt a random coil due to intramolecular properties. Random coils are segments of polymers that have flexible structure and they can easily be interspersed with other polymeric segments. The actual length of the polymer chain is shorter than its potential maximum length because of this random coil. The many available random coil conformations result in polymers being in a state of high entropy. However a polymer can be made up of chains of various segments including amorphous and entangled chains, crystallized polymer, intermolecular tie molecules, dangling end cilia and loops. Crystallized
polymer is a rigid section of polymer comprised of an organised regularly repeating three dimensional array of polymer segments. A polymer must be able to perform suitable rotations around bonds to attain a conformation of translational symmetry to undergo crystallization. Intermolecular tie molecules are a portion of molecules that bridge between two sections of polymer.

**Free volume**

The free volume\[12\] of a polymer and polymer composites is the difference between the actual specific volume (the ratio of total volume to unit mass) of the material and the specific volume of the occupied volume. The occupied volume is thought of as being a constant specific volume always occupied by the segments of a polymer i.e. the specific volume of a polymer can never be lower than its occupied volume\[13\]. However research has shown that the occupied volume can change with temperature\[14\]. Segmental motion in the polymer chains cannot occur at very low (sub-$T_g$) temperatures. The $T_g$ is the glass transition temperature. The free volume is constant and the specific volume is close or equal to that of the occupied volume at sub-$T_g$ temperatures. As the temperature increases small, side-chain groups gain energy and begin to rotate. As the temperature further increases larger parts of the molecule rotate. At temperatures equal to and greater than $T_g$, large chain segments of the amorphous component of the polymer can rotate resulting an increase in the free volume. Figure 1 represents the changes to specific, occupied and free volume with increasing temperature.

![Figure 1 Free volume changes with increasing temperature](image-url)


**Elastomers**

Elastomers are defined as polymers that behave like viscous fluids above their $T_g$ and sometimes flow under their own weight[15], and they must be lightly crosslinked to gain reversibility (recovery to original size dimension) under applied stress[16]. These polymers consist mainly of carbon and hydrogen atoms. Elastomers are able to undergo significant and rapid segmental motion since they are amorphous (and can have properties similar to that of a highly viscous liquid) at temperatures above their $T_g$. Therefore crosslinking (referred to as vulcanisation for rubbers) is sometimes employed to allow this motion to be reversible and not result in permanent strain deformation[17].

Elastomers are commonly referred to as rubbers, since the first elastomer introduced to Europe by Charles Marie de la Condamine was termed natural rubber[18]. Further observations were made by Joseph Priestley[19] who discovered that it could be used to erase pencil. Rubbers can be divided into two distinct groups; those that require sulphur vulcanisation, and those that cannot be vulcanised via sulphur compounds because of their chemical composition (due to saturation) and require other forms (e.g. a peroxide) of vulcanising agents[20]. Rubbers crosslinked via sulphur compounds include natural rubber, butyl rubber (a copolymer of isobutylene and isoprene), polybutadiene, styrene-butadiene (copolymer of styrene and butadiene), nitrile rubber, hydrogenated nitrile rubbers, chloroprene rubber and halogenated butyl rubbers.

Rubbers that cannot be cured by sulfur compounds include ethylene propylene rubber (a copolymer of ethylene and propylene), epichlorohydrin rubber, silicone rubber, fluoroelastomers, polyacrylic rubber, polyether block amides and fluorosilicone rubber[20].

The aforementioned examples are elastomers that require some form of crosslinking for reversible strain response. However there exist elastomers that are rigid enough initially for some applications and do not require crosslinking due to the presence regular crystallinity, physical crosslinks and internal bonding. Such elastomers can be classified as semi-crystalline elastomer and thermoplastic elastomers. Details of these elastomers will be expanded on in following sections.

**Poly(ethylene-co-propylene) diene monomer**

Poly(ethylene-co-propylene) diene monomer) (EPDM) is a member of the diene elastomers group (including ethylidene norbornene[21], dicyclopentadiene[22] and vinyl norbornene[23]). The varying ethylene, propylene and diene compositions and concentrations in EPDM elastomers are what will determine their properties.
EPDM has been employed for many uses such as seals[24], hosing[25], tubing[26] and electrical insulation[27]. It possesses many advantages over other elastomers including colour stability[28], resistance to ozone and oxidation[29], ability to absorb large volume fractions of oil and filler without creating instability[30] and low temperature flexibility[31]. These properties are largely attributed to their hydrocarbon nature and almost entirely saturated backbone[30]. Figure 2 represents a typical structure of an EPDM unit.

![Figure 2 Structure of EPDM with 5-ethylidenenorbornene side group](image)

Much research with EPDM has been dedicated towards performance enhancement, in particular reinforcement. Reinforcement of EPDM has been achieved by incorporation of filler as shown in the research by Ginic-Markovic et al[32]. Dynamic mechanical analysis was used to investigate the effect of carbon black loading in the EPDM over a wide range of time, temperature, strain, and frequency. The tensile stress relaxation results of the unfilled EPDM showed time-dependent but strain-invariant behaviour, whereas the filled system shows both strain and time dependence. The relaxation time spectrum of the filled system reveals nonlinear viscoelastic behaviour. They stated that the networks of carbon black formed at such a high loading contribute significantly to the relaxation process. Sohn et al researched the effect of silicon carbide particles (SiCps) at various volume fractions (0, 10, 20, 30, and 40 %.v/v), and various particle sizes (60, 36, and 6 µm), and other fillers (Al and Cu) on EPDM via dynamic mechanical analysis[33]. They observed that the tan δ values of the composite with 40 %.v/v SiCps were greater than the other EPDM-SiCps composites up to 70°C. The peak tan δ value of the composite with 20 %.v/v of Cu particles was lower than that of the composites with other particles (Al or SiCps) at the same volume fraction and attributed to more EPDM segments were adhering to the rough Cu particle surfaces. They noted that the amount of polymer rubber segments entrapped among the particles increased with the increase of the particle volume fraction resulting in a reduction in the mobility of the EPDM chains in the transition area from glassy to rubbery state.
Reinforcement via crosslinking was researched by Abd-El-Messieh et al in their work on the dielectric relaxation and mechanical investigation of EPDM with dicumyl peroxide and vulcanizing co-agents[34]. These results indicated that the addition of zinc chloride to EPDM cured with peroxide greatly improved the mechanical properties; however it had little effect on thermal stability. The ammonium iodide had little effect on either mechanical or thermal properties. This was of note as both zinc chloride and ammonium iodide are used as vulcanizing co-agents with conventional sulfur vulcanizing systems. Nicolas et al studied metallocene EPDM terpolymers with high diene and propylene content crosslinked with dicumyl peroxide and β-radiation[35]. They noted that the very high tertiary carbon content of EPDM resulted in chain scission reactions reducing significantly the efficiency of the crosslinking process either by dicumyl peroxide or β-radiation. However the presence of unsaturated carbon-carbon bonds favoured a fast curing rate compensating in part the consequences of the high scission levels and allowing the EPDM to reach the gelation point at reasonable levels of radiation doses or peroxide concentration. The crosslink densities and phase morphologies in thermoplastic vulcanizates including EPDM were researched by Ellul et al[36]. The degree of EPDM crosslinking during dynamic vulcanization of a PP-EPDM thermoplastic vulcanize (TPV) was modified by varying the weight fraction of the phenolic curative content. The rise in TPV viscosity and the reduction in swelling indicated an increase in EPDM crosslink density with increasing curative content. SEM morphologies of cryo-faced and ruthenium-stained TPVs with varying curative contents were analysed to determine the effects of cure on EPDM domain sizes and PP ligament thickness. A narrowing of the EPDM domain size distribution was observed with increasing EPDM crosslink density and the PP ligament number-average thickness was raised slightly.

Jain et al. investigated the effect of dynamic crosslinking on impact strength of polypropylene (PP) blended into EPDM[37]. The deformation and fracture behaviour of blends of isotactic PP-EPDM was compared with those of uncrosslinked blends of PP-EPDM with 10-40 %.wt of EPDM. Before crosslinking the impact strength moderately increased from 25 to 190 J/m with increasing EPDM weight fraction. After crosslinking there was a greater increase in the impact strength values from 25 to 86 J/m. The increase in impact strength as the EPDM content increased was attributed to the fact that rubber domains act as stress concentration sites for dissipation of shock or impact energies by controlling and promoting matrix deformation. The addition of rubber leads to relaxation of the stress concentration due to the release of constraints on strain by Poisson’s contraction between voids at the EPDM domains–polyolefin interfaces. As a result of this the nucleation of cracks at the sites of matrix deformation were suppressed and toughness was improved.
The effectiveness of EPDM as an adhesive has been studied by Ruch et al[38]. They observed the nonlinear relationship between peel strength and the number of bonds and attributed it to the very slow and unexpected diffusion of the elastomer chains due to the high degree of entanglements combined with chain branching introduced during the polymerization process. When crosslinking was achieved via a high temperature reaction (i.e. peroxide crosslinking) it was not possible to control interdiffusion and co-crosslinking separately; both phenomena occur simultaneously and were competitive.

**Poly(ethylene-co-methyl acrylate)**

Poly(ethylene-co-methyl acrylate) (EMA) is classified as a semi-crystalline elastomer. Semi-crystalline elastomers consist of crystalline and amorphous regions. Amorphous regions become trapped between the crystals as the crystals grow, hence the mobility of the amorphous region becomes hindered. With increasing amorphous content, semi-crystalline elastomers will become increasingly soft.

EMA is composed of sequences of ethylene (E) segments that can crystallise, and methyl acrylate (MA) pendant groups. Not only does the methyl acrylate reduce crystallinity in the co-polymer, it provides a polar functionality and bonding site. Figure 3 shows the composition of EMA with the two monomer units that comprise the random co-polymer.

![Figure 3 Structure of EMA comprised of two monomers where x and y represent the number of monomer units of polyethylene and methyl acrylate respectively](image)

The use of EMA possesses advantages over other polymers (e.g. poly(ethylene-co-vinyl acetate) and poly(vinyl chloride)) employed in similar applications such as superior melting temperatures and improved thermal stability. EMAs are used extensively in the production of disposable gloves, hygiene and medical products, adhesive applications and co-extrusion with other polyethylenes and polypropylenes to provide an adhesive layer. Research conducted by Generoso et al investigated the use of EMA for membranes employed as rate-controlling barriers for drug delivery systems[39]. They found that increasing the MA content in the copolymer significantly increased the elongation, decreased the tensile strength and modulus of elasticity, and increased the degree of swelling. Other recent research by Kanis et al
investigated the thermal, morphological and mechanical properties of EMA-poly(caprolactone-triol) (PCL-T) films[40]. The differential scanning calorimeter (DSC) thermograms showed that when PCL-T was added there were no changes to the melting and glass transition temperatures and with the addition of 40 \%.wt of PCL-T the film tensile strength decreased compared with pure EMA. Scanning electron micrographs showed a PCL-T domain in the EMA matrix indicating immiscibility of blend.

Cerezo, Preston and Shanks have investigated the morphology and mechanical properties of polypropylene and EMA blends[41]. The blend used for this research was a poly(ethylene-co-methyl acrylate) blended with acrylic acid (EMAA), combined with various forms of graphite oxide including exfoliated. The presence graphite oxide was a nucleating agent for the EMAA crystal growth. The addition of graphite to the EMAA matrix resulted in a remarkable decrease of stiffness. The storage modulus measured at -35 °C was observed to decrease with the addition of graphite oxide but increase for the storage modulus measured at 10 °C. The $T_g$ values of filled EMAA were found to be increased in the presence of all studied graphite oxides ascribed to the decrease in mobility of the polymer molecules due to the interaction between the polar groups of EMAA, and –COOH and –OH groups on the graphite layers of graphite.

The effect of EMA on thermal, morphological, and mechanical properties of polypropylene copolymer blown films was investigated by Gururajan et al[42]. Blends of polypropylene copolymer (PP-cp) and EMA were processed by blown film extrusion. As opposed to PP-cp the EMA-containing films exhibited a gradual yielding behaviour. The stress-strain tensile data of the blend films showed a visibly larger yield zone than that of neat PP-cp at 15 \%.wt EMA in PP-cp. The yield and tensile strengths of the blends were observed to decrease with increasing EMA \%.wt (at 2, 6 and 15 \%.wt) compared with neat PP-cp; however all blends possessed greater yield and tensile strengths compared with neat EMA.

Zhou et al investigated the morphology and electrical properties of linear low density polyethylene (LLDPE)-EMA blends filled with carbon black (CB)[43]. Both the characterization of SEM micrographs and the electrical properties confirmed that CB was mainly dispersed in the LLDPE phase. The selective distribution of CB in the nonpolar LLDPE phase was due to the lower viscosity of LLDPE when compared with EMA, although the interaction or interfacial energy between CB and EMA was stronger than that between CB and LLDPE.

The time-temperature creep behaviour of polypropylene and a polar polyethylene (EMA) copolymer blends was researched by Genovese and Shanks[44]. It was observed that when
the methyl acrylate content of EMA was 9 %wt that EMA had sufficient crystallinity and compatibility to impart some toughness and strength to the blends. Creep and recovery analysis over multiple analysis cycles showed changes in the viscoelastic behaviour of PP and blends containing EMA. These analyses proved valuable in describing the behaviour of PP and blends with EMA. The equilibrium modulus was found to decrease with each consecutive cycle and with increased copolymer in the blend. It is suggested that a small amount of EMA had markedly influenced the PP crystalline structure thereby causing longer relaxation times and lower creep modulus. Higher EMA weight fractions in the blends lead to less change in the relaxation times. It was observed that PP had the higher viscosity indicating that polymer flow would be less prevalent without the EMA contribution in the blends. The $T_g$ of PP (-3.7 °C) was only slightly modified by EMA.

**Thermoplastic polyurethanes**

Thermoplastic polyurethanes (TPUs) are a type of thermoplastic elastomers (TPEs) as distinct from thermoset elastomers (e.g. vulcanised rubbers). Thermoset elastomers are crosslinked via discrete covalent bonds usually formed during chemical reactions such as vulcanization. Thermoplastic elastomers are reinforced via inherent weaker dipole or hydrogen bonds (H-bonds)[45], and hard-sometimes crystalline segments. This allows for some TPEs to be melted and reformed upon cooling whilst thermoset elastomer will not melt as they will char. Thermoplastic elastomers possess both thermoplastic and elastomeric properties. Thermoplastic polyurethanes microphase separate[46] and form regular structures of block co-polymers. Their structures are usually comprised of a hard (bulky-steric hindering or crystalline) high $T_g$ or high $T_m$ (melting temperature; for crystalline segments) phase and a soft (amorphous) low $T_g$ phase.

Thermoplastic polyurethanes are formed by a polyaddition reaction of a polyisocyanate with a polyalcohol in the presence of a catalyst. The resultant TPU contains a urethane linkage (\(-RNHCOOR'\)). This urethane linkage is the site for H-bonding potential filler (with a polar surface) bonding in the TPU[47]. Figure 4 is a typical structure of thermoplastic polyurethane.

![Figure 4 Example of a structure of thermoplastic polyurethane](image)
TPEs are used in a range of applications such as snowmobile tracks, shoes soles, and blow-moulding applications due to their ease of processability.

Recent research on TPU has shown interest in their use in medical applications as observed by the work conducted by Hsieh et al. on the use of novel polyurethane-based root canal–obturation material and urethane-acrylate–based root canal sealer[48]. They developed a visible-light curable urethane-acrylate-tripropylene glycol diacrylate (UA-TPGDA) oligomer to serve as a root canal sealer and a zinc oxide-thermoplastic polyurethane (ZnO-TPU) composite to serve as a root canal obturation material and compared them with other materials. The results showed that the UA-PU groups had significantly higher bond strengths than the other groups. Douglas and Haugen’s research into coating of TPU scaffolds with collagen noted partial incompatibility lead to problematic application of aqueous collagen solution onto the hydrophobic scaffold[49]. This facilitated an invention of the coating of TPU with collagen by comparing crosslinking and coating techniques. The three different crosslinking approaches employed were chemical cross-linking agents of glutaraldehyde and N-cyclohexyl-N'2-morpholinoethyl-carbodiimide-methyl-p-toluolsulfonate (CMC) and by thermal cross-linking. It was observed that both thermal and glutaraldehyde methods showed validation of cross-linking; however glutaraldehyde seemed to be superior to the other methods. Subsequently three different coating techniques for TPU scaffolds were investigated: ultrasound, pressurized air and injection. The injection method performed most successfully with a complete coating of the TPU scaffolds.

Reinforcement of TPU by filler has been conducted in previous research conducted by Jell et al[50]. Thermoplastic polyurethanes in the form of foams manufactured by thermally induced phase separation were used as a scaffold and combined with multi-walled carbon nanotubes to form composites. This method proved to be a successful manufacturing route to three-dimensional, highly porous polymers containing well-dispersed carbon nanotubes. The results showed that the specific plateau stress of the foam reinforced with 5 % wt of carbon nanotubes increased by over 200% compared to the pure TPU foam. The thermal stability of TPU scaffolds was slightly increased for all weight fractions of carbon nanotubes; the onset of material degradation shifted from 300 °C for the pure TPU foam to approximately 315 °C with addition of carbon nanotubes. Dan et al researched the effect of solvent on the properties of thermoplastic polyurethane-clay nanocomposites prepared by solution mixing[51]. Two solvents; dimethylacetamide (DMAc) and tetrahydrofuran (THF) were used to dissolve two TPU (an ether and ester based TPU) and four types of clays (organically modified clays Closite C30B, C25A, and C15A, and the pristine montmorillonite) to create nanocomposites.

Dan et al. used ultrasound, pressurized air, and injection to coat the TPU scaffolds. The injection method performed the best, resulting in a complete coating of the TPU scaffolds.

Jell et al. conducted research on the reinforcement of TPU by filler. They used thermally induced phase separation to manufacture foams and combined them with multi-walled carbon nanotubes to create three-dimensional, highly porous polymers containing well-dispersed carbon nanotubes. The results showed that the specific plateau stress of the foam reinforced with 5% wt of carbon nanotubes increased by over 200% compared to the pure TPU foam. The thermal stability of TPU scaffolds was slightly increased for all weight fractions of carbon nanotubes; the onset of material degradation shifted from 300 °C for the pure TPU foam to approximately 315 °C with addition of carbon nanotubes.

Dan et al. studied the effect of solvent on the properties of thermoplastic polyurethane-clay nanocomposites prepared by solution mixing. They used two solvents: dimethylacetamide (DMAc) and tetrahydrofuran (THF) to dissolve two types of TPUs (an ether and ester based TPU) and four types of clays (organically modified clays Closite C30B, C25A, and C15A, and the pristine montmorillonite) to create nanocomposites.
It was observed that the clay C30B had best dispersion in DMAc attributed to the specific interaction originated from hydrogen bonding between carbonyl groups in TPU and hydroxyl groups in C30B, while C15A had the best dispersion with THF attributed to THF has better affinity to clay C15A than DMAc. This was attributed to the difference in solubility parameters between the solvents and the clays and that with increasing hydrophobicity of the clays THF was the best solvent while clays with reduced hydrophobicity are best dispersed in DMAc. However the researchers stated that the compatibility between clays and polymers becomes dominating in determining the final properties of nanocomposites, if there exists a specific interaction between the two as observed in nanocomposites containing C30B where good dispersion of clays was observed in this case regardless of the solvent.

The characterization of low hard segment thermoplastic polyurethane-carbon nanofibre composites with NMR was conducted by Powers et al[52]. They observed that the signals were broadened in the vicinity of the carbon nanofibres due to a difference in magnetic susceptibility between the carbon nanofibres and the polyurethane, but the molecular dynamics are not greatly changed. Spin diffusion appeared to be very sensitive to the onset of stress induced crystallinity, and stretching to high draw ratios promoted crystallite formation on the surface of the carbon nanofibres and lead to higher crystallinity and smaller crystallites. Buffa et al have researched the effect of single-walled carbon nanotube functionalization on the properties of single-walled carbon nanotube-polyurethane composites[53]. They observed that the inclusion of carbon nanotubes into a thermoplastic polyurethane with a high hard-segment content resulted in increases in the modulus, tensile strength, and strain at break. Functionalization of the nanotubes lead to slightly better dispersion at high nanotube weight fractions; however functionalization destroyed the inherent electrical conductivity of the nanotubes. The characterization of ester-based polyurethanes-silica nanocomposites in solution prepared with four different silica (hydrophobic and hydrophilic fumed silica, and hydrophobic and hydrophilic precipitated silica) was conducted by Torro-Palau et al[54]. The addition of silica to polyurethane in solution produced an increase in viscosity, but only the hydrophilic fumed silica imparts thixotropy and pseudo-plasticity. The addition of silica resulted in an increase in storage and loss moduli (measured via modulated force thermomechanometry in 3-point bend deformation geometry) of the PU nanocomposites. The greatest increase was observed in the nanocomposites containing hydrophilic fumed silica. The improved rheological properties of the PU composite containing hydrophilic fumed silica was ascribed to the creation of a network between the polyurethane chains and the silanol groups on the fumed silica surface. The addition of fumed silica did not affect the glass transition temperature of the nanocomposite compared with unfilled polyurethane.
Rheological properties were observed to decrease in nanocomposite films containing precipitated silicas.

**Crosslinking**

Elastomers require some form of reinforcement to provide dimensional reversibility. Reinforcement can be achieved by forming crosslinks within an elastomer. Crosslinking may be achieved via two methods, chemical crosslinking and physical crosslinking.

Chemical crosslinking is a process[16] that results in internal chemical bonding within a polymer. The first form of chemical crosslinking of a polymer was performed on natural rubber employing sulphur[20]; this process being termed ‘vulcanization’. Sulphur crosslinking has been widely used with a variety of polymers and sulphur crosslinking agents, however subsequent compounds and methods were developed to perform crosslinking, including reactive chlorine compounds, phenol resins, electron beam crosslinking, ultrasonic crosslinking, microwave crosslinking and peroxides[20].

Peroxides are a popular crosslinking agent due their ability to crosslink a wide variety of elastomers, including those which cannot be crosslinked via sulphur compounds[55]. The reaction path for peroxide crosslinking of elastomers involves a peroxide (to form a radical) removing a hydrogen atom from the elastomer creating a free radical site, which subsequently couples with sites in the polymer forming crosslinks[56]. Figure 5 displays the crosslinking mechanism for peroxide curing of EPDM and other unsaturated elastomers. Peroxide curing presents some advantages over other crosslinking methods, such as: short crosslinking time, possibility for transparent rubbers[57], simple compounding, less tension set, strain and heat aging resistance[58] and the ability to crosslink saturated elastomers[59]. A drawback with peroxide-induced crosslinking is the need for radicals; therefore antioxidants that are often included in polymers may hinder or even halt crosslinking reactions. Other drawbacks include cost and low mechanical strength of the resultant crosslinked elastomers.

\[
\begin{align*}
\text{heat or light} & \quad \text{ROOR} \quad \overset{\text{2RO}^*}{\longrightarrow} \quad \text{2RO}^* \\
& \quad \text{2RO}^* + \text{P-H} \quad \overset{\text{ROH + P}}{\longrightarrow} \ \text{2P}^* \\
& \quad \text{2P}^* \quad \overset{\text{PP crosslink}}{\longrightarrow} \quad \text{P(-H) + P(+H)}
\end{align*}
\]

*Figure 5 Peroxide crosslinking mechanism where P-H is an unsaturated polymer, reproduced from Akiba and Hashim[20]*
The crosslinking of diene monomers is of particular interest to this research. It has been stated[20] that peroxides are quantitative crosslinking agents, i.e. one mole of crosslinks are formed per one mole of peroxide. Dicumyl peroxide (the peroxide used in this research) is a common crosslinking agent of diene monomers. Advantages of employing dicumyl peroxide are that the resulting crosslinks are only composed of stable carbon-carbon (as opposed to carbon-sulphur-carbon bonds from sulphur crosslinking) and the compound is compatible with non-polar elastomers. Other peroxides which have been used to perform crosslinking include diacyl peroxides, t-alkyl peroxyesters and metal peroxides. EPDM has been crosslinked, hence shown to be reinforced with peroxides in previous research[60-62].

Chemical crosslinking is a non-reversible process and may result in adverse changes to the elastomer (due to its altered chemical nature). As mentioned previously another method of reinforcement of is crosslinking in the form of physical crosslinks, which can be achieved by the addition of fillers.

**Fillers**

Fillers are used to create crosslinking in elastomers by acting as physical links via adsorption onto multiple polymer segments (as opposed to forming chemical bonds between polymer segments). Fillers are able to bestow a number of properties onto elastomers apart from mechanical reinforcement including impact resistance[63], flame retardation[64], sound and vibration damping[65], roll resistance, abrasion resistance[66], and alter permeability to gases and moisture[67].

A number of factors influence the degree to which a filler will fulfil its desired effect and the maximisation of filler-polymer interaction. These include chemical composition (of both filler and polymeric matrix), size of filler particles, method and extent of dispersion of filler. Size dimensions of fillers ranging from the nano-sized to micro-sized, and coupling agents or surface treatments can be used to increase filler-matrix compatibility. Fillers are available in a range of chemical compositions including metals[68], glass fibres[69], synthetic fibres[70] and other polymers[71].

The fillers commonly used for elastomers are carbon black, clays and silicas. Carbon blacks have been incorporated into EPDM[33]. The relative abundance, non-polar chemical composition and stability of carbon black makes it an ideal candidate for use with EPDM and other non-polar matrix elastomers. Other fillers such as clays have been employed for reinforcing elastomers because of their polar groups (with non-polar coating)[72], and their ability to be intercalated with non-polar bonding regions[73].
To ensure that fillers adequately impart properties upon the polymeric matrix, maximum dispersion is required. Dispersion can be achieved by physical dispersion (shear mixing, ultrasonication), chemical (e.g. sol-gel[74]) or strain induced[75]. The particular fillers used in this research will be further detailed in the next two sections.

**Alumina**

Alumina is the trivial name for aluminium oxide (Al$_2$O$_3$) and its naturally occurring form is called corundum. The largest natural source of alumina is found in bauxite. The two main forms of alumina are $\alpha$-aluminium oxide (most common) and $\gamma$-aluminium oxide. Pure, metallic aluminium is very reactive with atmospheric oxygen. After being exposed to oxygen, a thin layer of alumina quickly forms on any pure aluminium surface, preventing any aluminium from further oxidising. Alumina is used in a variety of applications such as in water filters, ceramics, abrasives (sand paper), coatings for disc media and superconductors. The incorporation of alumina as filler into cured EPDM was researched by Abdel-Aziz et al [76]. They noted the changes in thermal and electrical properties after the incorporation of alumina with varying particle size. The thermal decomposition of EPDM occurred at higher temperatures (an average increase of approximately 20 °C) with the addition of all aluminas. There was an increase to electrical conductivity ($\varepsilon'$) when the particle size was 0.3µm. The $\varepsilon'$ was decreased when the particle size was reduced to 0.02 µm independent of temperature in the range studied. The alumina with 0.1µm particles size was observed to decrease the $\varepsilon'$ decreases compared to the raw EPDM. Prabu et al conducted research on the theoretical correlations amongst electrical and mechanical characteristics of EPDM-silicone and alumina based housing materials for outdoor insulators[77]. They predicted the improvement to tracking resistance and tensile strength at low to moderate weight fractions of alumina and a decline in tensile strength at the higher weight fractions of filler with multivariate analysis that was confirmed when compared with experimental data. The effect of alumina on the flame retardant and smoke inhibiting properties of an EPDM-polypropylene (PP) blend was investigated by Yu, Wang and Xiao[78]. They observed that an increase in flame retardant properties was attainable with the addition and subsequent increases in alumina concentration and particle size. The alumina had retarding effects on the evolution of the volatile compounds by barrier formation, but had a little effect on the thermal stability of the blend. Nagata et al investigated the reactivity of the alkoxy group in a silane coupling agent ($\gamma$-mercaptopropyltrimethoxysilane) employed for the compatibilisation between EPDM and inorganic filler surfaces including alumina[79]. Strong interactions were between the particle surface and the silane due to the hydrogen bonding and the ionic interaction was confirmed by
electron spectroscopy for chemical analysis (ESCA). Their influences on the mechanical properties of filled vulcanized rubber were investigated. The silane-treated filler particles showed ability as semi-reinforcing filler for vulcanized rubber; however the structure of the silane-layer on the particle surface had negligible affect on the mechanical properties of the composite. Yin et al presented a conference paper on the nano-aluminas with differing lattices (i.e. $\alpha$ and $\gamma$ forms) mechanically blended into EPDM[80]. It was observed that the $\gamma$-alumina was dispersed more uniformly than $\alpha$-alumina. Additionally, the mechanical properties of EPDM containing $\gamma$-alumina performed better than those of the composites containing the $\alpha$-alumina.

**Silica**

Silica is the trivial name for silicon dioxide ($\text{SiO}_2$). Silica is has a number of amorphous and crystalline forms. Most crystalline silicas involve a tetrahedral arrangement of $\text{SiO}_2$ molecules linked together where the bond lengths between silicon and oxygen in different crystal forms will vary.

The size of silica particles is dependent on synthesis with some particles being as small as 7 nm in diameter. Individual particles of silica rarely exist as described by Schaefer and Justice[81]. They commented on how these particles (called primary particles) tend to form aggregates, which are short chains of silica particles that cannot be disrupted even under severe shear conditions[81] as seen in Figure 6. These aggregates form what were termed hard agglomerates, which are clusters of the aggregates. Hard agglomerates can be broken apart under very high shear mixing (e.g. ultrasonication). In turn, hard agglomerates form what were termed as soft agglomerates. Soft agglomerates are clusters of hard agglomerates and can be disrupted via less-intense mixing methods (e.g. low shear mechanical mixing).

![Figure 6 Various arrangements of silica particles, as reproduced from Schaefer and Justice[81]](image)
Silica is used in a variety of applications such as glass, ceramics, thixotropic agent, microelectronics and the extraction of DNA and RNA due to its ability to bind to the nucleic acids under the presence of chaotropes[82].

Silica has been combined with elastomers, such as EPDM and thermoplastic elastomers. The rheological properties of polypropylene (PP)-EPDM-silica were investigated by Yang et al with a focus on the formation of filler networks[83]. Two types of nano-silica (one hydrophobic, one hydrophilic) and two processing methods (one-step or two-step) were employed to prepare the composites. Linear viscoelastic behaviour was observed for polypropylene-EPDM and PP/silica binary system, showing no evidence of the formation of filler-network structure. However, solid-like rheological behaviour, which was attributed to the formation of the filler-network structure as confirmed by SEM observation, was observed in some PP-EPDM-silica composites depending on the silica surface property, processing method and EPDM content. It was observed that hydrophilic silica was necessary for the formation of filler-network in PP-EPDM-silica composites. Guryia and Tripathy investigated the dynamic mechanical analysis of silica-filled closed-cell microcellular vulcanized EPDM[84]. The effect of blowing agent loading on the storage modulus and tan δ was found to have a complex nature. The viscoelastic behaviour of silica-filled microcellular EPDM was observed to be similar to that of solid rubber vulcanizates.

Isayev, Hong and Kim investigated the preparation on EPDM-silica composites, with and without silane coupling agents[85]. High power ultrasound was applied to disrupt silica agglomerates in the composites and to compatibilise plastic-rubber and rubber-rubber blends during extrusion process. Ultrasonically dispersed EPDM-silica composites without silane treatment of silica had significantly reduced sizes of silica agglomerates in comparison with those obtained by an internal mixer. The viscosity of the ultrasonicated compounds was found to be higher than that of the silane treated compounds while the extrudate swelling of both compounds were similar.

Thermoplastic polyurethanes-silica composites have been analysed in previous research. The properties and preparation of thermoplastic polyurethane-silica hybrids using a modified sol-gel process as investigated by Lai and Liu[86]. This modified approach used THF to extract poly(silicic) acid from aqueous sodium metasilicate solutions. A THF or aqueous solution containing solvated particles was mixed with dissolved TPU to form TPU-silica composites. Various mechanical tests were performed to analyse the composites, and it was noted that the storage modulus increased due to the reinforcement of the in-situ silica and tear strength
decreased significantly with increasing in-situ silica content. The cutting strength decreased slightly due to crack tip confinement.

The properties of thermoplastic polyurethane adhesives containing nano-silicas with different specific surface area and silanol group content were investigated by Vega-Baudrit et al[87]. Formation of agglomerates of nanosilica particles within the polyurethane matrix were favoured by increasing the silanol content, likely due to stronger hydrogen bond interactions between the silanol groups on the nanosilica over those between the polyurethane and the nanosilica. As a consequence, inter-urethane bonds formation rather than ester-urethane bonds were favoured, leaving the soft segment chains more free to interact between them. Thus, it was determined that the addition of nanosilica favoured phase segregation in the TPU. The addition of the nanosilica improved the mechanical tensile strength and elongation at break, and the viscoelastic properties of the polyurethane. The immediate adhesive strength of PVC-polyurethane adhesive joints increased in the filled adhesives.

Jauregui-Beloqui et al investigated the influence of the surface area of fumed silica on the adhesive and viscoelastic properties of TPU-silica composites[88]. Fumed silicas of surface areas ranging from 90–380 m$^2$/g were added to dissolved thermoplastic polyurethane, then the dispersions were dried. The viscoelastic properties of PU were improved by the addition of fumed silica and a solid-like behaviour in composites was obtained. The increase in specific surface area of the fumed silica increased the moduli of the composites. The glass transition temperature (obtained from DMA and DSC analysis) and the crystallisation rate of fumed silica-PU composites decreased with increasing surface area of the fumed silica. The contact angle values were similar in all the composites and the strength of PVC-fumed silica-PU composite joints was not affected by the specific surface area of the fumed silica.

**Admicellar polymerisation**

Some filler-matrix combinations may have poor compatibility due to differing properties such polarities, hardnesses and hydrophobicities. To overcome these incompatibilities surface modification of the filler can be employed, which will alter chemical nature of the filler particle surface. A novel technique for surface modification is that of *admicellar polymerisation*. Admicellar is a combination of the two terms, adsorption and micelle. It used to describe a method of coating filler (or other solid substrate) with polymeric layers introducing an intermediary layer.

Admicellar polymerisation is a four step process[89] involving step 1, the adsorption of surfactant onto surface of the filler, step 2, the solubilization of monomer into the surfactant-
filler solution resulting in monomer adsorption into surfactant bi-layer around filler, step 3, in-situ polymerisation of monomer in surfactant bi-layer and step 4, the removal of the top layer of surfactant. Once completed, this process results in filler coated in a layer of the desired polymer. Figure 7 is a graphical representation of this process.

![Figure 7 Schematic for functionalization of filler surface via admicellar polymerisation as seen in Xin Wei et al[90]](image)

Admicellar polymerisation not only functionalises a filler surface, but may benefit the damping properties of the filled system. When a rigid, hard particle is added to a soft elastomer, this difference between hardnesses may result in inefficient transfer of energy and cause failure. The layer of polymer on the filler surface can be used to bridge this difference between hardness. Ideally, the intermediary layer will have stiffness between the rigid filler and soft elastomer. This should allow for greater damping. A system that employs this approach has been termed a graded seal system. Pongprayoon et al employed a graded seal system in their research into the modification a sisal fibre surface with poly(methyl methacrylate) (PMMA) for the purpose of improving the compatibility between the sisal fibre and a surrounding polymeric matrix in a composite[91]. Hexadecyl pyridinium chloride (HDPyCl) was used as a surfactant in the admicelle formation. It was observed that the PMMA coating on the sisal fibres bestowed a hydrophobic character to fibres, as confirmed by its floating time, moisture absorption and surface charge measurements.

## Composites

Composites are materials in which a second component with different properties is added to the polymer matrix so that both components contribute to the properties of the product[16], in this case when fillers are added to elastomers. Fillers take up some free volume of the elastomer when forming a composite[92]. The properties of a composite will depend upon a
range of factors such as filler size[93], surface area[94], and surface chemistry[95] (affecting the interaction at the interface between filler and elastomer), method of dispersion[96], fractal nature of filler clustering[81] and volume fractions of the composite constituents. The surface area of filler provides the interfacial area on which elastomer can bond with the filler, hence larger surface area results in more potential bonding sites. Surface chemistry of filler will determine extent and bonding sites of the filler-elastomer interactions. Filler and matrices will interact in a variety of manners within a composite, an example containing various components and filler-elastomer interactions is given in Figure 8.

![Figure 8 Various composite segments and interaction as described by J.-L. Yang et al.[97]](image)

The presence of filler can remove some of the elastomer able to participate in molecular and segmental rotations. If there is attraction or clustering between filler particles (as observed[81] in silica) this may give rise to occlusion. Occlusion[98, 99] is when filler particles will completely envelope segments of an elastomer effectively removing it from the matrix. This results in an artificial increase in the volume fraction of filler in the composite as the occluded elastomer has limited molecular motion available for deformation. Figure 9 represents an example of a cluster of filler particles occluding that segment of matrix material from the rest of the system.
The various composite properties that affect the modulus as a function of strain were studied by Han, Zhang, Guo and Wu[100]. They described the various contributions of the filler-elastomer composite components to the modulus by investigating the effect on the mechanical properties of the addition of modified carbon black to SBR rubber. Figure 10 displays the various contributions to the modulus as a function of strain in the carbon black-SBR rubber composites. This figure describes how the modulus of an elastomeric composite is generated from the contributions of the elastomer network, hydrodynamic effect, the interactions between filler and matrix and filler-filler interactions (e.g. networks, clustering).
Chapter 2 Literature Review

Nanocomposites

Particle size plays a role in the extent of filler-elastomer interactions. The smaller the filler particle size, the greater the filler-elastomer interaction that can be achieved; however dispersion of filler becomes difficult with smaller particle size. A unique class of filler-elastomer compounds are known as nanocomposites. Nanocomposites are defined[101] as composites of more than one Gibbsian solid phase where at least one dimension of one of the solid phases (in this case, the dispersed phase) is in the 1 – 20 nm range. In filler-elastomer composites, filler particles are the dispersed phase of nano-sized dimensions and are referred to as nanoparticles. Nanoparticles have many advantages over other larger sized filler particles, such as increased surface area to volume ratio and the potential for greater dispersion in the polymer phase.

Testing and Analysis of polymeric composites

There are many methods for characterising various properties of polymer composites. Wide-angle and small-angle X-ray scattering methods have been used to detect the level of crystallinity in polymers[102] and the dispersion of fillers[103]. Optical microscopy is useful for observing micron-sized particle dispersion[104] and polarised light can be employed to observe birefringent materials[105]. Other techniques are characterise properties of polymers as a function of temperature. For this research the analysis techniques employed were thermogravimetric analysis, scanning electron microscopy and thermomechanometry.

Thermogravimetry

Thermogravimetric analysis (TGA) is defined as the continuous measurement of sample mass as a function of temperature and/or time[106]. It employs a thermobalance that measures the mass loss or gain with change in temperature and time. Experimental conditions that can be altered are: the atmosphere under which the analysis is conducted (e.g. ambient, oxygen, nitrogen, argon), analysis temperature range and heating rate. Cahn and Shultz[107] are usually credited for introducing the automatic thermobalance, which was subsequently improved upon[108].

Output from TGA is in the form of mass loss, fractional mass loss (where initial mass equals 100 %.w/w) and mass derivative (rate of mass loss as mg.min⁻¹). The minima in the mass derivative data correspond to the time or temperature at which fastest mass loss is observed (i.e. greatest mass loss over shortest time).
TGA has been used to determine degradation temperatures, moisture content, filler content and kinetics of reactions. Oezdemir[109] used TGA to characterise vulcanized EPDM via irradiation. He determined the thermal stability of the EPDM was increased with irradiation within the dose range studied. The maximum weight loss of non-irradiated EPDM was observed at 459 °C and that of 130 and 180 kGy irradiated ones were observed at about 468 °C. The derivatives of the TGA thermograms affirmed that the rate of weight loss was decreased with irradiation.

Li et al used thermogravimetry to characterise the thermal stability of EPDM-organo clay nanocomposites were prepared by melt extrusion in a twin-screw extruder. They observed that the organoclay improved the thermal stability compared with the unfilled EPDM[110].

Sirqueira and Soares[111] employed TGA to analyse the kinetics of thermal degradation of natural rubber-EPDM blends. The kinetic parameters of thermal degradation were evaluated from TGA experiments conducted at different heating rates. The inclusion functionalized copolymers in the blends resulted in a substantial increase of the activation energy at weight fractions as low as 2.5 %.wt. This indicated an increase in thermal stability.

Research has been conducted by Li et al[112] into the heat resistance of polyester-based thermoplastic polyurethane (TPU) with polyamide 1212 (PA-1212). The PA-1212 formed submicron dispersion domains in the TPU matrix indicating that there was good compatibility between the TPU and PA-1212. Due to the strong hydrogen-bonding interaction between TPU and PA 1212, the thermal stability of the blends was improved compared with the addition and each successive increase to PA-1212 concentration compared with the unblended TPU. This improvement was observed as a decrease to the rate of degradation; however the initial degradation temperature did not change with the addition of PA-1212.

Eceiza et al[113] employed TGA to characterise the thermal properties of TPU elastomers based on polycarbonate diols with different soft segment molecular weight and chemical structure. They noted that the urethane group was unstable at high temperatures and that, depending on the type of diisocyanate, the structure of the hard segment and the composition of polyurethane, thermal degradation reactions can occur during heating. The initial degradation temperature was observed at 290 °C.

Wang and Huang[114] characterised the thermal properties of novel thermoplastic elastomers prepared via step/chain transformation polymerization. They noted that the initial degradation was the degradation of the hard phase while the second degradation temperature was equivalent to the degradation of the soft phase and the third degradation temperature was
related to oxidation reactions of the MDI (4,4′-methylene bis(4-phenylisocyanate) and TPED (1,1,2,2-tetraphenyl-1,2-ethanediol: the free radical initiator) components in the hard phase.

**Scanning electron microscopy**

Scanning electron microscopy (SEM) is a microscopy technique that creates an image of a material surface via electrons[106]. The first prototype of an electron microscope was developed by Knoll and Ruska[115]. The scanning electron microscope was subsequently developed through the research of von Ardenne[116] and Oatley[117]. A high-energy beam of electrons is used to bombard the material surface with electrons. The electron beam is controlled by lenses consisting of magnetic fields. The electrons interact with the atoms at the surface of the material yielding secondary electrons and backscattered electrons, Auger electrons and X-ray radiation (caused by the electron beam removing inner shell electrons). The secondary and backscattered electrons are used to form an image that describes the surface topography. Scanning electron microscopy is performed under a vacuum and the resolution of the resultant image is dependant upon the voltage of the electron beam.

Scanning electron microscopy is used to observe surface topography of an analysed material, which in turn can be used to determine other material characteristics. Acharya et al used SEM to characterise the dispersion of layered silicate in EPDM-EVA blend nanocomposite[118]. It was observed that typical sea-island morphologies existed in which the EVA domains are dispersed in the EPDM matrix because of high melt viscosity of EVA; however, the phase morphology changes on addition of organoclay. It was found that the sea-island structure transforms into a co-continuous structure but the phase size is reduced with the addition of 4 and 8 %.w/w of montmorillonite. Fu et al employed SEM to analyse the compatibility of composite constituents in EPDM-graft-MS (a resin consisting of methyl methacrylate and styrene) composites[119]. The surface of EPDM/MS resin blends containing 25 %.w/w EPDM was composed of many fewer particles and cavitations (formed by desquamation of EPDM-g-MS particles) indicating that the compatibility between EPDM and MS resin was poor. Conversely, the surface of EPDM-g-MS/MS resin blends containing 25 %.w/w EPDM showed plastic flow and almost no cavitations, illustrating good compatibility between EPDM-g-MS and MS resin. Huang et al employed SEM to aid in the characterisation of morphology, melting behaviour, and non-isothermal crystallization of poly(butylene terephthalate)-poly(ethylene-co-methacrylic acid) blends[120]. The size of the dispersed phase was observed to increase when the weight fraction of PEMA increased from 10 to 50 %.w/w. When the PEMA content increased to 50 wt.% the mean size of dispersed phase increased and exhibited a sharp interface between PEMA domains and PBT matrix. PEMA
domains had a spherical shape and there were numbers of voids from which the dispersed PEMA were removed, indicating that the interfacial interaction between PBT and PEMA was poorer at higher content of PEMA.

**Thermomechanometry**

Thermomechanometry is an analysis technique that measures a change in dimension or mechanical property of an analysed material while subjected to a designated temperature program. It is useful for characterising the free volume and molecular relaxation transitions and times of materials. Thermomechanometry can be performed in a variety of test geometries such as tensile, compression, shear and 3-point bend modes determining different material characteristics.

There are three forms of thermomechanometry, dynamic force (df-TM), static force (sf-TM), and modulated force thermomechanometry (mf-TM). All forms employ the method of applying a force, given as stress (the ratio of force applied to area of the specimen) and measuring the resultant strain (ratio of change in size dimension to initial size dimension) as a function of time or temperature. Dynamic force thermomechanometry applies a constantly changing force. Static force thermomechanometry applies a constant force which can exceed the linear viscoelastic region resulting in some degree of non-reversible deformation. Modulated force thermomechanometry applies a force which does not exceed a materials linear viscoelastic region. In this region, deformation is comprised of elastic and viscoelastic deformation (i.e. fully reversible deformation) and the resultant modulus is constant.

**Dynamic force thermomechanometry**

**Stress-strain analysis**

Stress-strain analysis involves the constant deformation of a specimen via an applied force given as stress. This deformation can be achieved by applying a constantly changing stress rate and measuring the resultant strain response, or applying a varying stress to keep a constant strain deformation rate. A schematic of an example of the applied force required to maintain a constant strain rate during a stress-strain analysis is shown in Figure 11.
Figure 11 Applied force, strain rate schematic of stress-strain analysis: solid line indicates applied force; dotted indicates strain rate

Ideally a material analysed via stress-strain that is purely elastic will deform in a manner similar to that described by Hooke’s law, represented in Equation 1 as:

$$\sigma = k \gamma$$  \hspace{1cm} \text{Equation 1}$$

where $\sigma$ is stress, $\gamma$ is strain and $k$ is the spring constant. This would yield a single modulus value (defined as the ratio of stress to strain, termed Young’s modulus), which would equal the spring constant in Hooke’s law. However, most real materials do not behave in this manner and will deform in a manner between the two extremes of Hookean spring behaviour and viscous Newtonian behaviour. A Newtonian behaviour is that of a liquid, and can be described, as seen in Equation 2 as

$$\sigma = \eta \dot{\gamma} = \eta \frac{\partial \gamma}{\partial t}$$  \hspace{1cm} \text{Equation 2}$$

where $\eta$ is viscosity and $t$ is time.

A typical material response to stress-strain analysis involves initial elastic (instantaneously reversible) deformation viewed as linear stress-strain data, followed by curvature in strain data equating to viscoelastic and viscous (time-dependant reversible and time-dependant irreversible) deformation. The peak in stress value in the stress-strain data after the elastic deformation is equal to the stress at which yielding occurs. At and following yielding, less
stress is required to maintain a constant strain rate due to the uncoiling of polymer chain segments and molecular slippage. After yielding, the stress required for a constant strain extension may again increase due to crystal re-orientation or strain induced crystallinity. At a certain strain value the specimen will break, termed *failure*. Figure 12 represents an example of the typical data generated from stress-strain analysis with the various modes of deformation and material characteristics marked.

![Stress-strain curve](image)

**Figure 12 Example of stress strain analysis data**

Stress-strain analysis has been widely employed in the field of elastomer analysis. The research conducted by Nair et al employed stress-strain analysis to determine the effects of heat, ozone, gamma radiation, and water and ageing on the mechanical performance of EPDM blends[121]. They observed that tensile strength of the blends increased after thermal ageing for 96 h at 100 °C due to the continued crosslinking. It was noted that an increase in EPDM in the blends improved the ozone resistance of the blends. Crack initiation was noted only in blends with lower concentrations of EPDM and the cracks in such blends were found deeper, wider and continuous in the bulk. The tensile strength of the blends decreased with a 15 kGy irradiation dose while it increased with a 80 kGy dosage of \( \gamma \)-radiation. The elongation at break had a decreasing trend with increased dosage of \( \gamma \)-radiation.

The optimization of twin-screw extruder operational conditions for the preparation of EPDM-based composites and the effectiveness of in-situ sol-gel method of forming silica in EPDM was analysed via stress-strain analysis by Das et al[122]. The silane coupling agent bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (TESPT) was added to EPDM allowing for the growth of
silica particles inside the rubber matrix via in-situ sol-gel. The maximum tensile properties were achieved for the vulcanizate that was produced by a preheating procedure in the presence of the silane coupling agent. The corresponding unfilled vulcanizate had inferior tensile properties. The composite filled with 4.7 phr silica grown in situ at TESPT grafted EPDM had a pronounced reinforcement effect. The shape of the stress-strain curve was steeper compared with that observed for the elastomer and led to a higher maximum stress.

A series of thermoplastic polyurethanes based on 4,4'-dicyclohexylmethane diisocyanate were analysed via stress-strain analysis by Moravek et al[123]. Their work involved polyurethane synthesis based on dicyclohexylmethane diisocyanate and polyester polyols including, poly(butylene adipate) (BA), poly(D,L-lactide-co-glycolide) (PLGA), and BA-PLGA mixed polyols. The synthesised materials possessed excellent tensile properties and an operating temperature range of -40 to 80-90 °C.

Jeon et al used stress-strain analysis to mechanically analyse the synthesis and characterizations of waterborne polyurethane-silica hybrids filled via the sol-gel process and mechanical mixing[124]. They determined that the modulus and tensile strength increased with increasing nanosilica concentration, whereas the elongation at break showed the opposite tendency. It was observed that the reinforcing effect of nanosilica was more evident at large deformations due to the fact that alignment and extension of polyurethane chains in the rubbery state contribute to the improved performance of nanosilica. It was observed that the composites with mechanically mixed silica filler had higher moduli and tensile strength than the sol-gel silica polyurethane composites, whereas the trend of the elongation at break was the opposite. This was attributed to crosslink formations between polyurethane and silica in each respective system.

The Influence of silica on shape memory effect and mechanical properties of polyurethane-silica via sol-gel hybrids was analysed with stress-strain analysis by Cho and Lee[125]. The breaking stress and modulus of the composites increased slightly with increasing initial TEOS content up to about 10 %.wt then dropped again to a half of original pure polyurethane. Maximum breaking stress and modulus were obtained near 10 %.wt TEOS regardless of hard segment content. The elongation-at-break increased initially with TEOS content similarly to breaking stress; however they noted the elongation-at-break of composites usually decreased with increasing reinforcement. The mechanical properties of polyurethane appeared to be improved by the addition of relatively small amounts of 10 %.wt TEOS. This was supported by the authors’ results that as the TEOS concentration initially increased the formed silica composites were reinforced gradually without hindering elastic deformation of soft segments,
resulting in higher breaking strength and elongation-at-break. However, the incorporation of an excess of silica hindered the deformation of soft segments in polyurethane and thus led to lower breaking stress and elongation-at-break.

**Static force thermomechanometry**

Static force thermomechanometry involves the application of a constant force to a specimen resulting in a strain response as a function of time or temperature. This analysis is performed by controlling the strain deformation to maintain a constant stress during which temperature is usually held constant. Described below are two experimental procedures to carry out sf-TM.

**Creep and recovery analysis**

Creep and recovery analysis are two analysis procedures that are usually carried out in sequence. Creep analysis involves the instantaneous application of force held constant for a discrete time while measuring strain deformation. Recovery analysis involves the instantaneous removal of an applied force for a discrete time whilst measuring strain recovery. A schematic of the force application and removal with respect to time during creep and a subsequent recovery analysis is shown in Figure 13.

![Figure 13 Applied force schematic for a creep and subsequent recovery analysis](image)

Creep analysis will cause linear (elastic) and non-linear (viscoelastic) deformation, and non-reversible (viscous) deformation (as strain deformation exceeds the linear viscoelastic region) of the specimen. However non-linear and non-reversible deformations are only separately observable in a subsequent recovery analysis phase. Figure 14 represents an example of creep
and recovery strain-time data with the various modes of deformation and recovery labelled. During creep analysis, the elastic deformation is observable as the instantaneous increase in strain in response to applied force. The curvature observed in the strain-time data following elastic deformation is attributed to viscoelastic and viscous deformation.

When the applied force is removed during a recovery analysis there is an instantaneous decrease in strain which is equivalent to elastic recovery. This is followed by curvature in the time-strain data representing the viscoelastic recovery. The unrecovered strain in recovery analysis (the initial strain value at the removal of applied force minus the final strain value at completion of analysis) is equal to the viscous deformation that occurred during the application of force.

![Diagram](image-url)

**Figure 14 Creep and recovery analysis with the various modes of deformation and recovery labelled**

Beake et al employed nanoindentation creep to investigate the properties of various EPDM based rubbers[126]. They obtained the creep rates from creep testing the rubbers and plotted it as a function of $T_g - T_{\text{experimental}}$. From this they were able to determine the chain mobility of the materials based upon their creep rate values, relating creep behaviour to that of brittle solids.

Mohammadian-Gezaz et al researched the thermoformability of EPDM blends and composites by hot tensile and rheological tests[127] and determined via creep testing and other rheological tests that the blends had higher elasticity and more sag resistance. 10 phr of
calcium carbonate was incorporated into the blends to compensate for the reduction of modulus due to the presence of HDPE and EPDM.

Creep and recovery analysis were employed to investigate the changes in creep strain with regard to filler in a range of polyurethane thermoplastic elastomer montmorillonite nanocomposites by Rivera et al[128]. The introduction of the organo-clay increased the creep strain obtained while the nano-indenter was held at constant load for softer Shore hardness 80A materials. The increase in creep strain was greatest for materials containing an organo-clay modified with a hydrophilic quaternary alkylammonium surfactant and with highest concentrations of the hydrophilic organo-clay. This indicated the effect may be due to a plasticizing effect of the excess surfactant. The addition of the organo-clays to the Shore hardness 55D materials produced only a small decrease in the creep strain that was probably due to the interconnected hard domains in the material.

The long-term mechanical fatigue examination of two types of thermoplastic elastomers was researched by M. El Fray[129] via creep analysis. The thermoplastic elastomers used were PEDs-poly(aliphatic/aromatic-ester)s composed of poly(butylene terephthalate) and dimerized fatty acid, were combined with commercially available polyurethane (PU) elastomer. The PED copolymers showed superior fatigue properties compared with PU at high concentrations of hard segments (hardness 55 Shore D).

Creep mastercurves from the mechanical study of thermoplastic polyurethane-polypropylene blends have been constructed by Bajsic and Rek[130]. They observed a decrease of the creep modulus was faster at higher temperatures and the master curves were shifted to higher creep moduli with increasing polypropylene content. This is connected with molecular rearrangements that became more pronounced with time and were faster at higher temperatures. In blends with higher polypropylene content molecular rearrangements were reduced compared with blends with higher content of soft segments, i.e., higher thermoplastic polyurethane content.

A variation of a creep analysis is a stress-relaxation analysis. In this analysis, an applied force is allowed to vary to maintain a selected strain. A force, strain schematic of stress-relaxation analysis is represented in Figure 15. With time the stress required to maintain a constant strain is reduced as molecular segments randomise, relaxing into random coils.

Stress-relaxation analysis has been used by Jacob et al to analyse the effect of using ground, vulcanised EPDM as a filler in oil extended-EPDM[131]. They determined that although the tensile strength remained almost constant, the modulus, hardness, abrasion resistance, and tear
strength of the EPDM/EPDM composites progressively decreased with ground, vulcanised EPDM loading.

Spontak and Vratsanos analysed the rubber-filled low molecular weight polymers via the stress-relaxation analysis[132]. They modelled stress-relaxation data with a biexponential Maxwell model yielding two relaxation times, a short and long time. It was determined through analysis with respect changing rubber composition that the yielded long relaxation time exhibited Arrhenius behaviour. The composites that were uniformly dispersed obeyed this Arrhenius relationship whereas those that were significantly phase separated did not.

![Figure 15 Applied force, strain schematic of stress-relaxation analysis: solid line indicates applied force; dotted indicates strain](image)

**Modulated force thermomechanometry**

Multi force thermomechanometry (mf-TM) or dynamic mechanical analysis is the application of an oscillating force at designated frequency/ies over a discrete temperature range to a material, and analysing the material response to that force[15]. The application of force to a material will result in deformation, termed *strain*. The applied force is converted into stress (the ratio of applied force to cross-sectional area of a specimen) as stress is used for calculating dynamic mechanical moduli.

If a material is subjected to a sinusoidally oscillating stress, it is expected that the resultant deformation and recovery in the material will be relatively sinusoidal. The pseudo-sinusoidal relationship between stress and strain data holds true if the material is kept within its linear viscoelastic region. An equation describing the applied stress[15] is given in Equation 3.

\[ \sigma = \sigma_0 \sin(\omega t) \]  

**Equation 3**
where $\sigma$ is the stress, $\sigma_0$ is the maximum stress, $t$ is time and $\omega$ is the frequency of oscillation.

The elastic and viscoelastic strain deformation and recovery in response to an applied stress will be described by an equation accounting for these two components of deformation and recovery. When a material is in an elastic state, it will respond like a Hookean ideal spring as described by Equation 1. With regards to dynamic mechanical analysis, the elastic strain deformation and recovery can be described[133], as seen in Equation 4, as

$$\varepsilon(t) = E\sigma_0 \sin(\omega t)$$

Equation 4

where $\varepsilon(t)$ is strain, $E$ is Young’s modulus, $\sigma_0$ is the maximum stress (i.e. amplitude of the sinusoidal data).

Equation 4 can be rewritten as

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$

Equation 5

where $\varepsilon_0$ is the strain at maximum stress for purely elastic deformation and recovery.

Strain data described by Equation 5 will be in-phase with the stress data, i.e. no lag between the stress and strain curves along the time axis as seen in Figure 16.

![Figure 16 In-phase (elastic) material response to applied stress](image)

The other component of material response to applied stress is viscoelastic deformation. This response can be described as
\[ \varepsilon(t) = \eta \omega \sigma_0 \cos(\omega t) \quad \text{or} \quad \varepsilon(t) = \eta \omega \sigma_0 \sin(\omega t + \frac{\pi}{2}) \quad \text{Equation 6} \]

where \( \eta \) is the viscosity.

Equation 6 can be rewritten as

\[ \varepsilon(t) = \omega \varepsilon_0 \cos(\omega t) \quad \text{or} \quad \varepsilon(t) = \varepsilon_0 \sin(\omega t + \frac{\pi}{2}) \quad \text{Equation 7} \]

The resultant strain data from the viscoelastic component described by Equation 7 is displayed in Figure 17. It shows that for a viscous response, the strain data lags, or is delayed behind the stress data. The lag between the peak of the stress data and the peak of the strain data along the time axis is known as the phase lag, \( \delta \). The phase lag is given as an angle due to the trigonometric nature of the stress and strain data.

\[ \sigma(t) \]
\[ \varepsilon(t) \]

\[ \Delta \text{Phase Lag} = \pi/2 = 90^\circ \]

\[ \tau(t) \]

\[ \tau(t) \]

\[ \tau(t) \]

\[ \tau(t) \]

**Figure 17 Out-of-phase (viscoelastic) material response to applied stress**

Most materials will have strain deformation and recovery that is in between the elastic and viscoelastic extremes, therefore an equation is required that models this strain data. This equation[133] is

\[ \varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta) \quad \text{Equation 8} \]

Strain data modelled with Equation 7 is shown in Figure 18.
By separation of variables via trigonometric laws, the following equation can be determined:

\[
\varepsilon(t) = \varepsilon_0 [\sin(\omega t) \cos \delta + \cos(\omega t) \sin \delta]
\]  

Equation 9

From Equation 9, the viscoelastic and elastic components of a material can be described as the in-phase (\(\varepsilon'\)) and out-of-phase (\(\varepsilon''\)) components respectively, denoted by

\[
\varepsilon' = \varepsilon_0 \sin(\delta)
\]

Equation 10

and

\[
\varepsilon'' = \varepsilon_0 \cos(\delta)
\]

Equation 11

If the vector sum of Equations 9 and 10 is taken, the resultant equation is

\[
\varepsilon^* = \varepsilon' + i\varepsilon''
\]

Equation 12

where \(\varepsilon^*\) is the complex modulus and \(i\) is the complex number \(\sqrt{-1}\).

The complex modulus, \(E^*\), is a complex number and can be resolved into two components describing aspects of material behaviour; a real component representing the storage of energy, denoted \(E'\), and an imaginary component representing the loss of energy, denoted \(E''\). These variables are related trigonometrically[133] as shown in Figure 19.
The $E'$ modulus is a measure of elasticity (instantaneous deformation and recovery). $E'$ is sometimes referred to as the tensile (or flexural, shear, compressive) modulus due to the geometry of mechanical analysis, as described in a following section. $E'$ can be described\[134\], as seen in Equation 13, as

$$E' = \left( \frac{\sigma_0}{\varepsilon_0} \right) \cos \delta$$  \hspace{1cm} \text{Equation 13}$$

The value of $E''$ is a measure of viscoelasticity (time dependant deformation and recovery). It relates to the amount of energy a material will lose due to molecular and segmental motion and friction during recovery from deformation. $E''$ can be described\[134\] as

$$E'' = \left( \frac{\sigma_0}{\varepsilon_0} \right) \sin \delta$$  \hspace{1cm} \text{Equation 14}$$

When stress and strain data are compared, there is a lag between them given as an angle, $\delta$. When the tangent of this phase angle is taken ($\tan \delta$), the result is known as damping. Damping is the efficiency at which a material will lose energy and is the ratio of the loss to storage modulus, i.e.

$$\tan \delta = \frac{E''}{E'}$$  \hspace{1cm} \text{Equation 15}$$

The $E'$ and $E''$ moduli are usually used to describe modulus values obtained from mf-TM with tensile geometry. Changing the specimen analysis geometry probe will result in different modulus values. The different types of sample configurations are shown in Figure 20.
other moduli from different dynamic mechanical analysis deformation geometries include shear moduli (G*), compressive (E*) and flexural (E* or M*)[12]. Like the complex modulus these moduli can be resolved into real, in-phase and imaginary, out-of-phase components.

![Different modes of deformation in dynamic mechanical analysis](image)

**Figure 20 Different modes of deformation in dynamic mechanical analysis**

A modulated force analysis at a single frequency over a discrete temperature range will yield E* data that is usually resolved into its real and imaginary components, and tan δ. Figure 21 represents a typical plot of temperature-modulus and temperature-tan δ data.
Analysis is not restricted to a single frequency and can be performed at multiple frequencies during an analysis. These multi-frequency analyses are sometimes referred to as frequency sweeps. This creates multiple series of data, each representing a single frequency. Multiple frequencies may be tested in succession or extracted from a single pulse of a complex waveform (sometimes termed synthetic frequency.)

Modulated force thermomechanometry has been used to describe a number of material characteristics. Sarkhel and Choudhury employed it to characterise the properties of PE-EPDM based jute fibre composites[135]. Two types of jute-fibre were employed: an untreated jute fibre and a maleic anhydride grafted polyethylene (MAPE) modified jute fibre. It was observed that the storage modulus increased with reinforcement of the PE-EPDM matrix with both types of jute fibre. The damping peaks of treated-jute composites were of a lower magnitude compared with untreated composites and the tan δ values decreased with increases in both fibre content and MAPE concentration.

The dynamic mechanical properties of EPDM rubber blends the damping properties were investigated by Mao et al[136]. The damping properties of EPDM with aliphatic hydrocarbon (C94) resin were found to improve after addition of C94. With increasing content of the resin, the main tan δ peak shifted to higher temperatures and the valid temperature damping range was broadened. An addition of mica or acrylonitrile-butadiene rubber (NBR) was found to widen the effective damping range. With the addition of NBR into EPDM the effective damping range of the blends was evidently extended in the applicable temperature region,
especially when NBR content was 50 %.w/w. The excellent damping performance of the NBR-EPDM system was a result of the dispersed phase of NBR, which acted as a reinforcing filler at low temperatures and showed a distinguished tan δ peak because of its glass transition at room temperature. Moldovan et al used modulated force thermomechanometry in their research into EPDM-HDPE blends with different cure systems[137]. The groups of crosslinking agents used were sulphur, tetramethylthiuram disulfide (TH) and 2-mercaptobenzothiazole (M); sulfur, TH and zinc diethylthiocarbamate (ZDEC); sulfur, TH and diphenylguanidine (D). The composition of HDPE and EPDM was fixed at 50/50 by weight and the ratio cure accelerators/sulfur was varied from 0.4 to 6.34 by weight with the optimal ratio cure of accelerators to sulfur being 6.34 to 1.85. Results showed improved mechanical properties of those crosslinked in comparison with uncrosslinked blends.

The dynamic mechanical properties of polypropylene-EMA blends have been investigated by Genovese, and Shanks[138]. Blends of poly(propylene) (PP) were prepared with EMA having 9.0 and 21.5 %.w/w methyl acrylate comonomer. A similar series of blends were compatibilised by using maleic anhydride grafted PP. Modulated force thermomechanometry showed the crystal-crystal slip transition $T_{a^*}$ and $T_g$ for PP and EMA copolymer occurring at lower temperatures. The storage modulus of plain PP and the blends increased with annealing at 150 °C compared with isothermal crystallization at 130 °C. The storage modulus of the blends for isothermally crystallized PP increased with 5 %.w/w EMA and then decreased with subsequent increase to EMA weight fraction. The $T_g$ of the blends had only a slight change with differing EMA weight fraction.

Characterization of nanocellulose-reinforced shape memory polyurethanes using modulated force thermomechanometry was performed by Auad et al[139]. They observe that the main relaxation of the amorphous soft segment domains (related to the $T_g$ of PU soft segments) was sensitive to the presence of nanocellulose. The $T_g$ was slightly increased (approximately 1 °C) between the highest filled polyurethane (1 %.w/w of nanocellulose) and the unreinforced polymer. The magnitude of the change in tan δ peak with increasing nanocellulose weight fraction was noted. The addition of 0.1 %.w/w of nanocellulose produced essentially no change in the height of the peak. However, the addition of 0.5–1 %.w/w nanocellulose substantially reduced the height of the peak, indicating that less material was taking part in the transition. The change in tan δ peak was larger than expected from a dilution effect with only 1 %.w/w of cellulose. This was an indication of the strong interfacial interactions developed between the nanocellulose and the polymer. The authors noted the increase of $T_g$ was due to
the restricted mobility of amorphous polyurethane chains that resulted from the physical crosslinks induced by crystallization.

The effect of UV and hygrothermal (HT) aging (in accordance with ASTM D1183-05) on the mechanical performance of polyurethane (PU) elastomers were characterised via mf-TM by Aglan and Allie[140]. Mechanical analysis was performed from room temperature to 240 °C. Both storage moduli for UV and HT aged polyurethanes decreased with exposure time, although the storage modulus for the UV-aged PU decreased far more severely than the thermally aged PU. The storage modulus of the 3 mth UV-aged polyurethane decreased to 3037 MPa versus the storage modulus for the unaged material at 3784 MPa at 240 °C representing a decrease of 20%. The storage modulus of the UV-aged PU was observed to decrease by nearly 35% to 2480 MPa after 5 mth of aging. The storage modulus of the HT-aged sample at 5 mth decreased less than 15% to 3232 MPa. The values of tan δ at 240 °C showed that the tan δ for the UV-aged PU increased over the 5 mth duration from 0.033 for the unaged PU to 0.127 for the 5 mth UV-exposed PU. Thus, the loss modulus increased with UV exposure over time. The authors claimed that the loss of elasticity in the material and the increase in the loss modulus were indicative of the UV-aging process. The thermally-aged samples showed a slight decrease in tan δ (hence loss modulus) over time from 0.033 to 0.028. This indicated that the thermally-aged PU lost some of their viscoelastic properties with time but UV aging cause the most severe structural changes.

**Time-temperature superposition**

There are inherent limitations due to instrumental capabilities (e.g. frequencies not accessible by a dynamic mechanical analyser) when mechanically analysing a material. To overcome this problem and describe properties of a material at immeasurable analysis parameters, a method known as time-temperature superposition (TTS) can be employed. In general, TTS is a method of reduced variables that involves the translocation of data relative to a reference temperature[133]. Time-temperature superposition in based upon the principle that mechanical analysis at lower temperatures equates to an increasingly elastic response, whilst mechanical analysis at higher temperatures equates to an increasingly viscoelastic response[16]. Superposition of mechanical data allows for the construction of what are termed mastercurves.
**Mastercurves**

A mastercurve is a series of data that simulates material properties over a time or frequency not usually experimentally feasible[133]. An example of this method is employed with dynamic mechanical data. It involves analysing a material over a range of equidistant, isothermal temperatures at multiple frequencies. The resultant data from these analyses is plotted with dimensions of time or frequency and the desired material property (usually a modulus for dynamic mechanical analysis). A reference temperature is chosen after which data at other analysis temperatures are shifted creating continuous data possessing values for the analysed material property at times or frequencies beyond the original analysis range. The magnitude of the data shift is labelled a shift factor, \( a_T \). Shift factor values are related to relaxation times with respect to temperature[141], as seen in Equation 16 as:

\[
a_T(T) = \frac{\tau(T)}{\tau(T_0)}
\]

*Equation 16*

where \( \tau(T) \) is the relaxation time at a given temperature and \( \tau(T_0) \) is the relaxation time at the reference temperature.

Shift factors are sometimes required for the values of a desired material property to account for the change in density at different temperatures in some materials. This vertical shift factor, \( a_V \) is described in Equation 17 as

\[
a_V = \frac{T_s \rho_s}{T \rho}
\]

*Equation 17*

where \( a_V \) is the vertical shift factor, \( \rho_s \) is the density of material at the glass transition temperature, \( T \) is temperature and \( \rho \) is the density at \( T \).

Most mastercurves are based upon the time-temperature superposition principle. Dotson et al used mastercurves based upon simulated mechanical data modelled with the Kohlrausch Williams Watts equation in their research concerning the rheological complexity in simple chain models[142]. They found that for all cases a time-temperature master curve could be constructed even though the \( \beta \)'s (stretching exponents) for the individual response curves at each temperature varied systematically, while the onset of non-mastercurve behaviour appeared to be associated with the development of orientational hopping motion.

Mastercurves were employed by Zhoa et al in their research concerning the applicability of the time-temperature superposition principle in modelling dynamic response of a
polyurea[143]. The $T_g$ of polyurea (-49 °C) was used as the reference temperature for the mastercurve construction and it was observed that the mastercurve had good continuity between all data except at the highest analysed temperature (approximately 20 °C) due to higher mobility of molecules at this temperature. Cheng and Yang investigated the application of the time–temperature superposition principle to the transition kinetics of poly(N-isopropylacrylamide) in aqueous solution[144]. The resultant mastercurve data possessed dimensions of intrinsic viscosity ($\eta$) and logarithmic time, the reference temperature was taken at 304 °K. Mastercurves were modelled with an Arrhenius-like equation based upon reaction kinetics. From this modelling it was concluded that the reverse reaction of a globule to coil transition should be retarded, indicting that that the coil–globule transition of poly(N-isopropylacrylamide) in an aqueous solution was essentially a two-stage process.

Mastercurves were used by Nicolai et al to describe the viscoelastic relaxation of polyurethane at different stages of the gel formation[145]. The storage modulus master curves of polyurethanes at different stages of the gel formation were formed with a reference temperature of 5 °C above $T_g$. At high frequencies all the mastercurves showed the typical transition to solid-like behaviour plateauing at the same modulus value. At very low frequencies the extent of gel formation was proportional to the modulus values; the higher the gel formation the greater the modulus values. For polyurethanes containing gel content of 0.574 to 1 (where 1 is equal to fully grown gel) a terminal modulus was observed. Jahromi et al created mastercurves from shear mechanical data in research on the rheology of side chain dendritic isocyanates[146]. Mastercurves were constructed with a reference temperature at 80 °C. It was observed that the loss modulus was almost equal whereas storage modulus decreased as the generation number increased for polyisocyanates based on 1, 6-hexamethylene diisocyanate. It was stated that the size of the side groups did not markedly affect the viscoelastic part of the complex modulus but did modify the elastic contribution. This was attributed to the fact that the extent of intermolecular interactions, such as hydrogen bonding between urethane bonds in the main chain diminished as the isocyanates become more shielded by the surrounding dendritic side groups.

**Williams Landel Ferry shift factor model**

Shift factors and mastercurves are intrinsically related. Models have been created to describe the relationship between shift factors and temperatures that form mastercurves based upon TTS. The classic model for shift factors is the Williams Landel Ferry (WLF) model[147]. The WLF model is based upon the Doolittles theory of free volume, as seen in Equation 18 as
\[ \eta = B \times e^{\left( \frac{\beta}{v_f} \right)} \quad \text{Equation 18} \]

Where \( \eta \) is viscosity, \( B \) is a pre-exponential coefficient, \( \beta \) is an empirical constant often approximated to 1, \( v^* \) is the void volume required in order to jump-activate a chain segment and \( v_f \) is free volume. If the viscosities are taken at two temperatures, they can be written as

\[ \frac{\eta_1}{\eta_2} = \exp \left[ \frac{v^*}{v_f1} - \frac{v^*}{v_f2} \right] \quad \text{Equation 19} \]

If the free volume is defined as \( v_{f2} = v_{f1} + v_m \Delta \alpha (T_2 - T_1) \), where \( v_m \) is the unavailable volume and \( \alpha \) is the coefficient of thermal expansion, and the natural log is taken then at \( T_g \) Equation 19 becomes

\[ \ln \frac{\eta_1}{\eta} = \left( \frac{v^*}{v_{g1}} \right) (T - T_g) \quad \text{Equation 20} \]

where \( \eta_g \) is the viscosity at \( T_g \), \( v_g \) is the free volume at \( T_g \) and \( T \) is temperature. By taking the base ten log of Equation 20, it can be re-written in the classical WLF equation form of

\[ \log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad \text{Equation 21} \]

where \( \log(a_T) \) is the shift factor, \( T_r \) is temperature of the reference curve, \( C_1 \) and \( C_2 \) are numerical constants for the analysed material relating to free volume expansion (as seen in Equation 20).

To determine the numerical constants \( C_1 \) and \( C_2 \) in Equation 21 two methods can be employed. The first is a regression to find the best-modelling values for the shift factors. The second method involves plots of \( (T - T_r)/\log(a_T) \) versus \( (T - T_r) \). A linear relationship should be observed if the values are valid. From this plot, \( C_1 \) and \( C_2 \) can be derived via

\[ \text{If } y = mx + c, \text{ then:} \]

\[ C_1 = -\frac{1}{m}, \quad C_2 = \frac{c}{m} \]
Ideally the former method for determining the values of $C_1$ and $C_2$ is the most appropriate as it free from possible numerical artefacts and deviation in experimental results[148].

The WLF model is said to only apply over the temperature range from $T_r$ to $T_r + 100 \, ^\circ C$. Outside this range linearity in the aforementioned plot will be lost and data becomes convoluted due to increased mobility of molecules. Usually the reference temperature is designated as a material’s $T_g$.

The WLF model has been used extensively to model the shift factors derived from analysis of a range polymers. Abraham et al employed the WLF model in their research on the dynamic mechanical thermal analysis of copolymers comprised of all polypropylene (PP) [149]. $\alpha$-PP tapes were used as reinforcement in a $\beta$-PP based matrix. They found that the WLF equation was suitable to describe the temperature dependence of the shift factors of the mastercurve created from mechanical analysis of both beta and alpha polymorphic forms.

Research conducted by Schantz et al in poly(methyl methacrylate-co-ethyl acrylate) latex particles with poly(ethylene glycol) grafts employed the WLF model to aid with describing structure and film formation[150]. The model was found to accurately model shift factors derived from shear dynamic mechanical analysis mastercurve and an atomic force microscopy (AFM)-with force indenter attachment master plot. The researchers used a reference temperature of $25 \, ^\circ C$ and, $C_1$ and $C_2$ values of 11.2 and 65.2 respectively to model the mastercurve shift factors and AFM master plot data.

The rheological behaviour of polyhedral oligomeric silsesquioxane -polyurethane-urea nanocomposite films prepared by homogeneous solution polymerization in aqueous dispersions was researched by Madbouly et al[151]. They used the WLF model to model mastercurve data. It was observed that at higher temperatures a strong deviation from the master curve at the terminal zone of $G'$ was observed, and the WLF superposition principle was no longer valid in this temperature zone. They claimed that it was attributed to the fact that the polyurethane chemical structure is a multiblock copolymer comprised of alternating soft polyester and hard polyurethane-urea segments. These two segments undergo microphase separation into hard and soft phases respectively, below and above their glass transition temperatures. The $G''$ mastercurve data did not show any deviation in the terminal zone of the master curve, indicating that the stress induced in the system by the concentration fluctuations accompanying the microphase separation transition is mostly elastic in origin.

Le Huy and Evrard have previously researched methodologies for lifetime predictions of rubber (including EPDM) using Arrhenius and WLF models[152]. They used the WLF model
to predict polymer lifetimes when aging was controlled by a viscoelastic process (relaxation, creep). In particular they used creep analysis of styrene-butadiene-rubber-natural-rubber composites. The WLF model was used in research into the effect of molecular relaxation of acrylic elastomers on impact toughening of polybutylene terephthalate by Mekhilef et al[153]. $\tan \delta$ was used for WLF modelling. Within the analysis frequency range studied the WLF plots of the two analysed polymers (poly(ethyl hexyl acrylate) and poly(n-octyl acrylate)) coincided with each other, and there was no apparent sign of divergence suggesting that if extrapolated to higher frequencies, the peak $T_g$ value of the two polymers should still be very similar. This research used a variant of the WLF model incorporating the $T_g$ of the analysed materials into the model equation. $C_1$ and $C_2$ values obtained were 60 and 14 respectively, in fair agreement with the well-established empirical values of $C_1 = 51.6$ and $C_2 = 17.44$.

Zlatanic and Petrovic used the WLF model in the research into the viscoelastic properties of polyurethanes based on model triglycerides and polyurethanes[154]. Mastercurves were constructed for all materials covering a frequency range of more than 35 logarithmic decades via time temperature superposition. The temperature dependence of the shift factors was well modelled by the WLF model. The fractional free volume at the $T_g$ of the triolein-based network was calculated from $C_1$ and $C_2$ of the WLF equation and was more than two times higher than the fractional free volume of the trilinolein-based polyurethane. This was attributed to increased flexibility due to presence of dangling chains in the triolein-based network. Choi et al employed the WLF model in research into the effect of endgroup modification on dynamic viscoelastic relaxation and motion of hyperbranched poly(ether ketone)s[155]. They used the WLF model to model the shift factors derived from mastercurves constructed from the shear dynamic mechanical analysis data of the four materials. The materials were fluoro-terminated hyperbranched poly(ether ketone) (FHPEK) with their end groups modified with alkyl compounds of different chain lengths, i.e., hexyloxy (C6), dodecylxyloxy (C12), and octadecyloxy, (C18), to produce alkyl-modified HPEKs (HPEK-C6, HPEK-C12, and HPEK-C18, respectively). The temperature dependence of the shift factors was adequately modelled by the WLF model. The resultant $C_1$ and $C_2$ values were for FHPEK; 5.6 and 98, HPEK-C6; 5.1 and 97, HPEK-C12; 4 and 83, HPEK-C18; 5.8 and 101. From $C_1$ and $C_2$ values activation energies were calculated showing a decrease in activation energy with increasing temperature. However, at each temperature it was evident that the apparent activation energy of FHPEK was larger than that of the alkyl-modified HPEKs. The authors claimed this was due to the increase in free volume by substituting polar chain-ends of FHPEK into a nonpolar hydrophobic alkyl chains, acting as internal plasticizers.
Whilst the WLF model is an efficient model for predicting material response, there are limitations to its application. Not all materials will show similar predicted and actual responses due to chemical composition, levels of crosslinking and effects of temperature change. Other models have been developed for the interpretation and application of shift factors.

**Vogel Fulcher Tammann Hesse equation**

This Vogel Fulcher Tamman Hesse (VFTH) equation was constructed[156] from research conducted by Vogel[157], Fulcher[158], Tamman and Hesse[159]. It was originally designed to model the temperature dependence of viscosity for glass-forming liquids (i.e. only applicable for amorphous polymers). The modern interpretation of the VFTH equation is given as

$$
\tau(T) = \tau_0 \exp \left( \frac{B}{T - T_0} \right) \quad T_0 < T_g
$$

where $\tau(T)$ is the relaxation time as a function of temperature, $\tau_0$ is a pre-exponential factor, $B$ and $T_0$ are material specific parameters and $T_g$ is the glass transition temperature. The aforementioned relationship between shift factors and relaxation time (Equation 16) allows for the VFTH equation to model shift factor data as employed by Ferri and Lomellini[160]. They employed the VFTH equation to model the shift factors of mastercurves created from shear modulus data of melt rheology of randomly branched polystyrenes. It was stated that the $B$ parameter physically represents an Arrhenius-like temperature dependent activation energy called the *apparent activation energy* while $T_0$ represents the so called *ideal glass transition temperature*. They observed that the value of the apparent activation energy $B$ slightly increased with an increasing degree of branching and that greater temperature sensitivity of branched polystyrenes resulted in a greater $B$ value.

Alves et al employed the VFTH equation in their investigation into the molecular mobility in polymers studied with thermally stimulated recovery[161]. Mastercurves were constructed from shear modulus data obtained from dynamic mechanical analysis of poly(ethylene terephthalate) (PET) and the VFTH equation was used to model relaxation times calculated from shift factors used to construct mastercurves. They reported that the $\tau_0$ parameter was seen as a microscopic quantity related to the frequency of attempts to cross some barrier opposing the rearrangement of particles involved in the relaxation, or the time a molecule needs to move into some free space and $T_0$ is the diverging temperature implying the physical
impossibility of configurational changes in the solid, close to the Kauzmann temperature (the
temperature at which the difference of entropies between the liquid and solid becomes
zero)[162]. Their research found that the VFTH equation was useful for extrapolating the
characteristic relaxation times at temperatures above which analysis was performed.

The possibility to observe a compensation effect around the glass transition temperature was
investigated by Neagu et al[163]. They used the VFTH equation to study the compensation
effect near the glass transition obtained from dielectric analysis. It was observed there was a
relationship between activation energy, the temperature of the maximum current ($T_m$), the
VFTH temperature ($T_0$), the compensation temperature ($T_c$), and $\tau_0$.

Liu et al employed the VFTH equation in their research on the influence of long-chain
branching on linear viscoelastic properties and dielectric relaxation of polycarbonates[164].
They modelled the dielectric loss curve peak frequency data at various temperatures for a
linear polycarbonate and three branched polycarbonates. It was observed that the $\alpha$-relaxation
process (given as an activation energy $E_a$) could be expressed in terms of the $B$ and $T_0$
parameters in the VFTH equation.

**Expanded Van’t Hoff equation**

A shift factor model has been devised from recent research[165]. It is based on the Van’t Hoff
equation, given in Equation 23 as

$$\frac{d(\ln \dot{\varepsilon})}{dT} = \frac{E}{RT^2}$$  \hspace{1cm} \text{Equation 23}

Where $\varepsilon$ is the strain rate, $E$ is the change in specific enthalpy, $R$ is the universal gas constant
and $T$ is the temperature. Via a relation with Arrhenius equation, this equation was expanded
empirically as shown in Equation 24

$$\frac{d(\ln \dot{\varepsilon})}{dT} = \frac{A}{1 + C(T-T_g)^2}$$  \hspace{1cm} \text{Equation 24}

then integrated to give an arctan-based equation, described by Equation 25 as

$$\ln a_T = \frac{\int_{T_0}^{T} \frac{A}{1 + C(T-T_g)^2} dT = \frac{A}{\sqrt{C} \left[\arctan(\sqrt{C}(T-T_g)) - \arctan(\sqrt{C}(T_0-T_g))\right]} \hspace{1cm} \text{Equation 25}$$
where $A$ and $C$ are material dependant parameters $T_0$ is the reference temperature and $T_g$ is the glass transition temperature.

### Modelling of mechanical data

Models can be employed to model mechanical data such as strain and modulus as with shift factor data. Models such as the Fuoss-Kirkwood\[166\] empirical expression, as seen in Equation 26, is used to model the modulus at different relaxations.

\[
E = \sum_{i=\delta,\gamma} E''_{\text{max},i} \sec h \left( m_i \frac{E_{\text{a},i}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{max},i}} \right) \right)
\]

Equation 26

where $E$ is the modulus, $E_a$ is activation energy, $R$ is the universal gas constant, $T_{\text{max}}$ is the temperature where $E''$ has a maximum value and $m$ is a parameter ($0 < m \leq 1$) that is related to the broadness of the peak.

### Relaxation times

Mechanical analysis data can provide the strain and/or modulus data, but it does not give any indication of the time scale involved in these material responses. Therefore models have been used to describe an important component of mechanical analysis data, known as the relaxation time.

The relaxation time of a system is usually described as being the time-dependent response of that system to a defined external source. The specific meaning of a relaxation time is interchangeable and is dependant upon the area of research to which it is being applied. For example in RC (resistor-capacitor) circuits, relaxation time is equivalent to the time taken by a capacitor to discharge $1 - 1/e$ (approximately 63%) of its total, output voltage. In an astronomical sense, relaxation time is related to interactions between clusters of gravitational systems including star, galaxy and globular clusters.

Initial relaxation analysis was conducted using mostly dielectrics. Results obtained from dielectric analysis were in the form of $\varepsilon^*$, the dielectric constant can be used to calculate the relaxation time. The dielectric analysis relaxation time is defined as the time required for the moments to revert to a random distribution after the removal of the impressed (electric) field\[1\].

Relaxation times are not exclusive to dielectric analysis and can be obtained from both static and dynamic mechanical analysis. The definition of a relaxation time is usually given as the
amount of time for the strain to recover to 63.21% (or 1 - 1/e) of its original value after the removal of applied stress for static mechanical analysis. In dynamic analysis, the relaxation time is equivalent to the amount of time that the system (material, polymer, composite, etc) being analysed takes to fully recover after the removal of applied stress. Various models have been developed to determine relaxation time and other important characteristics from static and dynamic analysis data.

**Static force relaxation models**

Unlike dynamic mechanical analysis, static mechanical analysis does not resolve its resultant data; the output is a single strain (or in some cases a, stress) value. This is problematic as each individual strain value can be a sum of elastic, viscoelastic and viscous deformation. Various models have been developed to calculate the contributions of these various modes of deformation to strain values. The following models specifically model creep data, however in some models there is a requirement for using data from both analysis phases when only modelling a single phase.

**Maxwell model**

One of, if not the first model developed to model creep data was the Maxwell model developed by James Clerk Maxwell published in his book ‘Materials and Matter’ in 1876. The previously mentioned Hookean spring or a Newtonian viscous dashpot had been used to model mechanical deformation in a material; with poor results as materials do not usually exhibit these ideal behaviours. Maxwell suggested[134] that a spring and dashpot in series, representing and combining the Hookean and Newtonian deformation would better represent mechanical deformation. The Maxwell model is given[12] in Equation 27 as:

\[
\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta_E}
\]

where \(\varepsilon\) is the strain, \(t\) is time, \(E\) is the instantaneous modulus (elastic deformation), \(\sigma\) is the stress and \(\eta\) is the viscosity (viscous deformation).

Since the model was being applied to creep strain data, this meant that

\[
\frac{d\varepsilon}{dt} = \frac{\sigma_{E,0}}{\eta_E}
\]

Equation 28
Equation 28 was integrated from 0 until some time \( t \), and divided by \( \sigma_0 \) to give[134] Equation 29:

\[
\varepsilon(t) = \frac{\varepsilon_0}{\sigma_{E,0}} + \frac{t}{\eta_E} \quad \text{Equation 29}
\]

From Equation 29 it is seen that the term \( \varepsilon_0 / \sigma_{E,0} \) is equal to the instantaneous deformation in response to an applied force. The \( t / \eta_E \) term is equated to the viscous deformation, which is time dependant as indicated by possessing, \( t \) the time variable. Figure 22 represents typical data as modelled by a Maxwell element, spring-and-dashpot in series.

**Figure 22** Ideal creep and recovery data as described by the Maxwell model as a spring and dashpot in series, recreated from Menard[133]

**Voigt, or Kelvin model**

The Voigt, or Kelvin model is named after Woldemar Voigt[167] and William Thomson, 1st Baron Kelvin also known as Lord Kelvin. The Maxwell model, like the Voigt model, is based on the theory that mechanical deformation is a combination of the Hookean and Newtonian deformation. However they differ in that the Voigt model postulates that these deformations are in parallel rather than series. In the description[12] of this model the spring and dashpot deformations will operate together as they are in parallel. Deformation in response to stress will occur at a varying rate due to the stresses being shared between the spring and dashpot elements, i.e. deformation is entirely viscoelastic (time dependant). Combining Equations 1 and 2 for a Hookean spring and Newtonian liquid[16] respectively, Equation 30 was formed:
\[ \sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \]  \hspace{1cm} \text{Equation 30} \\

where \(\sigma\) is stress, \(E\) is the modulus (i.e. the spring constant of a Hookean spring), \(\varepsilon\) is strain, \(\eta\) is viscosity and \(t\) is time.

Via integration and rearrangement[12] the strain of this can be equated to, as seen in Equation 31 as,

\[ \varepsilon = \frac{\sigma}{E} \left(1 - e^{\frac{-t}{\tau}}\right) \]  \hspace{1cm} \text{Equation 31} \\

where \(\tau\) is the retardation time equivalent to \(\eta / E\).

The retardation time is equivalent to time taken for strain to reach \(1 - 1 / e\) of its equilibrium value during the creep phase. Figure 23 describes a typical strain response to an applied force modelled by the Voigt, spring-and-dashpot in parallel. The Voigt model has been compared with various other mechanical analysis data models (Maxwell model, operator equation, mechanical impedance function, creep curve, relaxation curve, and dynamic modulus function) for their suitability of modelling static and dynamic mechanical data by Alfrey and Doty[168]. Their personal preference was for the Voigt model but found that the Maxwell model was good at modelling mechanical data. It was concluded that the best approach to modelling mechanical analysis data was to model both dynamic (short time) and static (long time) data resulting in a series of parameters describing a wide time scale from the fastest frequency to the creep time.

Kudrna and Janacek used the Voigt equation to model the creep behaviour of polycaproamide fibres in various stages of homogeneous cold drawing[169]. They observed the dependence of the two parameters of the Voigt model (\(\eta\) and \(\tau\)) on the magnitude of deformation before onset of actual creep in partially oriented fibres at large tensile. The resultant strain indicated that the deformation consisted of destruction of microscopic regions, accompanied in a later stage by microcrack formation.

The Voigt model was employed to investigate the effects of creep and recovery on the dynamic properties of an unfilled and filled crosslinked maleic-type polyester dissolved in styrene with glass bead filler by Katz and Smooha[170]. It was found that in the case of lower stresses (150 and 175 kg.cm\(^{-2}\)) the Voigt model element in series with a viscosity dashpot characterized well the recoveries in both static and dynamic mechanical data whereas in the
case of the highest stress (193 kg cm⁻²) another Voigt model element was required in order to accurately describe the recoveries.

The Voigt model has been incorporated to form what is called the Terzaghi-Voigt combined model as used in the research of Christensen and Hinge about the influence of creep on cake solid volume fraction during filtration of core-shell particles[171].

![Figure 23 Ideal creep recovery data as described by the Voigt model as a spring and dash pot in parallel recreated from Menard[133]](image)

**Burgers or Maxwell-Voigt or 4 Element model**

The Maxwell and Voigt models assume material deformation under static mechanical analysis to be elastic and viscous, and viscoelastic respectively. However material deformation is a combination of elastic, viscoelastic and viscous deformation. Therefore a model combining all of these modes of deformation would be expected to more accurately model strain data than either the Maxwell or Voigt models. The first such model was the Burgers model, named after Johannes Martinus Burgers who developed this model in 1936[172]. The theory behind this
model was that a material deformation to applied force during a creep analysis is equivalent to all the aforementioned modes of deformation. Burgers model is described in Equation 32 as

\[ \varepsilon = \left( \frac{\sigma}{E_1} \right) + \left( \frac{\sigma}{E_2} \left( 1 - e^{-\frac{t}{\tau}} \right) \right) + \left( \frac{\sigma}{\eta_3} \right) t \]  

**Equation 32**

where \( \varepsilon \) is the strain, \( \sigma \) is the stress, \( E_1 \) is the elastic modulus of resistance to elastic deformation, \( \tau \) is the retardation time equal to \( \eta_2/E_2 \), \( E_2 \) and \( \eta_2 \) are the elastic and viscous contributions to resistance to viscoelastic deformation respectively, \( t \) is time and \( \eta_3 \) is the viscosity equated to irreversible flow.

The various modes of deformation modelled by the Burgers model as an arrangement of a spring (elastic deformation, \( E_1 \)), followed by a spring and dashpot in parallel (viscoelastic deformation, \( E_2 \) and \( \eta_2 \)) followed by a dashpot (viscous deformation, \( \eta_3 \)). Typical strain data modelled by Burgers model is represented in Figure 24. The Burgers model is known by other names such as the 4-element and Maxwell-Voigt model, and has been used to model the creep behaviour of EPDM as seen in the research conducted by Osanaiye and Adewale[173]. They employed a sandwich rheometer to measure the creep and recovery properties of EPDM and subsequently model creep data with Burgers model. It was observed that the \( \eta_3 \) viscosity modulus was \( 2.01 \times 10^7 \) Pa.s, \( G_1 \) shear modulus was 0.2077 Pa, \( G_2 \) shear modulus was 50,000 Pa and the \( \tau \) retardation time was 450 s. It was noted that for a polymer with many chains a single retardation time does not represent a realistic description of its viscoelastic compliance. The researchers proposed a model based upon Burgers model for relaxation analysis employing the same parameters.

Effect of mold temperature on the long-term viscoelastic behaviour of poly(butylene terephthalate) (PBT) was investigated with the use of Burgers model by Bantik and Mennig[174]. They observed with increasing mold temperature (14, 40 and 60 °C) \( E_1 \), \( \eta_2 \), \( \eta_3 \) increased and \( E_2 \) decreased. The increase in \( E_1 \) was attributed to the stiffening of the material when PBT is processed at higher mold temperature, while the results for \( E_2 \), \( \eta_2 \), \( \eta_3 \) were attributed to a decrease in viscosity as the mold temperature decreased. These observations were correlated to the microstructure developed in the molded parts, i.e. higher crystallinity as well as molecular packing in the specimens processed at higher mold temperature of 60 °C. This was expected to occur with an increase in the elastic modulus and viscosity manifesting during the creep test with reduced tendency to creep. Perez et al used Burgers model in their research into silicate-starch–polycaprolactone blend nanocomposites[175]. The \( E_1 \) parameter
was observed to have higher values with increasing clay content and lower values with decreasing temperature. This was related to the softening of the material at high temperatures that resulted in a decrease in the stiffness. The $\eta_3$ modulus was observed to increase with increasing clay content but decrease with increasing temperature. Polymer chains were thermally activated and large deformation of crystallized regions and irreversible transitions of amorphous regions took place at higher temperatures. The authors noted that the $\eta_3$ modulus could be related with the damage of crystalline polymer or oriented non-crystalline regions.

Figure 24 Ideal creep and recovery data as described by the Burgers model as a spring followed by a spring and dash pot in parallel, followed by a dashpot recreated from Menard[133]

Lemoine et al have presented a nanoindentation study to detect time-dependent deformations in non-polymeric hydrogenated amorphous carbon films using Burgers model[176]. They stated that term $\eta_3$ represented the constant and incremental disentanglements of chains, the viscous fluid-like steady-state creep as it occurs in liquids and more slowly in glasses, and the breaking of secondary bonds at the molecular level. The term $\eta_2$ corresponded to the disruption of secondary bonds but only those secondary bonds which take part in the covalent scaffold and, therefore cannot result in flow. The tensile creep analysis data of maleated and non-maleated polyethylene–montmorillonite layered silicate blown films were modelled by Ranade et al[177]. The Burger model parameters were greater in the montmorillonite layered silicate (MLS)-polyethylene-graft-maleic anhydride (PE-g-MA) films compared with when there is no PE-g-MA, only PE. The MLS-PE-g-MA maleated PE nanocomposites showed an increase in $E_1$ indicating improvement in the elastic properties of the material. The $\eta_2$ and $E_2$ parameters were analysed to determine the retardation time. They stated that ideal elastic
materials display an immediate recovery after loading and subsequent removal of the load. In
the case of viscoelastic materials there is time dependent recovery. Retardation time is the
delayed response to an applied force or stress. The maleated PE nanocomposites showed
smaller retardation times compared with non-maleated nanocomposites.

**Kohlrausch-Williams-Watts function**

The Burgers model is employed to model creep strain data and must account for the elastic,
viscoelastic and viscous material deformation. Models employed to model recovery strain
data need only account for the elastic and viscoelastic recovery (since the viscous deformation
is irreversible, there is no viscous recovery).

The most popular model for modelling relaxation strain data is the *stretched exponential
function*, also known as the Kohlrausch-Williams-Watts (KWW) function. This function is an
empirical description of relaxation rates and can be employed for modelling many physical
properties of complex systems. The first form of the KKW function was developed by the
Rudolf Kohlrausch[178] in 1854 and used to describe the discharge of a capacitor. This form
was used until the research conducted by G. Williams and D.C. Watts[179] in 1971 into the
characterisation of relaxation rates in polymers analysed via dielectrics. They further
expanded the modelling capabilities of the KWW function (and subsequently gave it its name)
by adding the exponential, $\beta$ factor. The form of the KWW function in wide use, is shown in
Equation 33.

$$\phi(t) = A \times e^{-\left(\frac{t}{\tau}\right)^\beta}$$

*Equation 33*

where $\phi(t)$ is a physical relaxation as a function of time, $A$ is a pre-exponential coefficient, $t$ is
time, $\tau$ is a characteristic relaxation time and $\beta$ is the stretched exponential factor where $0 < \beta 
\leq 1$.

The KWW function is applied to data in the time domain, which allows it to adequately
model recovery strain data. This form however prevents it being applicable to dynamic
mechanical data (as this data is frequency based). To counter this problem a Fourier transform
is performed[180] to transpose the KWW function from a time domain to a frequency
domain. The transposed KWW function is given in Equation 34 as

$$\frac{E^*(\omega) - E_\infty}{E_0 - E_\infty} = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{(\omega \tau)^n} \times \frac{\Gamma(n \beta + 1)}{\Gamma(n + 1)} \times \left( \cos \beta \frac{n \pi}{2} - i \sin \beta \frac{n \pi}{2} \right)$$

*Equation 34*
where $E^*$ is the complex modulus, $E_\infty$ is the infinite modulus (modulus at infinite frequency), $E_0$ is the zero modulus (modulus at zero frequency), $\omega$ is the frequency, $\tau$ is the characteristic relaxation time, $\beta$ is the stretched exponential factor, $n$ is the $n^{th}$ iteration, $\Gamma$ is the gamma function and $i$ is $\sqrt{-1}$. Frequency to time domain transforms for the KWW function have been performed by Havriliak and Havriliak[181].

The KWW function has been used extensively to model relaxations of polymers. Dotson et al conducted research about the rotation of molecular segments of supercooled glassy liquids under an applied force[142]. They noted that $\beta$ decreases as the relaxation time of the system increases, indicating that $\beta$ is a measure of the distribution of relaxation times. This meant that the distribution of relaxation times broadens as the glass transition is approached. The ideal glass transition was found to correspond to the limit of $\tau = \infty$.

Wu and Xu employed the KWW equation to model Legendre polynomials with respect to time obtained from molecular simulations of epoxy resins[182]. They used the KWW equation since the time-correlation functions of bond reorientation were not simple exponential ones and were modelled well by the stretched exponential function. The found that all the average relaxation times increased with the decreasing temperature, especially at 450 °K where this parameter increased by almost one order of magnitude. This was associated with glass transition of the polymer system.

The research conducted by Pang et al used a combined Weibull-KWW equation to model the viscoelastic recovery force data with respect to time of nylon fibres[183]. It was observed that the force growth rate decreased with increasing time, reflected in the $\beta$ value being less than 1. They summarized that their results were perhaps consistent from the viewpoint of a molecular network, that this function was associated with jump processes that may be governed by a hierarchy of constraints, despite the combined Weibull-KWW equation having no real theoretical basis.

Konyali et al investigated the modelling of long time stress relaxations of compounded natural rubber with the KWW equation[184]. They stated that the KWW equation in phenomenological theories may be taken as an indication of serial cooperativity where different pathways of relaxation exist in which one relaxation step depends on the occurrence of another. Or as stated in another way, relaxation goes through hierarchically constrained steps: sudden stretching of the network causes an affine-like deformation of chains. Chains deformed in this manner do not relax all at once. A group of chains relax first, this induces the relaxation of others, through network connectivity. Thus, according to this interpretation, relaxation propagates from one junction to its topological neighbours in a serial manner.
The torque Mooney viscosity of various rubbers was modelled with various models including the KWW equation, the others being the Maxwell, Wu–Abbott and Power law models, by G. Dean[185]. He found that the KWW equation was least well adapted for modelling the experimental data, however it still had an average $r^2$ value of 0.97 for modelling the data.

K.S. Fancey analysed the creep and recovery analysis data of nylon, propylene and polyether-ether-ketone with a Weibull-based equation similar to that of the KWW equation[186]. He stated that A pre-exponential parameter was equated to the initial viscoelastic strain on recovery after creep that the pre-exponential factor equated to initial viscoelastic recovery after removal of an applied force.

Other models

**Standard linear model**

The standard linear model (SLM) is a hybrid model comprised of the Maxwell and Voigt models. Unlike Burgers model, the SLM is based upon the theory that deformation in response to an applied force is equated to either a spring followed by a spring and dashpot in parallel, or a parallel arrangement of a spring and spring and dashpot in series, as seen in Figure 25. This model is usually attributed[12] as first being used by Zener[187]. Recent research employing the SLM includes it being adapted to model damping of aluminium[188], the biomechanics of single zonal chondrocytes[189] and predicting the response of the lumbar intervertebral disk to low-frequency vibrations[190].

![Figure 25 The spring and dashpot graphical representations of the Standard linear model](image)

**Eyring dashpot model**

The Eyring equation is based upon transition state theory and relates the reaction rate to temperature. The name of the function is derived from the work conducted by Henry Eyring and has subsequently been adapted to model creep data. The model is based upon the premise[97] that the creep deformation of a material is considered to be an rate activated
process involving the motion of segments of chain molecules over potential energy barriers. The visualisation of this model is of a single dashpot, where the movement of the dashpot is governed by a rate activated process. The Eyring dashpot model is described in Equation 35 as

$$\dot{\varepsilon}_E = \dot{\varepsilon}_{E0} e^{\Delta H / kT} \sinh \left( \frac{\nu \sigma}{kT} \right)$$  \hspace{1cm} \text{Equation 35}$$

where subscript E represents an Eyring process, $\dot{\varepsilon}_E$ is the strain rate, $\dot{\varepsilon}_{E0}$ is a pre-exponential factor $\Delta H$ is the energy barrier, $\nu$ is the activation volume, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $\sigma$ is the applied stress. This model has been used to calculate apparent viscosity related to activation energy[191], modelling stress enhanced yielding[192] and dielectric relaxations[193].

**Ogden model**

The Ogden material model is described as a hyperelastic material (an ideally elastic material whose stress-strain properties are based upon a strain energy density function) model that describes the non-linear stress-strain properties of an analysed material. This model was developed by Ray W. Ogden in 1972[194]. The Ogden model assumes that material behaviour under an applied force can be described by means of a strain energy function, from which the stress-strain relationships can be derived[16]. The materials modelled by the Ogden model are considered to be incompressible, isotropic and strain rate independent. The Ogden model is given in Equation 36 as

$$U = \sum_i \frac{\mu_i}{\alpha_i} \left( \lambda_1^{\alpha_i} + \lambda_2^{\alpha_i} + \lambda_3^{\alpha_i} - 3 \right)$$  \hspace{1cm} \text{Equation 36}$$

where $U$ is the strain energy function, $\mu$ is a material dependant variable, $\alpha$ is a material dependant variable and $\lambda$ is a principle stretch.

Mahmoud et al used a modified Ogden model in their research concerning the degradation and stability of high abrasion furnace black/acrylonitrile butadiene rubber and high abrasion furnace black/graphite/acrylonitrile butadiene rubber under cyclic stress-strain[195]. Their model incorporated a parameter representing the shear modulus, denoted $\mu_1$. The Ogden model was incorporated by Beda in his review of constitutive models for modelling hyperelastic behaviour of incompressible rubbers[196]. Andrew Norris used the Ogden model in his research into a method to analyse electromechanical stability of dielectric
elastomers[197]. He noted that results from uniaxial and for equibiaxial stress application provided further insight into the electromechanical stability model.

**Modulated force relaxation models**

Models used to determine characteristics such as relaxation time (τ) from static force thermomechanometry cannot be used with modulated force thermomechanometry as its data is frequency based (instead of time based), therefore other models must be used. When mf-TM is performed the resultant complex modulus, E* data is obtained. The complex modulus can be represented as a complex number, or Argand diagram in the form of $E^* = E' + iE''$, where the x-axis is real component of E*; the storage modulus and the y-axis is the imaginary component of E*; the loss modulus. A plot of the complex modulus produces a series of data possessing a semi-circular shape. The intercepts on the x-axis of this data are defined as $E_0$ and $E_{\infty}$, the terminal and plateau moduli respectively. The modulated force relaxation time is the time that a system takes to fully recover from an applied force. A number of models have been developed with the relaxation time, and the terminal and plateau moduli being common material parameters between them.

**Debye relaxation model**

One of the, if not first model for determining relaxation times from dynamic analysis was the Debye model[1]. This model was based on the relaxation of dipoles in polar gases and dilute polar liquids in response to an applied electric field. The Debye model is described by Equation 37.

$$
\frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{1 + i\omega\tau} \quad \text{Equation 37}
$$

where $\varepsilon^*$ is the complex dielectric constant, $\varepsilon_0$ is the dielectric constant value at low / zero frequencies (static frequency), $\varepsilon_{\infty}$ is the dielectric constant at high frequencies (infinite frequency), $\omega$ is the angular frequency (where frequency, $\omega = 2\pi f$), $i$ is $\sqrt{-1}$ and $\tau$ is the relaxation time.

As with the complex modulus, the Debye model equation can be resolved in to its real and imaginary components, denoted in Equations 38 and 39[198] respectively as

$$
\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + (\omega\tau)^2} \quad \text{Equation 38}
$$
where $\varepsilon'$ is the dielectric dissipation factor, and

$$
\varepsilon^* = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + (\omega \tau)^2}
$$

\textbf{Equation 39}

where $\varepsilon''$ is the dielectric loss factor.

The graphical representation of a complex modulus on an Argand, or complex plane, takes on a semi-circular shape. The Debye model can therefore be re-written in vector notation as

$$
u + \nu = \varepsilon_0 - \varepsilon_\infty
$$

\textbf{Equation 40}

where:

$$
u = \varepsilon^* - \varepsilon_\infty, \nu = i\omega \tau (\varepsilon^* - \varepsilon_\infty)
$$

The terms $u$ and $v$ are can be thought of as vectors that are perpendicular in the complex plane. Their vector sum is a real value according to Equation 40. The right angle created by the intersection of these two vectors creates a semi-circle whose diameter is $\varepsilon_0 - \varepsilon_\infty$ as seen in Figure 26. The resultant locus[199] (a set of data satisfying the same condition/s) from these vectors is the Debye model representation of the complex modulus as the frequency shifts from infinity to zero.

\textbf{Figure 26 Debye model of complex data}

The relaxation time variable alters the Debye curve locus. Altering the relaxation time will have differing effects on the resultant modelling curve as seen in Figure 27. As $\tau \rightarrow 0$, the
Debye model accuracy at modelling high \( \varepsilon' \) values (as \( \varepsilon' \to \infty \)) is reduced, and as \( \tau \to \infty \), the Debye model accuracy at modelling low \( \varepsilon' \) values (as \( \varepsilon' \to 0 \)) is reduced.

Figure 27 Theoretical Debye model modelling for complex data with \( \varepsilon_\infty = 80 \), \( \varepsilon_0 = 1 \) and varying relaxation times (\( \tau \)) of (a) 5 s, (b) 0.01 s and (c) 100 s

**Cole-Cole relaxation model**

Kenneth S. Cole, continuing from his previous work[200] with Robert H. Cole recognised the shortcomings of the Debye model for modelling dielectric relaxation data. In their research[198], they noted that they had produced and analysed a significant amount of experimental evidence to suggest that the Debye model was inadequate for modelling relaxation data, especially in liquid and solid dielectrics. The Debye model was only efficient in modelling complex modulus data that conformed to an exact semicircular shape (with its centre at \( \frac{1}{2}(\varepsilon_0-\varepsilon_\infty) \) on the \( \varepsilon' \) axis) in the complex plane. A large proportion of the data analysed by Cole and Cole, whilst displaying circular behaviour, had varying symmetries. Therefore a new model was required to adequately model this data.

The angle between the previously defined vectors \( u \) and \( v \) in the Debye model remains constant at 90° (\( \pi/2 \) radians), allowing only for loci with a single symmetry to exist. Cole and Cole introduced a new variable, \( \alpha \) to define the angle between the vectors \( u \) and \( v \) given as \( (1-\alpha)\pi/2 \), as seen in Figure 28. This new angle is equal to half the central angle subtended by the
The new variable, $\alpha$, allows the locus to be a variety of symmetries. Therefore the relationship between the vectors $u$ and $v$, including the variable $\alpha$, can be written as:

$$u + v = u\left[1 + f(\omega)e^{i(1-\alpha)\pi/2}\right] = \varepsilon_0 - \varepsilon_{\infty}$$

**Equation 41**

where $f(\omega)$ is a (real) undetermined function of the frequency and other parameters. Since $e^{i(1-\alpha)\pi/2} = i^{(1-\alpha)}$, and $u$ is equal to $\varepsilon_0 - \varepsilon_{\infty}$[198], Equation 37 can be rewritten as

$$\varepsilon^* - \varepsilon_{\infty} = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{1 + i^{(1-\alpha)}f(\omega)}$$

**Equation 42**

The dependence of the unknown function $f(\omega)$ on the frequency is indeterminable from Equation 42. However, it can be predicted that the $f(\omega)$ function dependence will be on $\omega(1-\alpha)$ since the complex form of the complex modulus results from the initial hypothesis of an applied field[1], written as:

$$E = E_0 e^{i\omega t}$$

**Equation 43**

where $E$ is the force, $E_0$ is the initial force, $i$ is $\sqrt{-1}$, $\omega$ is the number of vibrations in $2\pi$ seconds and $t$ is time.

Due to the $f(\omega)$ dependence upon $\omega$ and Equation 43, any linear operations performed on the frequency ($\omega$) variable must lead to the same operations on the imaginary unit, $i$[198].

![Figure 28 Cole-Cole model of complex data](image)
Therefore the complex modulus can be rewritten as what is recognised as the Cole-Cole (CC) model:

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega \tau)^{-\alpha}}$$  \hspace{1cm} \text{Equation 44}$$

The shape parameter, \(\alpha\) has a value of \(0 \leq \alpha < 1\). The CC model can alternatively be rewritten\[^{[201]}\] as:

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega \tau)^{\alpha}}$$  \hspace{1cm} \text{Equation 45}$$

As with the Debye model, the complex dielectric factor in the CC model can be resolved into its dissipation and loss components

$$\varepsilon' = \varepsilon_\infty + \frac{\left(\varepsilon_0 - \varepsilon_\infty\right)\left[1 + (\omega \tau)^{1-\alpha} \sin \frac{1}{2} \alpha \pi \right]}{1 + 2(\omega \tau)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau)^{2(1-\alpha)}}$$  \hspace{1cm} \text{Equation 46}$$

$$= \varepsilon_\infty + \frac{1}{2} \left(\varepsilon_0 - \varepsilon_\infty\right) \left[1 - \frac{\sinh(1-\alpha)x}{\cosh(1-\alpha)x + \cos \frac{1}{2} \alpha \pi}\right]$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)(\omega \tau)^{1-\alpha} \sin \frac{1}{2} \alpha \pi}{1 + 2(\omega \tau)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau)^{2(1-\alpha)}}$$  \hspace{1cm} \text{Equation 47}$$

$$= \frac{1}{2} \left(\varepsilon_0 - \varepsilon_\infty\right) \cos \frac{1}{2} \alpha \pi$$

$$\cosh(1-\alpha)x + \sin \frac{1}{2} \alpha \pi$$

where \(x = \log_e(\omega \tau)\)

In the CC model, the \(\alpha\) variable allows the broadness (i.e. the symmetry) of the modelling function represented on the complex plane to be altered. As seen in Figure 29, as \(\alpha \rightarrow 0\), the curve takes on a bell shaped symmetry where as \(\alpha \rightarrow 1\), the curve is extremely flat, approaching a linear shape.
Figure 29 Theoretical Cole-Cole model modelling for complex data with $\varepsilon_\infty = 80$, $\varepsilon_0 = 1$, $\tau = 1$ and varying $\alpha$ values of (a) 0.5, (b) 0.1 and (c) 0.9

Cole-Davidson relaxation model

Whilst the CC model accurately modelled some experimental data, there existed other dielectric analysis data that could not be modelled to a satisfactory degree of accuracy. Based upon research conducted during his PhD tenure and subsequently published in journal articles[202, 203], D.W. Davidson together with Robert H. Cole devised an alternative function to model dielectric analysis data. The resultant Cole-Davidson (CD) model is described in Equation 48 as

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + (i\omega\tau)^\beta)}$$

Equation 48

where $\beta$ is a shape parameter.

The CD model possesses a shape parameter termed $\beta$ (as opposed to the $\alpha$ parameter in the CC model). It determines the asymmetry (i.e. skewness) of the CD modelling data represented on a complex plane.

As with the CC model, the Cole Davidson model equation can be rewritten as
\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + (i\omega\tau))^{1-\beta}} \]  

Equation 49

Resolving the CD model equation into its real and imaginary components allows for the modelling of the dissipation and loss factors of dielectric analysis. The resolved equations are represented in Equations 50 and 51 as

\[ \varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)(\cos \varphi)^\beta \cos \beta \varphi \]  

Equation 50

and

\[ \varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)(\cos \varphi)^\beta \sin \beta \varphi \]  

Equation 51

where \( \varphi = \tan^{-1}(\tau_0\omega) \).

The \( \beta \) shape parameter alters the modelling data such that the skewness is shifted closer or further away from the low value end of the \( \varepsilon' \) axis. Figure 30 describes that as \( \beta \rightarrow 0 \), the curve is greatly skewed, where as \( \beta \rightarrow 1 \), and the curve is semi-circular (as with the Debye model data).

![Figure 30 Theoretical Cole-Davidson modelling for complex data with \( \varepsilon_\infty = 80, \varepsilon_0 = 1, \tau = 1 \) and varying \( \beta \) values of (a) 0.5, (b) 0.1 and (c) 0.9](image)
The CD model was used by Baker-Jarvis et al to determine relaxation times of three alcohols (1-propanol, 2-propanol, ethanediol) from dielectric analysis[204]. They studied time-domain differential equations for the polarization and related them to the resulting frequency-domain models of relaxation and resonance. The real and imaginary parts of the relaxation times were observed to depend on frequency, which insightful since relaxation times can be correlated with molecular interactions.

Hronsky et al investigated spin-lattice relaxation times in ultra-high molecular weight polyethylene fibres (undrawn ratio =1, draw ratios = 6, 9, 12, and 15)[205]. They modified the Cole-Davidson to model the $\alpha$, $\beta$ and $\gamma$ relaxation processes to determine which of dynamic-mechanical analysis (DMA), spin-lattice relaxation time (T1-NMR) and broad-line NMR measurements is the most efficient method for characterization of the relaxation processes. They found that DMA was the most efficient while the other two analysis methods provided some complimentary information on fibre-forming processes and those concerning of deformation processes. The $\beta$ shape parameter and relaxation time was observed to decrease with increasing draw ratio.

Gelfer et al investigated the frequency-based mechanical properties by applying a modified Cole-Davidson model to dynamic mechanical data of poly(ethylene-co-vinyl acetate) and poly(ethylene-co-methyl acrylate) nanocomposites[206]. They stated that the complex modulus was comprised of a frequency based and frequency independent component (implying the possibility of viscous energy loss) based upon data modelling results. The mechanical analysis data of the nanocomposites were observed to have decreasing frequency dependence as filler concentration increased. They suggested that these unusual rheological properties observed in nanocomposites were consistent with thermally induced physical gelation.

**Havriliak-Negami relaxation model**

The CC and CD model equations were successful to a degree in modelling dielectric analysis data of polymeric systems, however individually they still displayed shortcomings. S. Havriliak and S. Negami developed[207] the Havriliak-Negami (HN) relaxation model which incorporated both the $\alpha$-broadness and $\beta$-symmetry parameters into a single equation. The HN model equation is written as:

$$
\varepsilon^\ast = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (i\omega\gamma)^\alpha]^\beta}
$$

**Equation 52**
As with the other relaxation model equations, the HN model can be resolved into its dielectric analysis dissipation and loss factors. These are described as

\[ \varepsilon' = \varepsilon_{\infty} + \left( \varepsilon_0 - \varepsilon_{\infty} \right) r^{\frac{-\beta}{2}} \cos(\beta \theta) \]  

Equation 53

and

\[ \varepsilon'' = \left( \varepsilon_0 - \varepsilon_{\infty} \right) r^{\frac{-\beta}{2}} \sin(\beta \theta) \]  

Equation 54

where

\[ r = \left[ 1 + (\omega \tau)^{(1-a)} \sin \left( \frac{\alpha \pi}{2} \right) \right]^2 + \left[ (\omega \tau)^{(1-a)} \cos \left( \frac{\alpha \pi}{2} \right) \right]^2 \]  

and

\[ \theta = \tan^{-1} \left( \frac{(\omega \tau)^{(1-a)} \cos \left( \frac{\alpha \pi}{2} \right)}{1 + (\omega \tau)^{(1-a)} \sin \left( \frac{\alpha \pi}{2} \right)} \right) \]

Considering that the HN is essentially a combination of the Debye, CC and CD models, the HN model equation parameters alter the modelling curve the same as they did in the respective component models. Figure 31 demonstrates the effect of manipulating the \( \alpha \) and \( \beta \) parameters of the HN model equations in parallel.
Figure 31 Theoretical Havriliak-Negami modelling for complex data with $\varepsilon_\infty = 80$, $\varepsilon_0 = 1$, $\tau = 1$ and varying $\alpha$ and $\beta$ values of (a) $\alpha = 0.5$, $\beta = 0.9$, (b) $\alpha = 0.5$, $\beta = 0.1$ and (c) $\alpha = 0.9$ and $\beta = 0.5$

The Debye, CC, CD and HN models were originally conceived to model complex dielectric data (due to their theoretical grounding concerning the relaxation of dipoles) but they were eventually additionally employed to model complex mechanical data. Havriliak and Negami used their model for modelling mechanical analysis data in their research[7, 208] on the equivalence between dielectric and mechanical analysis data. Further research[180] used other models such as the CD model to model mechanical analysis data. However, the most frequently used models for modelling mf-TM data is the HN model[209-212]. The HN model equation is usually rewritten when applied to mechanical analysis data as

$$E^* = E_\infty + (E_0 - E_\infty) \times \frac{1}{[1 + (i\omega \tau)^\alpha]^\beta}$$

Equation 55

where $E^*$ is the mechanical complex modulus, $E_\infty$ is the storage modulus at infinite frequency and $E_0$ is the storage modulus at zero frequency. $E_\infty$ can be estimated from the values of E(modulus) data at low temperatures, high frequencies ($\omega \to \infty$) and $E_0$ can be estimated from E(modulus) data at high temperatures and low frequencies ($\omega \to 0$).
The temperature dependence of $E^*$ must be incorporated to use the HN model to characterize relaxation properties from mechanical and spectroscopic data. Typically, the only variable considered temperature dependant is $\tau$. The temperature dependence of $\tau$ can be accounted for when modelling the HN model to mastercurves. The modulus data in mastercurves has been shifted in relation to a reference temperature; hence it can be seen that all data is associated with a single temperature. Therefore, when $\tau$ is calculated from mastercurves no change in temperature needs to be accounted for since it is from single temperature data. However, Alig et al.[213] claimed that all the parameters in the HN equation are temperature dependant. They proposed the following approach as a method of incorporating temperature dependence into all of the HN model variables. It employed a nine-parameter method when using the HN equation to model mf-TM data. This method involved the use of the VFTH equation (Equation 22) to describe the relaxation time and temperature dependence being incorporated into seven parameters. The $\alpha$ and $\beta$ shape parameters were assumed to be constant and therefore independent of temperature. Alig et al. changed the $T - T_0$ denominator in the VFTH equation to $T_g - T_0$ due to the nature of the experiment. The unrelaxed ($E_\infty$) and relaxed ($E_0$) moduli were assumed to possess a linear dependence on temperature in the form of $E_\infty = a_1T + b_1$ and $E_0 = a_2T + b_2$.

The values for $a_1$, $a_2$ and $b_1$, $b_2$ were obtained from linear modelling of low frequency and high frequency mechanical spectroscopic data. A modelling program was used to select values for $\tau_0$, $\alpha$, $\beta$, B and $T_0$ that would minimize the difference between experimental and calculated modulus data. This process resulted in nine parameters being used to model data; $a_1$, $a_2$, $b_1$, $b_2$ (used to calculate $E_\infty$ and $E_0$), $\tau_0$, $\alpha$, $\beta$, B and $T_0$.

The five-parameter method is commonly used for applying the HN model to mechanical spectroscopic data. There are two approaches that can be taken to model experimental data with the five parameter model. Since the HN model is essentially modelling data on a complex plane (i.e. a combination of real and imaginary values) it can be resolved into real and imaginary components (like $E^*$ data is resolved into its $E'$ and $E''$ components). Therefore, modelling $E^*$ data with the HN model can be achieved by modelling $E^*$ in the form of $E^* = E' + iE''$, or by modelling $E'$ and $E''$ separately with the resolved HN model equations.

Szabo and Keough[214] used a method of directly modelling the four temperature independent HN parameters to the $E^*$ complex modulus, followed by direct calculation of the relaxation time. This HN equation modelling method relied on two fundamental assumptions; the complex plane representation of the modulus was independent of $\tau$, and that the only
temperature dependant parameter is $\tau$. $E^*$ was required to become temperature dependant, in addition to frequency dependence. This was achieved by making the relaxation time temperature dependant.

The first step of this method involved fixing $\tau = 1$ and setting the frequency range (in this research it was $10^{20} - 10^{15}$ Hz). Trial values for $\alpha$, $\beta$, $E_\infty$ and $E_0$ were then selected and adjusted to obtain the highest degree of modelling precision between experimental and HN model calculated modulus data. The degree of accuracy of the modelling was optimised by the use of two error functions, the Cole-Cole error and Wicket error functions. The Cole-Cole error function is based upon a Cole-Cole plot and is described in Equation 56 as

$$f_1 = \frac{\sum E^\prime \left|E^\prime_{\text{exp}} - E^\prime_{\text{calc}}\right|^2}{\sum E^\prime \left|E^\prime_{\text{exp}}\right|^2}$$  \text{Equation 56}$$

where $E^\prime_{\text{exp}}$ is the experimentally determined loss modulus and $E^\prime_{\text{calc}}$ is the calculated loss modulus values. The error function was computed over the range for which overlap occurred between $E^\prime_{\text{exp}}$ and $E^\prime_{\text{calc}}$.

The Wicket error function is based upon the Wicket plot that has $\log(\tan \delta)$ on the y-axis and $\log($storage modulus$)$ on the x-axis. Figure 32 displays a typical Wicket plot of data obtained form mf-TM. The Wicket error function, as given in Equation 22 is

$$f_2 = \frac{\sum E^\prime \left|\log(\tan \delta_{\text{exp}}) - \log(\tan \delta_{\text{calc}})\right|^2}{\sum E^\prime \left|E^\prime_{\text{exp}}\right|^2}$$  \text{Equation 57}$$

where $\tan \delta_{\text{exp}}$ is the experimentally determined damping and $\tan \delta_{\text{calc}}$ is the calculated damping.

Once the optimal values for $\alpha$, $\beta$, $E_\infty$ and $E_0$ had been determined, the relaxation time is calculated via Equation 58.

$$\tau = -i \times \exp \left( \log(\exp(\log(\frac{E_0 - E_\infty}{E^* - E_\infty})/\beta) - 1)/\alpha \right)$$  \text{Equation 58}$$

Since the relaxation time was calculated for each complex modulus obtained at each temperature analysis, the Equation 58 accounted for the temperature dependence of $\tau$. 

Figure 32 Example of a Wicket plot
Chapter 3 Materials and Method

Materials and processing

**Poly(ethylene-co-propylene) diene monomer-alumina composites**

Poly(ethylene-co-propylene) diene monomer (EPDM) rubber (Vistalon 7500) 2.7 \%\textit{mol} 5-ethylene norbornane, ethylene 60 \%\textit{mol}, propylene 37.3 \%\textit{mol}, density of 0.86 g·cm$^{-3}$ was used as supplied from Exxon Mobil corporation. Alumina was employed as filler and was provided in three forms; untreated alumina, alumina coated in sodium dodecyl sulfate (SDS) and alumina coated in SDS and polystyrene (PS). The crosslinking agent/curative used was dicumyl peroxide (DCP) present as 30 \% \textit{w/w in clay and supplied by Olex Australia Pty Ltd. n-Hexane (laboratory grade) was used as a solvent to dissolve EPDM and aid dispersion of filler and crosslinking agent.}

**Poly(ethylene-co-methyl acrylate)-silica nanocomposites**

The poly(ethylene-co-methyl acrylate) (EMA) elastomers that were employed for the synthesis of EMA-silica composites were: EMA 9 \% \textit{w/w methyl acrylate (hardness 35-40 Shore D, melting temperature 93 °C, density 0.93 g·cm$^{-3}$} in pellet form supplied by Sigma-Aldrich, and Lotryl 18MA02 EMA 19 \% \textit{w/w methyl acrylate (hardness 83 Shore A, melting temperature 87 °C, density 0.93 g·cm$^{-3}$} in pellet form supplied by Arkema Inc.

The silica used was Aerosil® 380 hydrophilic fumed silica (average particle diameter 7 nm, density 2.2 g·cm$^{-3}$) supplied by Degussa. Figure 33 displays SEM micrographs of the Aerosil 380 silica. It is evident that the silica agglomerates into different sized particles. Toluene (laboratory grade) was used as a solvent to dissolve EMA and aid dispersion of filler and crosslinking agent.
Figure 33 SEM micrographs of Aerosil 380 at 800X and 4000X magnification

**Thermoplastic polyurethane -silica nanocomposites**

The thermoplastic polyurethanes (TPU) that were employed for the preparation of polyurethane-silica composites were: polyester based Pellethane 2101-85A Polyurethane elastomer, consisting of 1,4-butandiol with poly(tetramethylene glycol), methylenediphenyl diisocyanate, methyloxirane and oxirane (Shore 85A hardness, T\textsubscript{g} of -24 °C, density of 1.13 g·cm\textsuperscript{-3}) and polyether based Pellethane 2103-85AE consisting of methylenediphenyl diisocyanate, 1,4-butandiol and poly(tetramethylene glycol) (Shore 85A hardness, T\textsubscript{g} of -38 °C, density of 1.14 g·cm\textsuperscript{-3}). Both polyurethanes were produced by Dow Chemical Company and supplied by Huntsman International LLC. The preparation of polyurethane-silica nanocomposites was made with Aerosil® 380 hydrophilic fumed silica (average particle diameter 7 nm, density 2.2 g·cm\textsuperscript{-3}) produced by Degussa. Tetrahydrofuran (THF, laboratory grade) was used as a solvent to dissolve the TPUs and aid dispersion of filler and crosslinking agent.

**Ultrasonicator**

The Ultrasonicator employed for the dispersion of crosslinking agents and fillers was an Autotune 500-Watt ultrasonic processor. It possessed a titanium alloy (Ti-6Al-4V) ultrasonic probe that produced a dispersion frequency of 20 kHz with variable amplitude.

**Vacuum oven**

The vacuum oven employed for the synthesis of composites was a Thermo Scientific Labline vacuum oven. It is temperature controlled and capable of a maximum vacuum pressure of 101 MPa.
Hot press

The hot press employed to compression mould and crosslink the EPDM-alumina composites, and compression mould EMA-based polyurethane-based materials was an IDM Instruments laboratory press model number L0003-1 (maximum applied load of 15 tonne, temperature range of ambient to 300 °C ± 2 °C, water as a coolant, platens with maximum separation of 150 mm).

Method - composite preparation

Poly(ethylene-co-propylene) diene monomer-alumina composites

The EPDM rubber was dissolved in hexane and then dicumyl peroxide (curative) was added. The extent of crosslinking in the EPDM was determined by the curative concentration. A series of EPDM films with varying concentrations of curative at 1, 2, 3, 4, 5, 7, 10 phr were prepared. The optimum concentration of dicumyl peroxide to give elasticity was found to be 2 phr.

EPDM rubber was dissolved in hexane and dicumyl peroxide and 30 %.w/w of the desired filler was added to prepare the EPDM-alumina composites. This filler concentration was used because it is similar to concentrations of carbon black used in car tyre formulations[215, 216]. The EPDM-curative-filler mixtures were then sheared to disperse the alumina using ultrasonification for 6 min at a 20 kHz frequency. The composites were cast into films and dried at room temperature for 48 h. They were then placed into a vacuum oven to remove any residual solvent. The composites were cured in a hot press at 150 °C under a load of 1 tonne for 1 h.

Poly(ethylene-co-methyl acrylate) - silica composites

The poly(ethylene-co-methyl acrylate) elastomers were dissolved in toluene with heating (at 70 °C) and stirred with a magnetic stirrer for 10 min. Silica was added to the dissolved elastomer in varying volume fractions (0.1, 0.5, 1, 5, 10 and 20 %.v/v). Preliminary dynamic mechanical analyses determined that the 0.1 and 0.5 %.v/v silica-EMA composites did not significantly change the moduli of unfilled EMA, hence these concentrations were not further analysed.

The dissolved EMA-silica mixtures were ultrasonified for 6 min at a 20 kHz frequency. The ultrasonified EMA-silica dispersions were then poured into a Petri dish and allowed to dry at room temperature for 48 h. The dried composites were subsequently placed into a vacuum
oven to remove any residual solvent. The composites were pressed into films using a hot press at 100 °C for 10 min.

**Thermoplastic polyurethane - silica composites**

The polyurethane elastomers were dissolved in THF and stirred with a magnetic stirrer for 10 min. Silica was added to the dissolved elastomer in varying volume fractions (0.1, 0.5, 1, 5, 10 and 20 %.v/v). The dissolved polyurethane-silica mixtures were ultrasonified for 6 min at 20 kHz frequency. The EMA-silica dispersions were then poured into a Petri dish and allowed to dry at room temperature for 48 h. The dried composites were subsequently placed into a vacuum oven to remove any residual solvent. The composites were pressed into films using a hot press at 175 °C for 10 min and were cut into specimens with shape dimensions of 0.5 × 10 × 8.5 mm$^3$ for creep-recovery and dynamic mechanical analysis, and into films with the shape dimensions of 0.5 × 25 × 10 mm$^3$ for stress-strain analysis.

**Instrumentation**

This section describes the instrumentation that was used in the work presented in this thesis. A detailed description of the experimental parameters and analyses is described.

**Scanning Electron Microscope**

Scanning electron micrographs were obtained on a Phillips FEI Quanta 200 environmental scanning electron microscope (ESEM). This microscope possessed the following instrumental capabilities:

- A high-performance thermal emission- SEM column with dual-anode source emission geometry, fixed objective aperture and through-the-lens differential pumping
- A maximum resolution of 3.0 nm (at 30 kV)
- An accelerating voltage range of 0.2 – 30 kV
- ESEM chamber vacuum of 10 – 2600 Pa
- Beam gas path length: 10 or 2 mm
- An image processor maximum resolution of 4096 x 3536 pixels

**Thermogravimetric Analyser**

The thermogravimetric analyser employed to conduct thermal stability and filler composition analyses was the Perkin-Elmer Pyris 1 TGA. Figure 34 displays a photograph of the
thermogravimetric analyser used to the experiments. This analyser possesses the following instrumental capabilities:

- A temperature range of ambient – 1000 °C
- Scanning rates of 0.1 – 200 °C.min\(^{-1}\)
- A temperature precision of ±2 °C
- The balance has the following characteristics:
  - Sensitivity of 0.1 µg
  - Accuracy higher than 0.02 %
  - Precision of 0.001 %
- A maximum pan capacity of 1300 mg
- An ion stream creates a curtain of charged particles surrounding the sample loading area to remove the static attraction between the sample pan and analysed material, and the sample pan and furnace wall

A quartz wire was used to suspend the sample pan assembly from the balance chamber. A gas-switching unit was used to automatically switch between nitrogen (inert) and air (oxidative) purge gases.

![Figure 34 Perkin-Elmer Pyris 1 TGA](image-url)
The Pyris 1 TGA was controlled via the Windows-based Pyris Version 5 thermal analysis software. Figure 32 represents a screenshot of the instrument view panel used to display real-time signals of the thermogravimetric analyser. This instrument view panel is able to control the furnace position, weight taring, sample weight, ion stream, isothermal conditioning and analysis commencement. Figure 35 displays the real time signal of temperature versus weight. Time can be used instead of temperature for the domain and weight fraction or weight loss derivative can be used for the range of the real-time signals.

![Figure 35 A screenshot of a typical instrument view for the Perkin-Elmer Pyris 1 TGA](image)

**Instron Universal Test Instrument**

An Instron Universal instrument was employed for dynamic force thermomechanometry (df-TM) of the EMA-based and polyurethane-based materials. An Instron conducts a tensile analysis on a test specimen by applying an extension and measuring the required load. The Instron is used to measure the stress-strain response of materials and constant stress-relaxation.
The Instron employed for this research was a 4465 model with the following instrumental capabilities:

- A load capacity range of 0.1 N – 5000 N
- A crosshead speed range of 0.001 – 1000 mm.min\(^{-1}\)
- A position control resolution of 0.118 µm
- A total vertical test space of 1249 mm
- Various test material clamps including tensile, three-point bend and compression

The Instron 4465 used for this research is shown in Figure 36, with the control panel for load calibration and setting of zero strain shown at the left.

![Figure 36 Instron model 4465 Universal Test Instrument](image)

The operation of the Instron universal tester was conducted via a Windows-based program (Merlin, version 5.31 Series IX). Figure 37 displays a typical instrument view panel screenshot. The properties being measured by the Instron, in this example the stress and strain, are displayed in real time. The Instron software is capable of performing a number of calculations upon the resultant analysis data. Some calculations performed on the data are shown at the bottom of the screen shot displayed in Figure 37. The calculations shown are
displacement at peak, load at peak, load at break, maximum strain displacement, energy at break, maximum load and Young’s modulus, although many other calculations can be performed on the data acquired. The Instron universal tester is calibrated against a 5 N load cell with internal electronic calibration before each use. This indicates that any errors in data are due to the inherent precision of the Instron universal analyser and errors associated with the dimensions and uniformity of the sample. Replicate analyses of the same material are a method of compensating for these errors and could be included in further work.

![Figure 37 A typical Instron instrument view panel screenshot](image)

**Dynamic mechanical analyser**

The dynamic mechanical analyser employed for this research to conduct df-TM, sf-TM and mf-TM was the Perkin-Elmer Diamond dynamic mechanical analyser. The Diamond DMA has a linear variable differential transformer (LVDT) to measure displacement. Employing an LVDT to measure displacement is based upon the relative position of a metal core between two secondary coils. Figure 38 represents a schematic of the components of a Diamond DMA. The operation of the DMA is combination of feedback between the oscillation phase angle calculation circuit and the DMA module central processing unit (CPU). These two components determine the force required to apply a predetermined strain to a specimen. The DMA module CPU is responsible for the control of temperature conditions, via a proportional integral derivative (PID) controller.
Chapter 3 Materials and Method

The Diamond DMA possesses the following instrumental capabilities:

- A sinusoidal frequency range of 0.01 – 100 Hz
- A synthetic frequency range of 5 frequencies, each approximately double the last, applied instantaneously
- A analysis temperature range of -150 – 600 °C with liquid nitrogen employed as a coolant
- A temperature scanning rate range of 0.01 – 20 °C.min$^{-1}$
- Maximum loads of +/- 10 N for static analysis and +/- 8 N for dynamic analysis

The key feature of the Diamond DMA is the synthetic frequency mode. This operates in a similar fashion to FTIR and NMR in that a complex waveform is applied to the test specimen, where the complex waveform is the sum of five successive frequencies. The material’s response to the complex waveform is then deconvoluted into the five original frequencies by Fourier transformation. Figure 39 demonstrates the convolution of five frequencies into a complex waveform.
Figure 39 Convolution of wavelengths into a complex waveform

The Diamond DMA is capable of analysing materials in variety of geometries such as tensile, single cantilever, dual cantilever, shear and compression. The deformation geometry used for this analysis was the tensile configuration. Figure 40 displays the Diamond DMA employed in this research. The small control unit beside the DMA in this picture is the liquid nitrogen cooling controller unit. The DMA module CPU communicates with the cooling controller unit, which in turn controls a heating probe inside a liquid nitrogen dewar. The heating probe slightly heats the liquid nitrogen forcing it to pass through tubing into the furnace encasement area. The inset picture represents the tensile sample clamps with an EPDM composite to demonstrate the placement of material specimens for analysis.

Figure 40 Perkin-Elmer Diamond DMA with inset picture magnifying tensile deformation sample clamps
The operation of the Diamond DMA was conducted on a computer workstation with Muse Measurement software (version 3.3U Build 637) from Seiko Instruments. Figure 41 displays the real-time measurement window with $E'$, $E''$ and $\tan \delta$ displayed with temperature. This measurement window displays in real-time the control temperature (the temperature of the furnace), the program temperature (the temperature of the heating program with respect to heating rate and time elapsed), the sample temperature (the actual temperature of the sample), the rate of extension ($dL$), applied force ($F_t$), position (probe position), and time or temperature and modulus or strain analysis data. The control panel has such controls to start and halt the analysis, test the suitability of the sample (discussed below), go to the initial experimental temperature and access to experimental parameters.

![Figure 41 Screenshot of the control panel of the Diamond DMA](image)

The DMA can test the sample before analysing a material to determine if its size dimensions are adequate for the application of the designated strain extension. It does this by applying the analysis frequency (if a multi-frequency analysis was selected then the applied frequency will be the median frequency) to obtain a storage modulus value. The log(modulus) value of this single frequency application is plotted against the log(geometry factor) value (determined from the sample size dimensions; length divided by the cross-sectional area). If this datum falls within the instruments analysis capabilities (represented as an envelope plot on the
log(modulus)-log(geometry factor) then these material and experimental parameters are suitable for mf-TM. The log(modulus) value is observed to be temperature dependant and the log(geometry factor) is dependant upon analysis configuration i.e. samples with the same size dimensions will possess different geometry factors if analysed in different analysis configurations. Figure 42 represents an example of the measurement range used for determining the viability of an analysis under the selected experimental parameters. Test data which lies inside the green dashed lines is ideal, whilst anything lying outside the red solid lines is considered unsuitable for analysis with the current experimental parameters. The ideal relationship between sample geometry and storage modulus demonstrated in Figure 42 indicates that with increasing modulus value the specimens must have a smaller dimensions.

The Diamond DMA has settings that can be applied for mf-TM measurements in tensile deformation mode. Figure 43 displays a screenshot of a typical mf-TM experimental parameters view panel. This figure displays the mf-TM experimental parameters L amplitude (the distance of extension which determines the applied strain), minimum tension/compression force (the minimum force the Diamond DMA will apply during an
analysis), tension/compression force gain (coefficient for changes related to the AC amplitude for tension/compression during analysis) and force amplitude default value (the initial force applied to a material to achieve desired L amplitude).

The Diamond DMA is calibrated against various standards: a stainless steel plate for compliance correction, time constant correction, F/L (Force/Length) gain, viscosity correction, probe mass and elasticity, standard mass for load calibration and an aluminium plate for calibration of tensile deformation mode. This indicates that any errors in data are due to the inherent precision of the Instron universal analyser and errors associated with the dimensions and uniformity of the sample. Replicate analyses of the same material are a method of compensating for these errors and could be included in further work.

Figure 43 An mf-TM experimental parameters view panel

Instrumental analysis parameters

The instrumental analysis parameters are described below for each base polymer system.
**Poly(ethylene–co-propylene-co-diene monomer)-based materials**

**Scanning electron microscopy**

Scanning electron micrographs were obtained on a Phillips FEI Quanta 200 scanning electron microscope. Composites were mounted on an aluminium stub with carbon tab tape. A 20 kV electron accelerating voltage, low vacuum of 0.5 torr and spot size 5 were used.

**Thermogravimetry**

Thermogravimetry was performed with a Perkin-Elmer TGA 7. The procedure for TGA is shown in Figure 44. The temperature range for weight analysis was 20 – 800 °C with a heating rate of 20 °C.min\(^{-1}\). A nitrogen atmosphere was used until the temperature reached 800 °C when the atmosphere switched to ambient air. The residue was heated at a constant 800 °C under an oxidative atmosphere for 5 min to remove any residual organic compounds. The mass loss and derivative data was collected and analysed.

![Figure 44 View program tab for the Perkin-Elmer TGA 7](image)
**Mechanical analysis – df-TM: Stress-strain analysis**

Stress-strain analysis was performed using the Perkin-Elmer Diamond DMA. Table 1 lists the experimental parameters used for these analyses. This stress-strain analysis involved constant extension of the test specimen at a given strain rate (calculated from a designated length extension per minute). The analysis continued until the specimens fractured.

**Table 1 Instrumental parameters employed for df-TM (stress-strain) of EPDM-based materials**

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force application rate</td>
<td>150 mN min⁻¹</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Isothermal at room temperature (i.e. 20 °C)</td>
</tr>
</tbody>
</table>

**Mechanical analysis – sf-TM: Creep and recovery analysis**

Creep and recovery analysis was performed on EPDM-based materials using the Perkin-Elmer Diamond DMA. Table 2 lists the experimental parameters used for these analyses.

**Table 2 Instrumental parameters employed for sf-TM (creep and recovery analysis) of EPDM-based materials**

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial force</td>
<td>10 mN</td>
</tr>
<tr>
<td>Applied force during creep cycle</td>
<td>200 mN</td>
</tr>
<tr>
<td>Creep time</td>
<td>600 s</td>
</tr>
<tr>
<td>Recovery time</td>
<td>Creep time × 4 = 2400 s</td>
</tr>
<tr>
<td>Number of analysis cycles</td>
<td>4</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Isothermal at room temperature (i.e. 20 °C)</td>
</tr>
</tbody>
</table>

**Mechanical analysis – mf-TM: Single frequency analysis**

Single frequency mf-TM was performed on EPDM-based materials using the Perkin-Elmer Diamond DMA. Table 3 lists the experimental parameters used for these analyses.
Table 3 Instrumental parameters employed for 1 Hz mf-TM of EPDM-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain amplitude</td>
<td>20 µm</td>
</tr>
<tr>
<td>Minimum tension force</td>
<td>0.01 mN</td>
</tr>
<tr>
<td>Tension force gain</td>
<td>1.5</td>
</tr>
<tr>
<td>Force amplitude default</td>
<td>100 mN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Dry nitrogen purge</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Analysed frequencies</td>
<td>1 Hz</td>
</tr>
<tr>
<td>Heating program</td>
<td>Ramp mode at 2 °C.min⁻¹</td>
</tr>
<tr>
<td>Temperature range</td>
<td>-80 – 150 °C.min⁻¹</td>
</tr>
</tbody>
</table>

Thermoplastic poly(ethylene-co-methyl acrylate)-based materials analysis parameters

**Thermogravimetry**
Thermogravimetry was performed with a Perkin-Elmer TGA 7. The procedure for TGA is shown in Figure 34. In this figure the temperature range for weight analysis was 20 – 800 °C with a heating rate of 20 °C.min⁻¹. A nitrogen atmosphere was used until the temperature reached 800 °C when the atmosphere switched to air (i.e. oxygen-enriched). The residue was heated at a constant 800 °C under an oxidative atmosphere for 5 min to remove any residual organic compounds. The mass loss and derivative data was collected and analysed.

**Mechanical analysis – df-TM: Stress-strain analysis**
Stress-strain analysis was performed on an Instron Universal Test Instrument 4465 model. Table 4 lists the experimental parameters used for these analyses. This stress-strain analysis involved extension of the specimen at a given strain rate (calculated from a designated length extension per minute). The analysis proceeded until the specimens fractured.

Table 4 Instrumental parameters employed for df-TM (stress-strain) of EMA-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosshead speed</td>
<td>8.33 mm.min⁻¹</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Isothermal at room temperature (i.e. 20 °C)</td>
</tr>
</tbody>
</table>

**Mechanical analysis – sf-TM: Creep and recovery analysis**
Creep and recovery analysis was performed on EMA-based materials using a Perkin-Elmer Diamond DMA. Table 5 lists the experimental parameters used for these analyses.
Table 5 Instrumental parameters employed for sf-TM (creep-recovery) of EMA-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial force</td>
<td>10 mN</td>
</tr>
<tr>
<td>Applied force during creep cycle</td>
<td>5000 mN</td>
</tr>
<tr>
<td>Creep time</td>
<td>600 s</td>
</tr>
<tr>
<td>Recovery time</td>
<td>Creep time × 4 = 2400 s</td>
</tr>
<tr>
<td>Number of analysis cycles</td>
<td>4</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Isothermal at room temperature (i.e. 20 °C)</td>
</tr>
</tbody>
</table>

Mechanical analysis – mf-TM

Single frequency analysis

Single frequency mf-TM was performed on EMA-based materials using a Perkin-Elmer Diamond DMA. Table 6 lists the experimental parameters used for these analyses.

Table 6 Instrumental parameters employed for 1 Hz mf-TM of EMA-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain amplitude</td>
<td>20 µm</td>
</tr>
<tr>
<td>Minimum tension force</td>
<td>0.01 mN</td>
</tr>
<tr>
<td>Tension force gain</td>
<td>1.5</td>
</tr>
<tr>
<td>Force amplitude default</td>
<td>100 mN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Dry nitrogen purge</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Analysed frequencies</td>
<td>1 Hz</td>
</tr>
<tr>
<td>Heating program</td>
<td>Ramp mode at 2 °C.min⁻¹</td>
</tr>
<tr>
<td>Temperature range</td>
<td>-80 – 120 °C.min⁻¹</td>
</tr>
</tbody>
</table>

Multi-frequency analysis

Multi frequency mf-TM was performed on EMA-based materials using the Perkin-Elmer Diamond DMA. Table 7 lists the experimental parameters used for these analyses.
Table 7 Instrumental parameters employed for multi frequency mf-TM of EMA-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain amplitude value</td>
<td>20 µm</td>
</tr>
<tr>
<td>Minimum tension force</td>
<td>0.01 mN</td>
</tr>
<tr>
<td>Tension force gain</td>
<td>1.5</td>
</tr>
<tr>
<td>Force amplitude default value</td>
<td>100 mN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Dry nitrogen purge</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Analysed frequencies</td>
<td>0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100 Hz</td>
</tr>
<tr>
<td>Heating program</td>
<td>Isothermal-step mode with 10 °C increments</td>
</tr>
<tr>
<td>Temperature range</td>
<td>-80 – 60 °C</td>
</tr>
</tbody>
</table>

Thermoplastic polyurethane-based materials analysis parameters

**Thermogravimetric analysis**

Thermogravimetry was performed with a Perkin-Elmer TGA 7. The procedure for TGA is shown in Figure 44. The temperature range for weight analysis was 20 – 800 °C with a heating rate of 20 °C.min⁻¹. A nitrogen atmosphere was used until the temperature reached 800 °C when the atmosphere switched to air (i.e. oxygen-enriched). The residue was heated at a constant 800 °C under an oxidative atmosphere for 5 min to remove any residual organic compounds. The mass loss and derivative data was collected and analysed.

**Mechanical analysis – df-TM: Stress-strain analysis**

Stress-strain analysis was performed using an Instron Universal Test Instrument 4465 model. Table 8 lists the experimental parameters used for these specimens. This stress-strain analysis involved the constant extension of the specimen at a given strain rate (calculated from a designated length extension per minute). The analysis continued until the specimens fractured.

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosshead speed</td>
<td>8.33 mm.min⁻¹</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Ambient (i.e. SLC: 20 °C)</td>
</tr>
</tbody>
</table>

**Mechanical analysis – sf-TM: Creep and recovery analysis**

Creep and recovery analysis was performed on polyurethane-based materials using a Perkin-Elmer Diamond DMA. Table 9 lists the experimental parameters used for these analyses.
Table 9 Instrumental parameters employed for sf-TM (creep and recovery analysis) of polyurethane-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial force</td>
<td>10 mN</td>
</tr>
<tr>
<td>Applied force during creep cycle</td>
<td>4000, 5000 mN</td>
</tr>
<tr>
<td>Creep time</td>
<td>600 s</td>
</tr>
<tr>
<td>Recovery time</td>
<td>Creep time × 4 = 2400 s</td>
</tr>
<tr>
<td>Number of analysis cycles</td>
<td>4</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ambient</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Heating program</td>
<td>N/A</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Ambient (i.e. SLC: 20 °C)</td>
</tr>
</tbody>
</table>

**Mechanical analysis – mf-TM**

**Single frequency analysis**

Single frequency mf-TM was performed on polyurethane-based materials using a Perkin-Elmer Diamond DMA. Table 10 lists the experimental parameters used for these analyses.

Table 10 Instrumental parameters employed for 1 Hz mf-TM of polyurethane-based materials

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain amplitude value</td>
<td>20 µm</td>
</tr>
<tr>
<td>Minimum tension force</td>
<td>0.01 mN</td>
</tr>
<tr>
<td>Tension force gain</td>
<td>1.5</td>
</tr>
<tr>
<td>Force amplitude default value</td>
<td>100 mN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Dry nitrogen purge</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Analysed frequencies</td>
<td>1 Hz</td>
</tr>
<tr>
<td>Heating program</td>
<td>Isothermal-step mode</td>
</tr>
<tr>
<td>Temperature range</td>
<td>-80 – 180 at 2 °C.min⁻¹</td>
</tr>
</tbody>
</table>

**Multi-frequency analysis**

Multi-frequency mf-TM was performed on polyurethane-based materials using a Perkin-Elmer Diamond DMA. Table 11 lists the experimental parameters used for these analyses.
Table 11 Instrumental parameters employed for multi-frequency mf-TM of polyurethane-based materials mastercurves

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain amplitude value</td>
<td>20 µm</td>
</tr>
<tr>
<td>Minimum tension force</td>
<td>0.01 mN</td>
</tr>
<tr>
<td>Tension force gain</td>
<td>1.5</td>
</tr>
<tr>
<td>Force amplitude default value</td>
<td>100 mN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Dry nitrogen purge</td>
</tr>
<tr>
<td>Deformation geometry</td>
<td>Tensile mode</td>
</tr>
<tr>
<td>Analysed frequencies</td>
<td>0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100 Hz</td>
</tr>
<tr>
<td>Heating program</td>
<td>Isothermal-step mode</td>
</tr>
<tr>
<td>Temperature range</td>
<td>-80 – 120 °C with 10 °C increments</td>
</tr>
</tbody>
</table>

Data manipulation and analysis methods

The resultant mechanical analysis data for static analysis – creep and recovery analyses were modelled with the 4-element model for the creep phase and the KWW function for the relaxation phase. Dynamic mechanical data was used to create mastercurves (from both single and multiple frequency analyses). Mastercurves created from multiple frequency analysis were modelled with various relaxation functions.

Modelling static analysis data: Creep analysis

The resultant time-strain data from creep analysis was modelled with the 4-element (Maxwell-Voigt) model as demonstrated by Menard[133].

The 4-element model consists of five parameters (the four deformation elements: $E_1$, $E_2$, $\eta_2$ and $\eta_3$, and the retardation time: $\tau$). The first three parameters that were calculated were the $E_1$ elastic modulus, $\eta_3$ viscosity and $\tau$ retardation time. The time-strain data used for the calculation of the $E_1$ and $\eta_3$ parameters is shown in Figure 45. The $E_1$ modulus parameter was calculated by division of the stress by the initial (instantaneous) increase in strain with the application of force. The calculation of the $\eta_3$ modulus parameter requires data from a subsequent relaxation analysis. This parameter is equal to the stress divided by the slope of the linear function that models the initial time-strain values (during the first analysis cycle, time and strain will equal 0 s and 0 mm.mm\(^{-1}\) respectively) and the time-strain datum which has the time equal to the time at the removal of force and the strain value equal to strain value at the final analysed time (i.e. the unrecovered strain) in the subsequent recovery analysis. The retardation time was calculated from a sigmoid function plot of log(time) and log(strain). The time at which the steepest section of this curve occurred (i.e. where the derivative was the largest) equated to the retardation time.
Figure 45 Components of creep-recovery data used to calculate the $E_1$ and $\eta_3$ moduli

After the $E_1$ and $\eta_3$ modulus parameters and retardation time were determined, the $E_2$ elastic component of the viscoelasticity of was calculated. It was calculated by rearranging the 4-element model equation as shown in Equation 32. This rearrangement resulted in Equation 59, given as

$$E_2 = \frac{\sigma \times \left(1 - \left(\frac{\tau}{\tau}\right)\right)}{\left(\varepsilon - \left(\frac{\sigma}{E_1}\right) - \left(\frac{\sigma}{\eta_3} \times t\right)\right)}$$

Equation 59

where $E_2$ is the elastic modulus parameter of the viscoelastic component, $\sigma$ is the stress, $\tau$ is the retardation time, $t$ is time, $\varepsilon$ is the strain, $E_1$ is the elastic modulus parameter and $\eta_3$ is the viscosity modulus parameter. Once $E_2$ has been calculated, the $\eta_2$ viscosity modulus parameter of the viscoelastic component was calculated since the retardation time is equal to $\eta_2$ divided by $E_2$.

Microsoft Excel 2003 edition was employed to perform 4-element model strain data modelling. Figure 46 represents a typical spreadsheet layout employed to model creep strain data and the sigmoidal function for calculating the retardation time.
Modelling of static analysis data: Recovery analysis

The recovery phase of creep-recovery analysis was modelled with the KWW equation model in the employed by Williams and Watts[179] in the form given in Equation 33. The KWW equation was modelled to the time-dependant recovery in the recovery phase, i.e. viscoelastic recovery. The initial, instantaneous (elastic) recovery was not modelled by the KWW equation only the subsequent time dependant recovery as displayed in Figure 47.
Figure 47 The KWW equation modelling recovery data where: (○-) is the recovery data; solid line indicates the KWW equation

The solver function in Microsoft Excel 2003 edition was employed to model the relaxation data obtained from recovery analysis. The solver function employed quadratic interpolation between data, forward derivatives and a Newton search method. Figure 48 represents a typical spreadsheet layout employed to model the KWW equation to strain recovery data. A sum-of-least-squares error function was employed to minimise the error between the experimental and calculated strain values.
Methods for mastercurve construction

Manually shifted mastercurves

Mastercurves created via a manual shift method were constructed via the following procedure. A series of multi-frequency, isothermal modulus data were created via the dynamic mechanical analysis method as previously described. Figure 49 displays an example of a frequency-modulus plot of these series of multi-frequency, isothermal storage modulus data for rheologically simple materials. The data with the greatest modulus values equates to analysis at the lowest temperature and vice-versa (as per time temperature superposition). The modulus values will decrease as the temperature increases; though this may not hold true for loss modulus data as there will sometimes be an increase in loss modulus values with increasing temperature at the onset of the glass transition[217, 218], and due to resonance frequency effects.
Figure 49 A series multi-frequency storage modulus data series

The frequency-modulus data series were converted into logarithmic data. From these series of logarithmic data a series at a specific temperature was chosen to be the reference temperature data. Figure 50 shows an example of three series of data where the median series was chosen to be the reference temperature data. The reference temperature was usually chosen to be the $T_g$ or a particular operating temperature.

Figure 50 Three multi-frequency storage modulus data series where (-♦-) is the reference temperature data
Once the reference data has been designated, the other curves are shifted in the positive or negative direction of the log(frequency) axis to create a single continuous data series. Figure 51 displays an example of the shifting of the data series (seen in Figure 50) to form a single data series. The shifted data possesses log(frequency) values which are greater and smaller that those of the original multi-frequency, isothermal storage modulus data series. The shift in the log(frequency) was described as a shift factor, labelled $a_T$.

![Figure 51 Multi-frequency modulus data series shifted in relation to the reference temperature data](image)

All of the data series are shifted until a single series of data existed comprised of various data obtained from analyses at various temperatures; hence there is a shift factor associated with each analysis temperature. Figure 52 displays a mastercurve created from the multi-frequency, isothermal storage modulus data series seen in Figure 49.
Havriliak Negami shifted mastercurves

A further method employed in this research to create mastercurves used the Havriliak-Negami dynamic relaxation model, based upon the procedure described Madigosky, Lee and Niemiec[141]. A series of multi-frequency, isothermal modulus data curves were created via the dynamic mechanical analysis as for the manually shifted method. Next a reference temperature was chosen from the storage modulus data series. The HN relaxation equation was then used to model the reference curve data. If the log(frequency) values are extended beyond those of the reference curve data, the HN function (using the parameters used to model the reference curve data) models the modulus values as the frequency approaches zero and infinity, as shown in Figure 53. This process derives values for the five HN parameters ($E_\infty$, $E_0$, $\alpha$, $\beta$, $\tau$) when modelling the reference temperature data. The $E_\infty$, $E_0$, $\alpha$ and $\beta$ parameters are material dependent but temperature independent; hence can be applied to each series of data at the analysed temperatures without change while the relaxation time ($\tau$) variable is temperature dependant and therefore must be calculated for each other data series.

Figure 52 Multi-frequency storage modulus data shifted via shift factor to form a single, mastercurve
Subsequently all other multi-frequency, isothermal modulus data series were modelled with the HN equation, as shown in Figure 54. Each set of HN parameters (one set per data series) possessed the same $E_\infty$, $E_0$, $\alpha$ and $\beta$ parameter values for all temperatures but differing $\tau$ values. The HN equation mastercurve construction method, as with the manual shift method employs shift factors to alter the frequency values of the modulus-frequency data; however the method of determining shift factor values is different. Shift factors were determined by taking the logarithmic value of the ratio between the relaxation time (derived from HN equation modelling) at the analysed temperature and the relaxation time at the reference temperature, i.e.

$$a_T = \log \left( \frac{\tau}{\tau_0} \right) \quad \text{Equation 60}$$

where $a_T$ is the shift factor, $\tau$ is the relaxation time at the analysed temperature and $\tau_0$ is the relaxation time at the reference temperature.

Figure 53 Havriliak-Negami equation modelling the reference temperature data and extended over a hypothetical frequency range
Each of these HN curves possessed the same $E_\infty$, $E_0$, $\alpha$ and $\beta$ values but differing $\tau$ values. With the relaxation time calculated for each series of data (resulting in a relaxation time associated with each analysis temperature) shift factors were able to be calculated. Once the shift factors are calculated and applied to the data series a single continuous mastercurve was formed. The mastercurve was observed to possess similar modulus values to the values calculated via the HN equation, as shown in Figure 55.
Chapter 3 Materials and Method

Method of applying relaxation equations

Dynamic relaxation equations applied to multi-frequency mastercurve data

The Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami relaxation were employed to model dynamic mechanical analysis mastercurve data. The forms of the equations used to model the storage and loss modulus for each of the D, CC and CD models were as given in the original references (Equations 38 and 39, Equations 46 and 47, and Equations 50 and 51 respectively). The forms of the HN relaxation equation used to model the storage and loss modulus data were as given by Kwak et al.[211], as

\[ E' = E_m + \left( E_0 - E_m \right) \times \frac{\cos(\gamma \theta)}{\left[ 1 + 2(\omega \tau_{HN})^\alpha \cos\left(\frac{\alpha \pi}{2}\right) + (\omega \tau_{HN})^{2\alpha} \right]^{\frac{1}{2}}} \]  

Equation 61

and

\[ E'' = (E_0 - E_m) \times \frac{\sin(\gamma \theta)}{\left[ 1 + 2(\omega \tau_{HN})^\alpha \cos\left(\frac{\alpha \pi}{2}\right) + (\omega \tau_{HN})^{2\alpha} \right]^{\frac{1}{2}}} \]  

Equation 62

where

\[ \theta = \tan^{-1} \left( \frac{(\omega \tau_{HN})^\alpha \sin\left(\frac{\alpha \pi}{2}\right)}{1 + (\omega \tau_{HN})^\alpha \cos\left(\frac{\alpha \pi}{2}\right)} \right) \]

The following procedure was used to model the mastercurve modulus data with the four aforementioned relaxation equations. The storage and loss mastercurves were simultaneously modelled with the resolved components of the complex relaxation equations. The Wicket error function (Equation 57) was employed to determine the best modelling equation parameters for each of the relaxation equations. The storage modulus mastercurve was given preference over the loss modulus mastercurve due to two factors; the storage mastercurve modulus values were larger than their loss modulus counterparts (hence error functions will preferentially model the largest values), and the storage modulus mastercurves were created.
Chapter 3 Materials and Method

first with the same derived shift factors then being applied to form the loss modulus mastercurve.

Relaxation equation modelling was performed using a spreadsheet (Microsoft Excel 2003). The solver function employed quadratic interpolation between data, forward derivatives and a Newton search method. Figure 56 represents a typical spreadsheet layout employed to model dynamic relaxation equations to mastercurve data.

Dynamic relaxation model applied to single frequency data

Modelling dynamic mechanical data with relaxation equations usually requires multi-frequency analysis, however a method described by Szabo and Keough[214] allows for the modelling of single frequency modulus data with relaxation equations; in this instance the HN equation was used.

Storage and loss modulus data were obtained from single frequency (for this research, 1 Hz) dynamic mechanical analysis, with the resultant data was plotted with the dimensions of temperature and modulus. This method of modelling modulus data with the HN equation
required the modulus data to be replotted with dimensions of modulus and frequency, as shown in Figure 57. The frequency range used in previous research employing this method was $10^{15}$ – $10^{15}$ Hz. When plotting the frequency-modulus data the high frequency values must be correlated to the low temperatures whilst high temperatures are correlated with low frequencies, adhering to the TTS principal.

![Temperature-frequency and storage modulus data from single frequency dynamic mechanical analysis](image)

**Figure 57 Temperature-frequency and storage modulus data from single frequency dynamic mechanical analysis**

The HN relaxation equation was used to model the modulus data after the temperature-frequency superposition. An arbitrary value for the relaxation time parameter, $\tau$ (given as 1 s in the literature) was set, then the remaining HN parameters ($E_\infty$, $E_0$, $\alpha$ and $\beta$) were adjusted to determine their best-modelling values. The Wicket error function was used to minimise the distance between experimental and calculated modulus values. The relaxation time was subsequently recalculated for the modulus values at each analysis temperature once the optimal values of the other HN parameters had been determined. However this time the frequency was held constant (at the analysed frequency) and the relaxation time parameter became the variable of the HN equation, i.e. instead of the HN calculated modulus having frequency as the independent variable in $E(\omega)$ the relaxation became the independent variable as in $E(\tau)$. This is because the relaxation time as previously mentioned is temperature dependant, and therefore must be calculated for each modulus value at a different temperature. The result was single frequency modulus data modelled with the HN equation, as seen in Figure 58 with a calculated relaxation time for each analysed temperature.
Figure 58 Single frequency modulus data (-●-) and the modelling HN equation is the continuous line.
Chapter 4 Alumina surface chemistry and thermal properties of poly(ethylene-co-propylene) diene monomer-alumina composites

Introduction

The elastomer poly(ethylene-co-propylene) diene monomer (EPDM) is an amorphous hydrocarbon polymer. Its hydrocarbon nature means it possesses weak internal forces (as opposed to strong internal forces such as H-bonding or dipole-dipole bonding). An ideal elastomer possesses a network structure allowing instantaneous (elastic) reversibility, which maintains relative local chain position within the material. Real elastomers exhibit time dependent reversibility due to molecular entanglements, loops and dangling ends. Time dependent reversibility occurs when entanglements untangle and local chain movement cannot occur until other nearby molecular movement has happened. This gives rise to damping which uses the energy available from finite intermolecular forces (e.g. covalent forces). When the intermolecular forces are exceeded the time dependant deformation (or creep) becomes irreversible, primarily caused by insufficient crosslinking.

EPDM can be crosslinked with either or both chemical and/or physical crosslinking processes. Chemical crosslinking (curing/vulcanisation) involves radical induced reactions initiated by a peroxide to cause bonding between molecules, while physical crosslinking involves the addition of a filler to bond molecules by adsorption.

Carbon black has been one of the most widely used fillers in elastomers such as EPDM due to its abundance and compatibility with hydrocarbons. Other fillers that have been used are silicas, clays, carbon-silica dual phase materials and alumina. Silica and alumina can sometimes agglomerate whereby a filler will self associate in clusters rather than be separately dispersed within an elastomeric matrix. Agglomerates of filler can occlude sections of elastomer effectively removing them from participating in deformations in response to applied forces.
Polar fillers such as silica and alumina require surface treatments (altering surface polarity) to optimise the compatibility between elastomer and filler. An example of surface treatment is admicellar polymerisation. Admicellar polymerisation is a multi-step process that involves incorporating a filler particle into a micelle and coating it with a surfactant bilayer. Monomer is dissolved into this bilayer where polymerisation occurs and finally the top layer of surfactant is washed leaving only the filler particle coated with a polymeric layer.

The degree to which elastomers and fillers interact is dependent upon a variety of factors; including particle size, surface chemistry and dispersion. Optimal interaction will lead to the highest strength interfacial adhesion between filler and polymer. Debonding between filler and polymer, and deagglomeration between filler can occur under high strains.

The effectiveness of fillers in elastomers is determined by changes to bulk (characteristics on a macroscopic scale) properties of an elastomer-filler composite when compared with the pure elastomer. These changes can be analysed via mechanical testing. Dynamic and static mechanical thermomechanometry (df-TM and sf-TM) characterises the physical crosslink strength in a composite, i.e. the bonding between elastomer and filler and modulated force thermomechanometry (mf-TM) characterises damping (dissipation of energy) performed within the linear-viscoelastic region.

The objectives of this study were to prepare EPDM-alumina composites with aluminas possessing varying surface chemistry and analyse their thermal and thermomechanical properties to study what effect of the differing surface chemistry of alumina had on there properties.

**Experimental**

**Preparation of EPDM-alumina composites**

Three types of alumina fillers were combined with EPDM; untreated alumina, alumina coated with sodium dodecyl sulfate (SDS) and alumina coated with SDS and polystyrene (SDS-PS). Composites were prepared via the method described in Chapter 3. Samples of composite films were to cut to appropriate sizes to fit the stage and the sample pan for scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) respectively. Material specimens were cut into rectangular strips of dimensions $8.5 \times 10 \times 0.5 \text{ mm}^3$ (length $\times$ width $\times$ thickness for df-TM, sf-TM and mf-TM. The compositions and naming scheme of the composites are summarised in Table 12.
Table 12 EPDM-alumina composite composition and sample designation

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Elastomer</th>
<th>Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>xE</td>
<td>xE – crosslinked EPDM</td>
<td>No filler</td>
</tr>
<tr>
<td>xE-SDS</td>
<td>xE – crosslinked EPDM</td>
<td>SDS – alumina coated with SDS</td>
</tr>
<tr>
<td>xE-SDS-PS</td>
<td>xE – crosslinked EPDM</td>
<td>SDS-PS – alumina coated with SDS and PS</td>
</tr>
<tr>
<td>xE-UT</td>
<td>xE – crosslinked EPDM</td>
<td>UT – untreated alumina</td>
</tr>
</tbody>
</table>

Composite characterisation

The methods employed to characterise thermal; filler composition and thermal stability, and the thermomechanical properties; stress required for constant strain rate, creep and recovery, single frequency mf-TM, and data analysis; 4-element model and Kohlrausch-Williams-Watts (KWW) equation applied to creep and recovery data, and the Havriliak-Negami (HN) relaxation equation applied to mf-TM data, of the EPDM-alumina composites were described in Chapter 3.

Results and discussion

Dispersion of alumina fillers within EPDM matrix

Scanning electron microscopy was employed to observe the dispersion of alumina within the EPDM matrix of the composites. Figure 59 displays the micrographs taken at 200X and 800X magnifications of xE. There were only minimal features observed such as surface contours. Figure 60 represents micrographs taken at 200X and 800X magnification of xE-SDS. The alumina coated in SDS is observed as well dispersed particles with only minimal clustering. Figure 61 displays micrographs taken at 200X and 800X magnification of xE-SDS-PS. The alumina is observed as bright, white spots in the darker matrix. The 800X magnification micrograph shows good dispersion of alumina in the EPDM matrix was achieved. The distinct shape of the alumina particles is not observable in Figure 61. This suggests that the coated alumina has been wetted by the EPDM matrix.

Figure 62 shows micrographs taken at 200X and 800X magnification of xE-UT. The untreated alumina particles appear as clusters. This was due to a difference in polarities between the untreated alumina and EPDM matrix. The untreated alumina will agglomerate after shearing in solution, during solvent evaporation resulting in uneven distribution of alumina since the alumina will preferentially bond to itself rather than EPDM. It is seen that the alumina particles are of a regular, cuboid shape and demonstrate clustering. This reaffirms that the untreated alumina is attracted to itself in the EPDM matrix. It can be observed from Figure 59-62 that the surface treatments effected the dispersion of the alumina in EPDM.
Coating the alumina in SDS provided better dispersion when compared with the dispersion of the untreated alumina; however the alumina particles were still clearly observable as cuboid shapes in the EPDM matrix. Coating the alumina in SDS and PS resulted in better dispersion of alumina when compared with the untreated alumina and SDS-coated alumina since the particles were well dispersed and their shape could not be readily observed (they appeared as white areas in the matrix).

Figure 59 200X and 800X magnification of xE

Figure 60 200X and 800X magnification of xE-SDS
Filler composition and the effect of alumina surface chemistry on thermal stability

Thermogravimetry was performed on the EPDM-based materials to characterise the filler composition (i.e. the weight fraction) and the effect of filler composition on thermal stability. The results from these analyses are represented in Figure 63. The xE material had approximately 0 %.wt since all material was pyrolysed before completion of TG at 900 °C. The xE-SDS and xE-SDS-PS composites had alumina weight fractions close to that of the desired 30 %.wt (at 32 %.wt and 29 %.wt respectively). The xE-UT thermogravimetric analysis determined the weight fraction of untreated alumina to be 43 %.wt. The higher concentration of alumina occurred during the solvent casting film preparation method where
filler clusters were retained in the central film region (due to their preferential attraction to each other rather than the EPDM), while solvent and polymer flowed further at the edges.

![Graph showing filler composition and thermal stability](image)

**Figure 63** Filler composition and thermal stability: xE (−○−); xE-SDS (−◊−); xE-SDS-PS (−□−); xE-UT (−∆−)

There were changes to thermal stability with differing filler content. Table 13 represents the temperature at which each composite had undergone a 50 % w/w loss. The xE-SDS and xE-SDS-PS composites provided a 12 °C and 15 °C enhancement, while the untreated alumina provided the highest increase to thermal stability at 23 °C. The increase in thermal stability with addition of the SDS and SDS-PS treated aluminas was attributed to adsorption of volatiles and decreased diffusion of degradation volatiles through the matrix at 30 % wt. The untreated alumina caused the greatest increase in thermal stability due to the increased filler concentration (43 % w/w) compared to filler concentration of the other composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature at 50 % w/w loss °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>xE</td>
<td>478</td>
</tr>
<tr>
<td>xE-SDS</td>
<td>490</td>
</tr>
<tr>
<td>xE-SDS-PS</td>
<td>495</td>
</tr>
<tr>
<td>xE-UT</td>
<td>501</td>
</tr>
</tbody>
</table>

**Table 13** Temperatures at which composites have undergone 50 % w/w loss

**Alumina surface chemistry and composite stress-strain response**

Dynamic force thermomechanometry via stress-strain analysis was employed to characterise the effect of varying alumina surface chemistry on physical crosslink strength in each
Chapter 4 Alumina surface chemistry and thermal properties of poly(ethylene-co-propylene) diene monomer-alumina composites

Figure 64 represents the results from these analyses. Interpretations of the results are based upon the assumption that all the EPDM-based materials possessed the same amount of chemical crosslink density. The xE-UT composite possessed a greater modulus than xE but had a lower strain at break. This was due to the untreated alumina surface being weakly bonded to the EPDM, so there was little transfer of stresses between them resulting in low reinforcement.

![Graph showing stress vs. strain for EPDM composites](image)

**Figure 64 Strain extension from increasing applied stress rate for EPDM composites, represented as: xE (O-); xE-SDS (◊-); xE-SDS-PS (□-); xE-UT (△-)**

The xE-SDS and xE-SDS-PS composites showed the greatest reinforcement compared with xE and xE-UT composite. Both of these composites had a higher modulus than that of xE and demonstrated a yield stress then further extension until breakage. The xE-SDS-PS composite had a higher initial modulus than xE-SDS. Since physical crosslinks with filler predominate at lower strains as the molecular segments begin to uncoil and the greater compatibility between filler and matrix provided by the styrene coating explains why xE-SDS-PS had the greatest initial modulus. The composite xE-SDS had the next greatest modulus followed by xE-UT then xE. This indicated that while the addition of any of these fillers will increase the initial modulus, increasing compatibility between filler and EPDM will result in further increases of the modulus values.

Higher extension (after yielding) caused whitening of the xE-SDS and xE-SDS-PS composites at high stress, although no whitening was observed in either of the xE or xE-UT materials. No whitening in xE implied that the whitening was not caused by strain induced
crystallinity. These results may imply that whitening in the xE-SDS and xE-SDS-PS composites was caused by voiding at the filler surface.

The xE-SDS-PS composite was observed to have the strongest filler-matrix interface as evidenced by it requiring the highest stress for similar strain values until breakage. The xE-SDS composite had the highest strain at breakage, followed by xE-SDS-PS, xE and xE-UT. The xE-SDS composite had the highest strain at breakage due to the surfactant on the alumina acting as lubricant allowing for molecular segments to slip past each other. The untreated alumina decreased the maximum strain extension due to the poor interface between filler and matrix.

Alumina surface chemistry and composite creep and recovery response

Static force thermomechanometry via creep and recovery analysis was employed to characterise the effect of varying alumina surface chemistry on physical crosslink strength for each composite. Figure 65 illustrates creep-recovery data obtained from creep and recovery, which were subsequently modelled with the 4-element model (creep phase) and the KWW equation (recovery phase). All of the composites and unfilled elastomer were analysed at low forces as they showed little resistance to higher (> 200 mN) tensile forces. Each of the composites and xE demonstrated a combination of instantaneous and time dependant recoveries, and permanent deformation.

![Creep and recovery analysis data: xE (-○-); xE-SDS (-△-); SDS – xE-SDS-PS (-□-); xE-UT (-△-); Solid lines indicate modelling by the 4-element (creep analysis) and KWW (recovery phase) functions](image-url)

Figure 65 Creep and recovery analysis data: xE (-○-); xE-SDS (-△-); SDS – xE-SDS-PS (-□-); xE-UT (-Δ-); Solid lines indicate modelling by the 4-element (creep analysis) and KWW (recovery phase) functions
The xE material had the largest instantaneous, elastic deformation in response to applied forces (indicated by the strain value at the first analysis time). The xE-UT composite possessed the second largest elastic deformation followed by xE-SDS and xE-SDS-PS. This trend indicated that the greater the compatibility between filler and elastomer the smaller the initial elastic deformation; however all fillers reduced the initial creep extension. A combination of viscoelastic and viscous deformation occurred after the elastic deformation. The non-linearity in the time-strain data (equated to viscoelastic deformation) was most prevalent in xE, followed by xE-UT, xE-SDS and xE-SDS-PS. The filled composites possessed faster recovery indicated by the increased linearity of the strain-time data in the viscoelastic recovery region of the recovery time-strain data compared with xE time-strain data. The observations in both the creep and recovery analyses were consistent in subsequent analysis cycles.

Creep and recovery models

The 4-element model and Kohlrausch-Williams-Watts (KWW) equation were employed to model creep and recovery data, respectively to determine moduli and relaxation properties. Table 14 contains the values of the parameters obtained when the 4-element model was used to model creep data. The order of the instantaneous elastic modulus and elastic component of the viscoelastic creep ($E_1$ and $E_2$ respectively) of the EPDM-based materials in terms of size was xE < xE-UT < xE-SDS < xE-SDS-PS. The order of the viscous component of the viscoelastic creep ($\eta_2$) in terms of size was xE < xE-SDS < xE-PS < xE-UT. The order of the viscosity ($\eta_3$) in terms of size was xE-UT < xE-SDS < xE-PS < xE. The unfilled crosslinked EPDM possessed the lowest $E_1$, $E_2$ and $\eta_2$ values indicating it had the least resistance to instantaneous and time dependant uncoiling and extension of molecules; but possessed the greatest $\eta_3$ value indicating that it had the most resistance to permanent flow. This was due to the chemical crosslink structure predominating allowing it to have a much higher stain extension than the filled materials.
Table 14 4-element model parameters obtained from modelling EPDM-based materials creep analysis data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycle</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$\eta_2$</th>
<th>$\eta_3$</th>
<th>$\tau$</th>
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<td></td>
<td></td>
<td>(kPa)</td>
<td>(kPa)</td>
<td>(kPa.s)</td>
<td>(MPa.s)</td>
<td>(s)</td>
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<td></td>
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<td></td>
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<td>xE-UT</td>
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<td></td>
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<td>283</td>
<td>543</td>
<td>526</td>
<td>3.10</td>
<td>0.22</td>
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</tbody>
</table>

The xE-SDS composite was expected to have weak interaction between filler and EPDM but good wetting due to the presence of SDS. The uncoiling of molecules was limited compared with the xE material (determined from their $E_1$ values). The time dependant uncoiling gave lower strain ($E_2$) and occurred over a moderately shorter time ($\eta_2$). Irreversible flow took place over a moderately short time (determined from the $\eta_3$ value). The xE-SDS-PS was expected to have the greatest compatibility between filler and EPDM. This composite had the highest $E_1$ value indicating that molecular uncoiling was limited due to the filler-EPDM interactions. Time dependant uncoiling gave lower strain ($E_2$) similar to that of xE-SDS but required a longer time ($\eta_2$) than xE-SDS. The irreversible flow ($\eta_3$) required a longer time than xE-SDS to occur though it was less retarded than the highly extended unfilled elastomer. The xE-UT composite was expected to have the weakest interactions between filler and EPDM (consisting mainly of mechanical adhesion at the filler-matrix interface). Instantaneous uncoiling ($E_1$) was limited by filler (though not to the extent of the SDS or SDS-PS fillers) even though weak interactions were present. The resistance to time dependant uncoiling ($E_2$) was moderately limited by the untreated alumina but took place over the longest time ($\eta_2$) compared with the other materials. The irreversible flow ($\eta_3$) took place over the shortest time compared with the other analysed materials.

Data obtained from the recovery analysis of the EPDM-based materials were modelled with the KWW equation; the resultant parameter values can be seen in Table 15. Relaxation of the
elastic component of the viscoelastic modulus ($E_2$) has been equated to the $A$ parameter. The $\beta$ parameter was equated to the distribution of relaxation. The distribution of relaxation is exponential if $\beta$ equals 1; however as $\beta$ approaches zero the distribution become increasingly skewed.

Table 15 KWW equation parameters obtained from modelling EPDM-based materials recovery analysis data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycle</th>
<th>$A$ mm.mm$^{-1}$</th>
<th>$\tau$ min</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
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<td>4.84</td>
<td>0.025</td>
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<td>0.011</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td>4.50</td>
<td>0.010</td>
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<td>0.019</td>
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<tr>
<td>xE-UT</td>
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<td>0.005</td>
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<td></td>
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<td></td>
<td>4</td>
<td>0.378</td>
<td>5.00</td>
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The xE material had the second largest value for $A$; slightly smaller than xE-UT therefore they possessed similar resistance to viscoelastic recovery. The xE material had low interactions (dispersive forces) and a low level of crosslinking (similar between all materials). The relaxation time of the recovery of xE was relatively low since the molecules had low impediments to relaxation. The distribution factor values implied that xE had the least constraints to the operation of relaxation modes. Further modes became progressively available as described by the stretched exponential function as relaxation progressed. Molecular orientation during the straining (creep) phase will leave some molecules with limited free volume in which to relax. Constrained molecules will become unhindered allowing relaxation to occur as relaxation progresses.

The xE-SDS composite had less resistance to relaxation than that of xE or xE-UT (determined from their $A$ values). Even though there was filler present the SDS surfactant on the filler surface provided a lubricating effect on the relaxation processes. This was observed in the relaxation time values where xE-SDS had the lowest $\tau$ value. The value of the distribution
factor of the modelled xE-SDS relaxation data was lower than that of xE-UT indicating that there were steric constraints inhibiting relaxation modes.

The xE-SDS-PS composite had low resistance to recovery (determined from A values) contrasted with the longest relaxation time. The distribution factor value was similar to xE indicating low constraints to the release of relaxation modes. This and the increased relaxation time were expected due to the higher interaction between the PS-layer on the alumina and EPDM.

The xE-UT composite had the highest A value which was associated with the greatest resistance to recovery. While the interactions between filler and EPDM are expected to be low, the untreated alumina has been linked to clustering of filler particles with the entrapment of elastomer molecules. The relaxation time determined was towards the longer value compared with xE-SDS but not significantly different from xE-SDS-PS and even XE. The value of $\beta$ for xE-UT was the lowest giving xE-UT the most skewness, consistent with the steric hindrance by filler particles in clusters that progressively release relaxation modes of the elastomer.

**Alumina surface chemistry and composite elasticity, damping and properties glass transitions**

Modulated force thermomechanometry was employed using a single frequency modulation to characterise the elasticity and damping properties of all EPDM-based materials. Figure 66 shows the storage modulus values for all materials obtained from analysis at 1 Hz over the designated temperature range. The increase in $E'$ of xE-UT at the onset of glass transition temperature ($T_g$, approximately -45°C) is proposed to be caused by the increased availability of rotational modes of molecular segments previously inhibited by the clustering of the untreated alumina, causing the xE-UT sample to contract. This required the Diamond DMA to apply a greater force than previously required to maintain the chosen strain, resulting in a greater applied stress, hence an apparent increased modulus value. The increase in modulus values continued with increasing temperature until $T_g$, after which the modulus values decreased. The $E'$ of the other materials was observed to decrease slightly at the onset of $T_g$.

The xE-UT composite had the largest storage modulus at post-$T_g$ temperatures, which was consistent with entrapped EPDM in filler clusters being unable to exercise elasticity and the highest volume fraction of filler present (as seen in the TGA results). This is in contrast to the weak interactions with fillers that would cause a lower $E'$.

The PS-coated alumina was well dispersed and expected to have the highest interactions with EPDM, as seen by the xE-SDS-PS composite having an enhanced $E'$ at post-$T_g$ temperatures,
compared with xE. The xE-SDS modulus values appear anomalous in having a higher post-$T_g$ $E'$ than xE-SDS-PS, however this was consistent with recovery analysis data model parameters where the resistance to recovery (A value) was lower than xE-SDS-PS, but xE-SDS had the faster relaxation time.

![Figure 66 Storage modulus versus temperature: xE (O-); xE-SDS (O-); xE-SDS-PS (□-); xE-UT (△-)](image)

The term *temperature of failure* was used to describe the temperature at which the material was unable to support the analysed frequency/ies (for the EPDM-based materials, 1 Hz) vibrations. The order of EPDM-based material temperatures of failure from highest of lowest was xE-UT, xE-SDS-PS, xE-SDS then xE. The xE-UT composite was the highest due to the entrapped polymer artificially increasing the volume fraction of filler and the real filler volume fraction being higher than the filler volume fraction in other composites, resulting in greater thermal stability. The xE-SDS-PS composite was next due to this composite having the highest interactions between filler and EPDM. The moderate interactions between the SDS-coated alumina and EPDM provided some temperature resistance in the xE-SDS composite. The unfilled EPDM only possesses chemical crosslinking to resist thermal motion hence it had the lowest temperature of failure of all of the EPDM-based materials.

The loss modulus values obtained from analysis at 1 Hz of all EPDM-based materials are shown in Figure 67. The xE-SDS-PS and xE-SDS $E''$ modulus values were approximately equal, and the largest followed by xE and the xE-UT composite which had the lowest $E''$ modulus values at pre-$T_g$ temperatures. This indicated that good interaction between filler and EPDM increased the loss modulus values whilst poor interactions resulted in decreased loss.

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modulus values. The lower xE-UT $E''$ values were due to the free volume effect and weak interactions.

All materials had approximately the same loss modulus values at $T_g$, meaning that xE-UT had the greatest increase in $E''$ values with the onset of $T_g$. The $E''$ (viscoelasticity) corresponds to absorption of energy and conversion to heat at post-$T_g$ temperatures. The xE and xE-SDS materials were observed to have similar energy loss until xE fractured, as indicated by their similar $E''$ values. The lubricating effect of the SDS gave it the same energy loss properties as the unfilled elastomer. The xE-UT composite had the highest loss of energy due to its apparent higher volume fraction (EPDM entrapped in filler clusters) and actual higher volume fraction of filler (as seen in TGA results). The xE-SDS-PS composite had the lowest loss of energy at post-$T_g$ temperatures due to stronger interactions.

The tan δ values obtained from analysis at 1 Hz over the designated temperature range of all composites is seen in Figure 68. All materials were observed to have a single sharp peak at approximately the same temperature (~40 °C ± 1). The unfilled elastomer had the lowest $E'$ and second lowest $E''$ values but the highest tan δ values. This was expected as there were only chemical crosslinks to inhibit energy dispersion. The xE-SDS-PS composite had the second lowest and lowest $E'$ and $E''$ values respectively, but the second highest tan δ values. Therefore the SDS-PS-coated filler contributed mainly to the viscoelastic modulus resulting in better energy dispersion compared with the other fillers; however this filler still inhibited energy dispersion compared with the unfilled elastomer. The xE-UT composite had the lowest
tan δ but the highest $E'$ and $E''$ values, therefore the filler in xE-UT contributed mostly to increasing the elastic modulus, not energy dispersion. The xE-SDS composite had moderate $E'$, $E''$ and tan δ values. This indicated that the SDS-coated filler contributed to both increasing elasticity and energy dispersion but to a lesser extent than the untreated alumina filler that mainly contributed to elasticity, and the SDS-PS coated alumina filler that mainly contributed to energy dispersion.

![Figure 68 Tan δ versus temperature: xE (○); xE-SDS (○); xE-SDS-PS (□); xE-UT (△)](image)

**Figure 68 Tan δ versus temperature: xE (○); xE-SDS (○); xE-SDS-PS (□); xE-UT (△)**

**Plateau and terminal modulus, and relaxation times derived from the Havriliak-Negami relaxation equation**

The HN relaxation equation was employed to model the plateau modulus ($E_\infty$), terminal modulus ($E_0$) and relaxation time for each EPDM-based material to determine the effect of alumina surface chemistry on the resultant parameters. The method used for modelling single frequency mechanical analysis data with the HN relaxation equation was described in Chapter 3, based upon the method used by Szabo and Keough[214]. Data obtained at 5 °C intervals was used for modelling with the HN equation. Figure 69 displays the Cole-Cole plots of the dynamic mechanical data from 1 Hz analysis of the EPDM-based materials. Figure 70 displays the simulated EPDM-based dynamic mechanical analysis data from modelling with the HN equation. Figures displaying the dynamic mechanical data modelled with the HN equation for each individual EPDM-based material are shown in Appendix 1.1.
Figure 69 Cole-Cole plots of 1 Hz dynamic mechanical data: xE (-O-); xE-SDS (-◊-); xE-SDS-PS (-□-); xE-UT (-△-)

Figure 70 HN modelling data of EPDM-based material frequency data: xE (-O-); xE-SDS (-◊-); xE-SDS-PS (-□-); xE-UT (-△-)

Table 16 lists the resultant parameters from the data modelling and the associated Wicket errors. The Wicket error was observed to be smallest for the xE-UT composite followed by the unfilled elastomer. The xE-SDS and xE-SDS-PS composites possessed the largest wicket error.
The presence of filler was observed to increase the $E_0$ modulus compared with the unfilled elastomer. The three filled materials had similar $E_0$ modulus values with a range of 5 MPa between them. The addition of the SDS-coated and SDS-PS-coated alumina to EPDM increased the value of the $E_0$ modulus. The untreated alumina caused a reduction in $E_0$ value due to the increasing $E'$ modulus at the onset of $T_g$, caused by the Diamond DMA applying a greater force than previously required to maintain the chosen strain, resulting in an apparent increased modulus value.

The $\alpha$ shape parameter (relating to symmetry) was observed to decrease with the addition of all fillers in comparisons between the $\alpha$ values of the unfilled elastomer and the composites. The SDS-coated and SDS-PS-coated aluminas only slightly reduced the $\alpha$ value (by 0.010 and 0.023 decrease respectively) whereas the untreated alumina caused the greatest reduction in $\alpha$, by 0.103. The $\beta$ shape parameter (related to skewness) was observed to slightly decrease with the addition of the SDS-coated and SDS-PS-coated alumina (0.002 and 0.005 decrease respectively) but $\beta$ increased with the addition of the untreated alumina (0.088 increase), compared with the values for the unfilled elastomer.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_\infty$ GPa</th>
<th>$E_0$ MPa</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>Wicket error</th>
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<td>xE</td>
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</tr>
<tr>
<td>xE-UT</td>
<td>3.40</td>
<td>28.00</td>
<td>0.550</td>
<td>0.143</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure 71 represents the calculated relaxation times at each temperature where the 1 Hz data was modelled with the HN equation. The relaxation times of the EPDM-based materials differed greatest at pre-$T_g$ temperatures. The xE and xE-SDS-PS materials had the longest calculated relaxation times at these temperatures, while xE-SDS had a moderately fast times and xE-UT had the fastest calculated relaxation times. The calculated relaxation times of all the EPDM-based materials were approximately equal at $T_g$ and post-$T_g$ temperatures.
Conclusion

The SDS-PS treated alumina was observed to have excellent dispersion properties in an EPDM matrix compared with the untreated alumina, as observed in SEM micrographs. The SDS-coated alumina was well dispersed but was not completely wetted by the EPDM matrix. Thermal reinforcement was provided by the presence of all fillers, with greater compatibility resulting in increased thermal stability for the composites containing treated aluminas due to adsorption of volatiles and decreased diffusion of degradation volatiles through the matrix. However the presence of UT alumina resulted in the greatest increase in thermal stability due to higher weight fraction of UT alumina present (due to the solvent casting film preparation method).

The results from stress-strain analysis indicated that xE-UT possessed a greater modulus than xE but had a lower strain at break due to the untreated alumina surface being weakly bonded to the EPDM. The xE-SDS and xE-SDS-PS composites showed the greatest reinforcement; their modulus values were greater than those of xE and xE-UT and their stress-strain data demonstrated a yield stress then further extension until breakage. The xE-SDS-PS composite possessed the greatest initial modulus since physical crosslinks with filler predominate at lower strains as the molecular segments begin to uncoil and the greater compatibility between filler and matrix provided by the styrene coating. This indicated that while the addition of any of these fillers increased the initial modulus, the modulus will increase greatest with increasing compatibility between filler and EPDM. The xE-SDS and xE-SDS-PS composites
were thought to have had voiding at the filler surface during stress-strain analysis as indicated by whitening under extension. The xE-SDS-PS composite was observed to have the strongest filler-matrix interface as evidenced by it requiring the highest stress for similar strain values compared with the other EPDM-based materials until breakage. The xE-SDS had the highest strain at breakage due to the surfactant on the alumina acting as lubricant allowing for molecular segments to slip past each other. The untreated alumina decreased the maximum strain extension due to the poor interface between filler and matrix.

Results from creep and recovery analysis showed that xE had the largest instantaneous, elastic deformation in response to applied forces followed by xE-UT, xE-SDS and xE-SDS-PS. This trend indicated that the greater the compatibility between filler and elastomer the smaller the initial elastic deformation; however all fillers reduced the initial creep extension. The viscoelastic and viscous deformation following elastic extension was most prevalent in xE, followed by xE-UT, xE-SDS and xE-SDS-PS indicating that greater compatibility between matrix and filler resulted in greater resistance to viscoelastic and viscous deformation; however all fillers reduced these deformations. The filled composites possessed faster recovery in the viscoelastic recovery region of the recovery time-strain data compared with xE time-strain data.

Modelling of creep analysis data revealed that xE had the least resistance to instantaneous and time dependant uncoiling and extension of molecules; but the greatest resistance to permanent flow. The uncoiling of molecules in xE-SDS was limited compared with the xE material while time dependant uncoiling was at a lower and occurred over a moderately shorter time. Irreversible flow took place over a moderately short time. The xE-SDS-PS had the highest E1 value indicating that molecular uncoiling was limited due to the filler-EPDM interactions while time dependant uncoiling was at a lower strain similar to that of xE-SDS but required a longer time for time dependant uncoiling. The irreversible flow of xE-SDS-PS required a longer time than xE-SDS to occur though it was less retarded than xE-UT. The instantaneous uncoiling of xE-UT was limited by filler (though not to the extent of the SDS or SDS-PS fillers) even though only weak interactions were present. The resistance to time dependant uncoiling was moderately limited by the untreated alumina but took place over the longest time compared with the other materials. Irreversible flow of xE-UT took place over the shortest time compared with the other analysed materials.

Modelling of recovery analysis data revealed that xE possessed similar resistance to viscoelastic recovery as xE-UT. The relaxation time of the recovery of xE was relatively low since the molecules had low impediments to relaxation. The distribution factor values implied
that xE had the least constraints to the operation of relaxation modes. The xE-SDS composite had less resistance to relaxation than that of xE or xE-UT. Even though there was filler present the SDS surfactant on the filler surface provided a lubricating effect on the relaxation processes as observed in the relaxation time values where xE-SDS had the lowest $\tau$ value. The value of the distribution factor of the modelled xE-SDS relaxation data was lower than that of xE-UT indicating that there were steric constraints inhibiting relaxation modes. The xE-SDS-PS composite had low resistance to recovery contrasted with the longest relaxation time. Its distribution factor value was similar to xE indicating low constraints to the release of relaxation modes. The xE-UT composite had the greatest resistance to recovery since the untreated alumina had been linked to clustering of filler particles with the entrapment of elastomer molecules. The relaxation time determined was towards the longer value compared with xE-SDS while the value of $\beta$ for xE-UT was the lowest giving the most skewness. These results were consistent with the steric hindrance by filler particles in clusters that progressively release relaxation modes of the elastomer.

Modulated force thermomechanometry characterised the elasticity and damping properties of composites. The increase in $E'$ of xE-UT at the onset of glass transition temperature was proposed to be caused by the increased availability of rotational modes of molecular segments, requiring the Diamond DMA to apply a greater force than previously used to maintain the chosen strain. This resulted in a greater applied stress, hence an apparent increased modulus value. The $E'$ of the other materials was observed to decrease slightly at the onset of $T_g$. The xE-UT composite had the largest storage modulus at post-$T_g$ temperatures, which was consistent with entrapped EPDM in filler clusters being unable to exercise elasticity and the highest volume fraction of filler present. The xE-SDS modulus values appear anomalous in having a higher post-$T_g$ $E'$ than xE-SDS-PS, however this was consistent with recovery analysis data model parameters where the resistance to recovery was lower than xE-SDS-PS but xE-SDS had a faster relaxation time. The order of EPDM-based material temperatures of failure from highest to lowest was xE-UT, xE-SDS-PS, xE-SDS then xE. The xE-UT composite had the greatest modulus value due to the entrapped polymer artificially increasing the volume fraction of filler and the real filler volume fraction being higher than the filler volume fraction in other composites, resulting in greater thermal stability. The xE-SDS-PS composite was next due to this composite having the highest interactions between filler and EPDM. The moderate interactions between the SDS-coated alumina and EPDM provided some temperature resistance in the xE-SDS composite.
The loss modulus values obtained from analysis indicated that at pre-$T_g$ temperature the xE-SDS-PS and xE-SDS $E''$ modulus values were the largest followed by xE then xE-UT indicating that good interaction between filler and EPDM increased the loss modulus values whilst poor interactions resulted in decreased loss modulus values. The lower xE-UT $E''$ values were attributed to the free volume effect and weak interactions. All materials had approximately the same loss modulus values at $T_g$. The xE and xE-SDS materials were observed to have similar $E''$ modulus values until xE fractured. The lubricating effect of the SDS gave it the same energy loss properties as the unfilled elastomer. The xE-UT composite had the highest loss of energy due to its apparent higher volume fraction (EPDM entrapped in filler clusters) and actual higher volume fraction of filler. The xE-SDS-PS composite had the lowest loss of energy at post-$T_g$ temperatures due to stronger interactions.

The tan $\delta$ data obtained from analysis were observed to have a single sharp peak at approximately the same temperature (-40 °C ± 1). The unfilled elastomer had the highest tan $\delta$ values as was expected since there were only chemical crosslinks to inhibited energy dispersion. The xE-SDS-PS composite had the second highest tan $\delta$ values indicating the SDS-PS-coated filler contributed mainly to the viscoelastic modulus resulting in better energy dispersion compared with the other fillers; however this filler still inhibited energy dispersion compared with the unfilled elastomer. The xE-UT composite had the lowest tan $\delta$ the filler contributed mostly to increasing the elastic modulus, not energy dispersion. The xE-SDS composite had moderate tan $\delta$ values indicating the SDS-coated filler contributed to both increasing elasticity and energy dispersion but to a lesser extent than the untreated alumina filler that mainly contributed to elasticity, and the SDS-PS coated alumina filler that mainly contributed to energy dispersion.

The HN relaxation equation modelled the plateau modulus, terminal modulus and relaxation time. The presence of filler was observed to increase the $E_0$ modulus compared with the unfilled elastomer. The three filled materials had similar $E_0$ modulus values with a range of 5 MPa between them. The addition of the SDS-coated and SDS-PS-coated alumina to EPDM increased the value of the $E_x$ modulus while the untreated alumina caused a reduction in $E_x$ value due to the Diamond DMA applying a greater force than previously required, resulting in an apparent increased modulus value.

The $\alpha$ shape parameter was observed to decrease with the addition of all fillers. The SDS-coated and SDS-PS-coated aluminas only slightly reduced the $\alpha$ value whereas the untreated alumina caused the greatest reduction. The $\beta$ shape parameter was observed to slightly
decrease with the addition of the SDS-coated and SDS-PS-coated alumina but increase with the addition of the untreated alumina. The calculated relaxation times of the EPDM-based materials differed greatest at pre-\(T_g\) temperatures with \(xE\) and \(xE-SDS-PS\) having the longest calculated relaxation times while \(xE-SDS\) had a moderately fast times and \(xE-UT\) had the fastest calculated relaxation times. The calculated relaxation times of all the EPDM-based materials were approximately equal at \(T_g\) and post-\(T_g\) temperatures.
Chapter 5 Methyl acrylate, silica and the thermal properties of poly(ethylene-co-methyl acrylate) - silica nanocomposites

Introduction

Poly(ethylene-co-methyl acrylate) (EMA) is an elastomeric semi-crystalline random copolymer prepared by the high pressure polyethylene process. EMA is analogous to low-density polyethylene with interspersed methyl acrylate units. Methyl acrylate units are excluded from the crystals so the amorphous phase consists of chain segments containing more than the average methyl acrylate content. The amorphous phase provides elastomeric properties. The crystalline phase contains chain segments only consisting of ethylene units. The crystals form physical crosslinks to provide cohesion to EMA. The crystallinity is decreased with increasing methyl acrylate content.

Addition of filler provides increases cohesion. The silica filler is expected to bond predominantly to the polar methyl acrylate units, which will increase stiffness of the amorphous phase. This is especially expected since hydrophilic silica was used. A secondary effect of silica may be to nucleate crystallisation though this may be restricted by preferential adsorption of methyl acrylate units onto silica.

The objectives of this part of the project were to prepare nanocomposites from a thermoplastic elastomer where chemical crosslinking was not required, to determine the contribution of the polar functional groups, and to investigate their thermal, dynamic force, static force and modulated force thermomechanical properties. These properties will be interpreted using relaxation models that have been described in Chapter 2, and applied to EMA composites in Chapter 5.
Chapter 5 Methyl acrylate, silica and the thermal properties of poly(ethylene-co-methyl acrylate) - silica nanocomposites

Experimental

Preparation of poly(ethylene-co-methyl acrylate) – silica nanocomposite sheets

Composites were prepared with hydrophilic nano-particulate silica (Aerosil 380) and two poly(ethylene-co-methyl acrylates) with methyl acrylate contents of 9 %,w/w and 19 %,w/w. The nanocomposites were prepared by solution dispersion and pressing into sheets according to the method described in Chapter 3. The compositions and naming scheme for the EMA-based materials is shown in Table 17. Thermogravimetry (TGA) was performed on the materials using samples of approximately 2 mg. TGA was used to confirm the actual silica composition and to identify any EMA thermal stability conferred by the silica filler. The detailed TGA method for analysis and data processing is described in Chapter 3.

Composite characterisation

Stress-strain analysis (dynamic force thermomechanometry (df-TM)) was performed in tensile mode using rectangular specimens of length × width × thickness 25 × 10 × 0.5 mm. Creep and recovery analysis (static force thermomechanometry (sf-TM)) was performed in tensile mode using rectangular specimens of length × width × thickness 8.5 × 10 × 0.5 mm. Single and multi-frequency modulated force thermomechanometry (mf-TM) were performed in tensile mode using a heating rate of 2 °C·min⁻¹ for single frequency analysis, and a stepwise isothermal temperature program for multi-frequency analysis. Details of these methods are described in Chapter 3.

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</thead>
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</tr>
<tr>
<td>EMA9Si1</td>
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<tr>
<td>EMA19Si20</td>
<td>19</td>
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</tr>
</tbody>
</table>

Table 17 EMA-based materials formulation designation and composition
Mechanical characterisation data analysis

Data from thermomechanometry experiments were analysed and interpreted using several theoretical models. Numerical solutions were obtained for the modelling with an iterative calculation using Excel Solver. Creep data was described using the four element elastic, viscoelastic and viscous model. Recovery data were modelled using the KWW stretched exponential model to allow for delayed or constrained recovery. Modulated force frequency-temperature data were used to construct mastercurves that were then modelled using each of the Debye (D), Cole-Cole (CC), Cole-Davidson (CD) and Havriliak-Negami (HN) relaxation equations.

Results and Discussion

Thermal stability dependence on methyl acrylate content and silica composition

TG was performed on the EMA elastomers and EMA-silica nanocomposites to confirm silica composition and assess any contribution of thermal stability from the silica or methyl acrylate content. The TG data for EMA9 and the EMA9Si composites is shown in Figure 72. A single step mass loss decomposition occurred with an onset above 400 °C over a temperature range of approximately 20 °C. The plateau after decomposition was used to calculate the actual silica content. Confirmation of complete polymer degradation was demonstrated by the lack of residue from the pure EMA9. The degradation temperatures increased slightly with increased silica composition.
Figure 72 Filler composition and thermal stability: EMA9 (-○-); EMA9Si1 (-□-); EMA9Si5 (-△-); EMA9Si10 (-×-); EMA9Si20 (-○-)

Figure 73 shows the corresponding TG data curves for the EMA composites with 19 %·w/w methyl acrylate and varying silica compositions. All of the EMA19-based materials exhibited a single step mass loss with onset above 400 °C and a slightly shorter temperature range than obtained for the EMA9-based materials.

Figure 73 Filler composition and thermal stability: EMA19 (-○-); EMA19Si1 (-□-); EMA19Si5 (-△-); EMA19Si10 (-×-); EMA19Si20 (-○-)

The decomposition of each material was taken at the temperature (T₀.5) for 50 %·w/w mass loss. This temperature was chosen because there was a single decomposition mass loss event.
for each material. Figure 74 shows the decomposition temperature plotted against the filler volume fraction (Φ). Thermal stability increased with silica volume fraction with curvature indicating a plateau stability would occur above 20 %·v/v. Logarithmic curves were fitted to each data set to give Equations 63 and 64 for EMA9-based and EMA-19 based materials respectively.

\[
T_{0.5} = 7.18 \cdot \ln(\Phi) + 480 \quad \text{Equation 63}
\]

\[
T_{0.5} = 6.51 \cdot \ln(\Phi) + 472 \quad \text{Equation 64}
\]

The EMA9 degradation temperature was raised by 20 °C and EMA19 degradation temperature by 19 °C for the 20 %·w/w filled composites compared with the pure polymer.

The increased degradation temperature was attributed to adsorption of polymer and pyrolysis products on the silica resulting in a decreased rate of volatiles loss at a particular temperature, in this case the temperature from a constant mass loss of 50 %·w/w. EMA9-based materials were more stable than their EMA19-based counterparts for the pure polymers and each filler composition. The methyl acrylate derived ester groups were shown to be the less stable parts of the polymers.
thermogravimetric analysis) of the EMA composites converted to volume fraction from the TG weight fraction output. Each composite possessed actual silica volume fractions near to the desired volume fractions as listed. The unfilled EMA9 and EMA19 TG data indicated that there was a small amount of residue from the EMA matrix remaining at completion of analysis. This would partly account for a slight difference between desired and actual silica content remaining in other composite TG data. The EMA9-based materials possessed an overall higher volume fraction remaining at the conclusion of TG than their EMA19 counterparts. This difference is the result of an excess in carbon residue due to the EMA9 variety possessing greater amount of polyethylene compared with EMA19. The EMA9Si20 composite had a maximum difference of 1.3 %.v/v compared with other composites where the largest difference was 0.8 %.v/v (for EMA9Si10).

**Table 18 Final mass remaining after TGA converted to volume fraction**

<table>
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<tr>
<th>Material</th>
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</tr>
</thead>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>EMA19Si10</td>
<td>10.6</td>
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<tr>
<td>EMA19Si20</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Direct comparisons between each composite with differing MA weight fractions but similar silica volume fractions were graphed. The EMA9 composites possessed a higher decomposition temperature and remaining volume fraction as expected from the previously discussed results. Figure 75 represents a comparison of TG data between the EMA9Si20 and EMA19Si20 composites. Other comparison figures can be found in Appendix 2.1.
Stress-strain response with methyl acrylate and silica composition

Dynamic force thermomechanometry as stress-strain analysis was employed to characterise the effect of varying methyl acrylate and silica content on physical crosslink strength in each material. Figure 76 represents stress-strain analyses of the EMA9-based materials. The data generated from these analyses were based upon the original sample dimensions (as stated previously), resulting in engineering stress-strain data being generated. It was not possible to obtain true stress-strain data because the Instron did not have an optical encoder extensometer attachment that could measure the instantaneous sample dimensions. Young’s modulus (as listed in Table 24 in the comparison of elastic moduli section) increased with increasing filler content. This was expected as filler effects predominate at lower strains. The materials EMA9, EMA9Si1, EMA9Si5 each displayed a yield followed by further extension. Each of these materials fractured at approximately the same strain (2.75); however none had strain-induced stiffening, as indicated by their plateauing of stress required for continual strain extension after yielding. EMA9 and EMA9Si1 had the similar stress values required for continual strain extension from approximately 1.5 strain value and onwards until breakage. EMA9Si10 displayed onset of yielding but fractured before any further strain extension could be performed and EMA9Si20 did not exhibit a yield before fracturing. These results indicated that the inclusion of 1 and 5 % v/v of silica increased the strength but had little effect on the toughness compared with unfilled EMA9. The strength increased but toughness was reduced at silica concentrations of 10 and 20 % v/v indicating the brittleness of the composites.
Figure 76 Stress-strain data: EMA9 (-◇-); EMA9Si1 (-◇-); EMA9Si5 (-△-); EMA9Si10 (-×-); EMA9Si20 (-○-)

Figure 77 represents stress-strain analyses of the EMA19-based materials. There was an increase in modulus with increasing filler content (as listed in Table 24 in the comparison of elastic moduli section) since filler effects predominate at lower strains. EMA19, EMA9Si1, EMA9Si5 and EMA9Si10 had yielding and subsequent extension without strain-induced hardening. The materials EMA19, EMA19Si1, EMA19Si5 each slipped from the clamps before breakage could occur due to thinning of the sample at high strains. The EMA19Si20 composite did not exhibit a yield before fracturing. These observations indicate that all of the designated volume fraction additions of silica resulted in stronger composites when compared with EMA19. The EMA19Si10 and EMA19Si20 composites were observed to have reduced toughness compared with EMA19, EMA19Si1 and EMA19Si5. The toughness of EMA19Si1 and EMA19Si5 cannot be commented upon in relation to EMA19 as they slipped before fracturing.
Comparisons were made between the stress-strain analyses of the EMA9-based and EMA19-based materials to observe the effect of differing methyl acrylate weight fractions at different silica volume fractions. Figure 78 represents the stress-strain analysis data for the EMA9Si10 and EMA19Si10 composites. Each of the EMA9 and EMA9Si composites were observed to have a greater modulus than the EMA19 and similarly filled EMA19Si composites, as listed in Table 24. The EMA9-based materials possessed Young’s moduli double, or triple that of the EMA19-based materials. The increase of modulus with increasing silica volume fraction was largest in the EMA9-based materials. The EMA9 elastomer and EMA9Si composites yielded at higher stresses than EMA19 and the similarly filled EMA19-based materials. This and the modulus results indicated that the EMA9-based materials were the strongest due to the increased crystallinity. The EMA19-based materials extended to longer strains than their EMA9 counterparts; except for the 5% v/v silica filled composites where the final strain extension value was similar (although the EMA19Si5 composite did not break but slipped from the Instron clamps). These results indicated that the EMA19-based materials were tougher than their EMA9 counterparts due to the plasticising effect of their greater methyl acrylate weight fraction. Other comparison figures of EMA-based materials are in Appendix 2.2.
Chapter 5 Methyl acrylate, silica and the thermal properties of poly(ethylene-co-methyl acrylate) - silica nanocomposites

Creep and recovery response of materials with methyl acrylate and silica composition

Static force thermomechanometry as creep and recovery analysis was employed to characterise the effect of varying methyl acrylate and silica content on physical crosslink strength for each composite. The analysis method used for creep and recovery analysis (Chapter 3, page 89, Table 5); which applied a constant force to each material was employed as this would yield information about the effect of filler on resistance to deformation and recovery. Another method that could be employed is to apply a force (or a sample extension) that would correspond to a designated fraction of maximum tensile strength (or fraction of an extension) to all materials; however this would require the maximum tensile strength of each material to be already known. A similar method to this is outlined in ASTM D 2990 – 0; which requires several analyses with applied forces that result in strains above and below the designated strain (1 % for this testing method). Interpolation is then used to determine the applied force required for 1 % strain. This would make the elastic strain constant, while the viscoelastic and viscous strains would vary, along with the force required, so the results for different materials would be difficult to compare.

Figures 79 and 80 show the resultant creep and recovery time-strain data obtained from these analyses. The highest silica volume fraction EMA composites (the 10 and 20 %.v/v SiO₂ filled composites) were observed to have greatest resistance to creep when compared with the unfilled elastomers and other silica volume fractions. This was indicated by these composites having a small initial elastic strain extension. The 10 and 20 %.v/v SiO₂ filled composites
exhibited less curvature in the viscoelastic data, and less viscous creep compared with the unfilled elastomers and other composites; greater curvature in time-strain data indicates longer times for viscoelastic deformation. These results indicated that the composites with highest silica volume fractions were time-dependently and permanently deforming less with respect to time than the other materials.

Figure 79 Creep and recovery analysis data: EMA9 (○-); EMA9Si1 (□-); EMA9Si5 (△-); EMA9Si10 (□-); EMA9Si20 (○-); solid lines indicate modelling by the 4-element model (creep phase) and KWW function (recovery phase)

All materials displayed some instantaneous (elastic) recovery before time dependant (viscoelastic) recovery, represented by the curvature in time-strain recovery data. The 10 and 20 % v/v silica filled composites had little curvature in their recovery data indicating reduced viscoelastic recovery compared with the other materials. This was expected due to these composites displaying less viscoelastic deformation in the creep phase. The unfilled elastomers and lower silica volume fraction composites showed broader curvature in their recovery time-strain data (as expected due to the curvature in the creep time-strain data). The inclusion of silica into the elastomer resulted in faster retardation and relaxation times from these observations.

The maximum strain in the creep phase data increased slightly over subsequent creep and recovery analysis cycles. The largest increase was observed in the unfilled elastomers and with increasing silica volume fraction this increase was reduced. The minimum strain value in the recovery phase data (equated to the permanent or viscous deformation) was observed to increase over subsequent analysis cycles. The change in permanent strain after recovery was
reduced with increasing silica volume fraction, consistent with the trend observed during the creep phase.

![Graph showing creep and recovery analysis data for EMA9, EMA19Si1, EMA19Si5, EMA19Si10, and EMA19Si20 composites. Solid lines indicate modelled by the 4-element model (creep phase) and KWW function (recovery phase).]

Figure 80 Creep and recovery analysis data: EMA19 (-◊-); EMA19Si1 (-□-); EMA19Si5 (-△-); EMA19Si10 (-×-); EMA19Si20 (-○-); solid lines indicate modelled by the 4-element model (creep phase) and KWW function (recovery phase)

The EMA9 elastomer and EMA9Si composites were observed to have a reduced maximum creep and minimum recovery strain values under application and removal of stress with increasing silica volume fraction. The EMA19-based materials did not follow a similar pattern with regard to strain values and silica volume fraction. The highest creep strain value exhibited by any of the EMA19-based materials was observed for EMA19Si5. This result may be attributed to interactions between the EMA and silica particles. The silica may have inhibited nucleation of polyethylene crystals within the EMASi composite. However at the highest silica volume fractions (10 and 20 %:v/v), EMA19Si10 and EMA19Si20 had the second lowest and lowest creep strain values respectively. This indicated that at these volume fractions, the silica is dominating the reinforcing effect of the EMA19Si composites compared with crystallinity (since EMA19 has less crystallinity than EMA9).

The EMA9 elastomer and EMA9Si composites were observed to creep less than their EMA19Si counterparts, as evidenced by the EMA19 elastomer and EMA19Si composites having higher creep strain value maximums at each silica volume fraction. This was due to the increased crystallinity in the EMA9-based materials. The curvature in the creep and recovery time-strain data was more pronounced in the EMA19 elastomer and EMA19Si composites compared with the EMA9-based materials due to the increased methyl acrylate weight fraction resulting in less resistance to viscoelastic deformation.
Creep and recovery models

The 4-element model and Kohlrausch-Williams-Watts (KWW) equation were employed to model creep and recovery data, respectively to determine moduli and relaxation properties. The 4-element model provides five parameters though only four are independently calculated (since $\tau = \eta_2 / E_2$). The four parameters $E_1$, $E_2$, $\eta_2$, $\eta_3$ describe different phenomena but they are not independent since $E_1$ occurs first and the other parameters are consequential on the state of the material after elastic deformation. The viscoelastic ($E_2$ and $\eta_2$) and viscous ($\eta_3$) events occur simultaneously but the molecular motions involved are coupled. The provisions make consistent trends difficult to indentify. The material variables were filler content, methyl acrylate content and crystallinity that are determined by the previously mentioned parameters, for this research.

The resultant parameters from applying the 4-element model to the creep analyses are shown in Table 19 and Table 20 for the EMA9-based and EMA19-based materials respectively. The elastic modulus ($E_1$) consistently increased with silica content for the EMA9-based materials. An increasing modulus trend was less consistent for the EMA19-based materials, where increased methyl acrylate polar groups will give stronger adsorption to the silica but crystallinity will be more severely constrained. The elastic modulus values of EMA9 and each EMA9Si composite were overall larger than their EMA19-based counterparts indicating that greater crystallinity in the EMA9-based materials resulted in increased resistance to elastic deformation.
The time dependent uncoiling of molecules was observed to occur at increasingly lower strains ($E_2$) and longer times ($\eta_2$) with increasing silica volume fraction for the EMA9 series of materials. There was an overall decrease in the strain and increase in time required for time dependent uncoiling of molecules and deformation although the changes with each subsequent increase in silica volume fraction were inconsistent for the EMA19 series of materials. The $E_2$ and $\eta_2$ values of the EMA9 elastomer and each EMA9Si composite were larger than their EMA19-based counterparts for each silica volume fraction. This was due to the increased crystallinity in the EMA9-based materials and increased methyl acrylate weight fraction in the EMA19-based materials. The irreversible flow ($\eta_3$) was observed to occur at increasingly longer times with increasing silica volume fraction for the EMA9 series of materials. There was an overall increase in the time for irreversible flow to occur although the changes with each subsequent increase in silica volume fraction were inconsistent for the EMA19 series of materials. The $\eta_3$ values of the EMA9 elastomer and EMA9Si composites were greater than their EMA19 counterparts for each silica volume fraction due to the increased crystallinity in the EMA9-based materials and increased methyl acrylate weight fraction in the EMA19-based materials. The retardation times were observed to decrease with increasing silica volume fraction for both the EMA9 and EMA19 series of materials and were

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<th>$E_2$</th>
<th>$\eta_2$</th>
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of similar value between the two series of materials with the greatest difference being 0.03 min between the unfilled elastomers.

Table 20 4-element moduli values for EMA19Si composites obtained from modelling creep data

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<tr>
<th>SiO₂ volume fraction</th>
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<th>E₂</th>
<th>η₂</th>
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<td>MPa.s</td>
<td>GPa.s</td>
<td>min</td>
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The KWW equation parameters obtained from modelling the recovery time-strain data of the EMA9 and EMA19 series of materials are listed in Tables 21 and 22 respectively. The resistance to relaxation (as indicated by the A, pre-exponential coefficient) was observed to consistently decrease with increasing silica volume fraction for the EMA9 series of materials. The A values obtained from modelling of the EMA19 series of materials overall decreased with increasing silica volume fraction however there was no consistent trend observed in changes between the silica volume fractions. The A values of the EMA19 elastomer and EMA19Si composites were observed to be larger than their EMA9 series counterparts for the unfilled elastomers and each silica volume fraction due to the plasticising effect of the increased methyl acrylate weight fraction. The A values of both the EMA9 and EMA19 series of materials were observed to increase over subsequent analysis cycles.
Table 21 KWW equation parameters for EMA9Si composites obtained from modelling recovery data

<table>
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<td>4</td>
<td>4.999</td>
<td>0.022</td>
<td>0.013</td>
</tr>
</tbody>
</table>

An overall slight decrease was observed in the β shape parameter values for both the EMA9 and EMA19 series of materials however no consistent trend was observed in either series of materials with respect to increasing silica volume fraction. The β values of the EMA19 series of materials were observed to be overall larger indicating they had the least constraints to the operation of relaxation modes. Over subsequent analysis cycles the β values were observed to decrease for both series of materials. All of the KWW equation parameters are simultaneously optimized to minimise variance when modelling recovery time-strain data. However if parameters are optimized sequentially they may not be significantly altered, or changed at all if a single parameter can be altered to minimise variance. This may account for the irregular β values trend with regards to silica volume fraction. Another explanation may be that the β shape distribution parameter is dependant upon free volume, entanglements, obstruction by filler and crystallinity. As each composite possesses a unique molecular environment with differing amounts of these characteristics (which may not necessarily change consistently with increasing filler), the β values may need to change in a complex pattern to account for all of these characteristics. The relaxation times of the EMA19 series of materials were longer than their EMA9 counterparts for the unfilled elastomers and at each silica volume fraction.
The relaxation time was observed to slightly decrease with increasing silica volume fraction for the EMA9 series of materials. An overall slight decrease in relaxation time with respect to increasing silica volume fraction was observed for the EMA19 series of materials however there was no consistent trend observed. The relaxation time was observed to slightly increase over subsequent analysis cycles for the unfilled elastomers and each silica volume fraction for both series of materials.

**Table 22** KWW equation parameters for EMA19Si composites obtained from modelling recovery data

<table>
<thead>
<tr>
<th>SiO&lt;sub&gt;2&lt;/sub&gt; volume fraction %v/v</th>
<th>Cycle</th>
<th>τ min</th>
<th>β</th>
<th>A mm.mm&lt;sup&gt;-1&lt;/sup&gt;</th>
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</thead>
<tbody>
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<td>5.000</td>
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<td>0.096</td>
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<tr>
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<td>5.000</td>
<td>0.024</td>
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<td>3</td>
<td>5.000</td>
<td>0.028</td>
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<tr>
<td>20</td>
<td>4</td>
<td>5.000</td>
<td>0.025</td>
<td>0.033</td>
</tr>
</tbody>
</table>

**Material glass transitions and damping properties with methyl acrylate and silica content**

Modulated force thermomechanometry (mf-TM) was employed using a single frequency (1 Hz) to characterise the contributions of methyl acrylate and filler on glass transition temperature and damping. Figure 81 shows the resultant storage modulus of the EMA9 elastomer and EMA9Si composites from mf-TM. The storage modulus was observed to consistently increase with each increase to silica volume fraction at all temperatures for the EMA9-based materials. This indicated that the resistance to elastic deformation increased with increasing silica content. The storage modulus values of all materials were constant from
the initial analysis temperature to approximately -27 °C upon which they continually decreased until the final analysis temperature. There appeared to be a transition in the temperature range of approximately 10 °C – 55 °C which may be similar to the polyethylene crystal-crystal transition. The mf-TM analysis of EMA9Si20 ended prematurely due to the test specimen fracturing at 102 °C. All other materials possessed a temperature of failure at temperatures above 114 °C as irreversible deformation had occurred.

Figure 81 Storage modulus versus temperature: EMA9 (-◊-); EMA9Si1 (-□-); EMA9Si5 (-△-); EMA9Si10 (-×-); EMA9Si20 (-○-)

Figure 82 represents storage modulus values of the EMA9-based materials obtained at 20 °C. The storage modulus was observed to increase with increasing silica volume fraction. Slight increases in the storage modulus were observed with the addition of 1, 5 and 10 %v/v silica. The largest increase in modulus occurred between the 10 and 20 %v/v silica filled composites. These observations indicate that the presence of silica inhibits elasticity and that the increase from 10 to 20 %v/v silica results in the greatest inhibition. The increase in modulus with increasing silica content seemed to model an exponential trend.
Figure 82 Storage modulus versus silica volume fraction of EMA9 elastomer and EMA9Si composites at 20 °C

Figure 83 represents the loss modulus data for the EMA9 elastomer and EMA9Si composites. The loss modulus was observed to consistently increase with increasing silica volume fraction indicating that absorption of energy and conversion to heat increased with increasing silica content. The previously mentioned transition in the temperature range of 10 °C – 55 °C appeared in the loss modulus. All of the EMA9-based materials loss modulus values were observed to peak at $T_g$ then continually decrease at post-$T_g$ temperatures until temperature of failure.
Table 23 lists the temperatures at which the loss modulus maxima occurred for EMA9 and the EMA9Si composites. It was observed that the $T_g$ decreased with increasing silica volume fraction. The addition of 1 %.v/v of silica decreased the $T_g$ by 0.1 °C which is negligible, whilst the largest decrease of 2.6 °C was observed with the addition of 20 %.v/v. This indicated that the silica had little effect on the $T_g$ at the given volume fractions.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ °C</th>
<th>Loss modulus, E'' MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA9</td>
<td>-25.7</td>
<td>231</td>
</tr>
<tr>
<td>EMA9Si1</td>
<td>-25.8</td>
<td>286</td>
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<tr>
<td>EMA9Si5</td>
<td>-26.8</td>
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<tr>
<td>EMA9Si10</td>
<td>-27.5</td>
<td>333</td>
</tr>
<tr>
<td>EMA9Si20</td>
<td>-28.3</td>
<td>608</td>
</tr>
</tbody>
</table>

Figure 84 represents loss modulus values of the EMA9-based materials obtained at 20 °C. It was observed that the loss modulus increased with increasing silica volume fraction. Slight increases in loss modulus values were observed with the addition of 1, 5 and 10 %.v/v silica and the largest increase in modulus occurred between the 10 and 20 %.v/v silica filled composites as with the storage modulus. This indicated that the presence of silica in any of the designated volume fractions increased the dispersion of energy however 20 %.v/v of silica resulted in the greatest increase.
Figure 84 Loss modulus versus silica volume fraction of EMA9 elastomer and EMA9Si composites at 20 °C

Figure 85 represents the tan δ data of EMA9 and the EMA9Si composites. The tan δ values were observed to decrease with increasing silica content indicating that silica contributed mainly to the viscoelastic modulus. The materials possessed constant tan δ values from the initial analysis temperature then exhibited a single broad peak from approximately -28 – 56 °C, after which their tan δ values were constant until the onset of failure when they rapidly increased.

Figure 85 Tan δ versus temperature: EMA9 (-◇-); EMA9Si1 (-□-); EMA9Si5 (-△-); EMA9Si10 (-×-); EMA9Si20 (-○-)
Figure 86 represents the maximum tan $\delta$ values (tan $\delta_{\text{max}}$) obtained from mf-TM of the EMA9 series of materials. It was observed that with the exception of EMA9Si1, the tan $\delta_{\text{max}}$ values reduced with increasing silica volume fraction. The presence of 1 %.v/v of silica caused the tan $\delta_{\text{max}}$ to increase slightly. This indicated that the silica increasingly reduced damping with further increase to the silica volume fraction. The decrease in tan $\delta_{\text{max}}$ values with increasing silica volume fraction was observed to be a linear trend.

Figure 87 represents the storage modulus of EMA19 and the EMA19Si composites. The storage modulus increased with increasing silica volume fraction at all temperatures indicating that the resistance to elastic deformation increased with increasing silica content. The storage modulus was observed to be constant for each material at low (pre-$T_g$) temperatures (equivalent to the plateau region observed in frequency space). There was a reduction in modulus that occurred with the onset of glass transition (approximately -28 °C) for all materials. There was a transition in the temperature range of approximately 10 °C – 55 °C that was present in the EMA9 material modulus data appeared in the EMA19 material modulus data, related to the polyethylene crystal-crystal transition. This reduction continued until the temperature of failure. The mf-TM analysis of EMA19 ended prematurely due to the test specimen fracturing at 94 °C. All other EMA19-based materials possessed a temperature of failure at temperatures above 115 °C where irreversible deformation occurred.
Figure 87 Storage modulus versus temperature: EMA19 (-◇-); EMA19Si1 (-□-); EMA19Si5 (-△-); EMA19Si10 (-×-); EMA19Si20 (-○-)

Figure 88 displays the storage modulus values of EMA19 and the EMA19Si composites obtained from mf-TM at 20 °C. It was observed that with the addition of silica the storage modulus increased meaning that elasticity of EMA19 was being inhibited at all designated volume fractions of silica. A slight increase in storage modulus was observed with the addition 1 %.v/v of silica followed by moderate increases for the 5 and 10 %..v/v silica filled composites. The greatest increase occurred in the EMA19Si20 composite indicating that this volume fraction of silica most inhibited elasticity. The increase in modulus with increasing silica content appeared to model an exponential trend.
Figure 88 Storage modulus versus silica volume fraction of EMA19 elastomer and EMA19Si composites at 20 °C

Figure 89 represents the loss modulus data of EMA19 and the EMA19Si composites. The loss modulus values increased with increasing silica content at all temperatures. This indicated that absorption of energy and conversion to heat increased with increasing silica content. The loss modulus values were observed to be constant at pre-$T_g$ temperatures for all materials. The loss modulus values increased for all materials at the onset of $T_g$, then peaking at $T_g$. There was a transition in the temperature range of approximately 10 °C – 55 °C related to the polyethylene crystal-crystal transition. The modulus values of all materials subsequently decreased after glass transition until temperature of failure.
Figure 89 Loss modulus versus temperature: EMA9 (–◇–); EMA9Si1 (–□–); EMA9Si5 (–△–); EMA9Si10 (–×–); EMA9Si20 (–○–)

Figure 90 shows the loss modulus values of the EMA19-based materials obtained at 20 °C. It was observed that the loss modulus increased with increasing silica volume fraction. Slight increase in the loss modulus was observed with the addition of 1 %v/v silica while moderate increases were observed with the additions of 5 and 10 %v/v silica. The largest increase in modulus occurred between the 10 and 20 %v/v silica filled composites (as with the storage modulus values). This indicated that the presence of silica at any of the designated volume fractions increased the loss of energy however 20 %v/v of silica resulted in the greatest increase.
The glass transition temperature \( T_g \) was taken to be the temperature of the maximum loss modulus value. Table 24 lists the temperatures at which the maximum loss modulus values occurred for EMA19 and the EMA19Si composites. It was observed that the \( T_g \) decreased with increasing silica volume fraction. There was a negligible decrease of 0.2 °C with the addition of 1 %.v/v silica. The largest decrease of 2.8 °C was observed with the addition of 20 %.v/v silica to the unfilled elastomer.

**Table 24 Glass transition temperature and \( E'' \) of EMA19 and EMA19Si composites**

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_g ) °C</th>
<th>Loss modulus, ( E'' ) MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA19</td>
<td>-27.1</td>
<td>359</td>
</tr>
<tr>
<td>EMA19Si1</td>
<td>-27.3</td>
<td>390</td>
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<td>EMA19Si5</td>
<td>-29.2</td>
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<td>EMA19Si10</td>
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<td>509</td>
</tr>
<tr>
<td>EMA19Si20</td>
<td>-29.9</td>
<td>614</td>
</tr>
</tbody>
</table>

Figure 91 represents the tan δ values of EMA19 and the EMA19Si composites. The tan δ values were observed to decrease with increasing silica volume fraction at all temperatures. This indicated that silica contributed mainly to the viscoelastic modulus. The tan δ values of all materials were constant from initial analysis temperature until they exhibited a broad peak over the temperature range of approximately -40 °C – 20 °C (encompassing the \( T_g \) range). These peaks consisted of two shoulders at -19 °C and 5 °C. The tan δ values plateaued until a
sharp increase near the temperature of failure at temperatures above the temperatures of the peaks.

![Figure 91 Tan δ versus temperature: EMA19 (-◇-); EMA19Si1 (-□-); EMA19Si5 (-△-); EMA19Si10 (-×-); EMA19Si20 (-○-)](image)

Figure 92 represents the maximum tan δ values (tan δ_{max}) obtained from mf-TM of the EMA19 series of materials. It was observed that the tan δ_{max} values decreased with increasing silica volume fraction. The largest reductions were observed between the increases from 1 \%v/v to 5 \%v/v, and 10 \%v/v to 20 \%v/v silica. This indicated that the silica increasingly reduced damping with further increase to the silica volume fraction the tan δ_{max} though only slight reductions were observed between some increases in silica volume fraction. The decrease in tan δ_{max} values with increasing silica volume fraction was observed to be a linear trend.
Figure 92 Tan $\delta_{\text{max}}$ versus silica volume fraction of EMA19 elastomer and EMA19Si composites

Figure 93 displays the storage modulus data of EMA9Si5 and EMA19Si5. The storage moduli of these composites were approximately equal at pre-$T_g$ temperatures since crystallinity effects and methyl acrylate weight fraction did not influence modulus values due to segmental rotation not being able to occur. The EMA9Si5 composite possessed the larger storage modulus at post-$T_g$ temperatures due to the increased crystallinity in EMA9, until nearing the temperature of failure when these composites possessed approximately the same modulus values. These observations were consistent with other comparisons between the unfilled elastomers and materials with similar silica volume fractions but differing methyl acrylate weight fractions. Comparison figures for other materials with similar silica volume fractions can be found in Appendix 2.3.
Figure 93 Storage modulus versus temperature: EMA9Si5 (■); EMA19Si5 (■)

Figure 94 displays the loss modulus data of EMA9Si5 and EMA19Si5. The EMA19Si5 composite had the largest modulus at the pre-$T_g$ temperatures. EMA19Si5 had a largest increase in loss modulus at the onset of $T_g$. It was observed that EMA9 and the EMA9Si composites possessed higher glass transition temperatures for the unfilled elastomers and each volume fraction of silica (as listed in Tables 24 and 25). The loss moduli of EMA9 and the EMA9Si composites were greater than that of EMA19 and the EMA19Si composites at post-$T_g$ temperatures due to the increased crystallinity in EMA9, until nearing the temperature of failure when these composites possessed approximately the same modulus values. The polyethylene crystal-crystal transition in the temperature range of $10 \, ^\circ C - 55 \, ^\circ C$ resulted in greater modulus values in the EMA9Si5 composites since the higher methyl acrylate weight fraction in the EMA19Si5 composite inhibited polyethylene crystallinity. These observations were consistent for comparisons between other similarly silica filled composites, except for the composites possessing 20 \% v/v of silica where the EMA9Si20 loss modulus was larger at pre-$T_g$ temperatures. Comparison figures for other materials with similar silica volume fractions can be found in Appendix 2.3.
Figure 94 Loss modulus versus temperature: EMA9Si5 (-□-); EMA19Si5 (-■-)

Figure 95 displays the tan δ data of EMA9Si5 and EMA19Si5. Both composites possessed constant tan δ values at pre-$T_g$ temperatures followed by a single broad peak then a plateau and final increase in their tan δ values near the temperature of failure. EMA19Si5 possessed the greatest tan δ$_{\text{max}}$ due to its increased methyl acrylate weight fraction, while EMA9Si5 possessed a broader peak in their tan δ data. These observation were consistent for comparisons between the unfilled elastomers and other similarly silica filled materials. Comparison figures for other materials with similar silica volume fractions can be found in Appendix 2.3.
Theoretical and experimental copolymer glass-transition temperatures

The Fox equation was employed to determine the theoretical $T_g$ of the EMA9 and EMA19 copolymers. The Fox equation takes the form as seen in Equation 65.

$$\frac{1}{T_{g,\text{comp}}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$  \hspace{1cm} \text{Equation 65}$$

where $T_{g,\text{comp}}$ is the glass transition temperature of a blend with the components which possess, $w_n$ and $T_{gn}$ which are the weight fractions and glass transition temperatures, respectively. The $T_g$ of poly(ethylene) was taken to be -81 °C[219] and the $T_g$ of poly(methyl acrylate) was taken[220] to be -1 °C.

The theoretical $T_g$s of the EMA9 and EMA19 copolymers where calculated to be -17.8 °C and -9.5 °C respectively via the Fox equation. The experimentally derived $T_g$s were calculated from the peak loss modulus value in 1 Hz mf-TM, as previously stated, and were found to be -25.9 and -27.9 for EMA9 and EMA19 respectively. It should be noted that the Fox equation predicts that EMA19 will have a higher $T_g$ than EMA9; however via mf-TM, it was observed that EMA19 had the lowest $T_g$. This was because the greater crystallinity in the EMA9 materials made the amorphous regions lose degrees of freedom.
Theoretical single frequency mf-TM modulus values

The single frequency mf-TM experimental storage modulus values of the EMA-based materials were compared with modulus values calculated from two “rule of mixture” equations. Equation 66 describes the upper limit of calculated moduls while Equation 67 describes the lower limit as

\[
E_{\text{composite}}(x) = (x \times E_{\text{filler}}) + ((1 - x) \times E_{\text{matrix}})
\]

\[
\frac{1}{E_{\text{composite}}(x)} = \frac{x}{E_{\text{filler}}} + \frac{1 - x}{E_{\text{matrix}}}
\]

where \( E_{\text{composite}} \) is the modulus of the composite, \( x \) is the volume fraction of the filler, \( E_{\text{filler}} \) is the modulus of the filler and \( E_{\text{matrix}} \) is the modulus of the matrix. The experimental moduli of the unfilled elastomers and composites were taken to be the storage moduli obtained from analysis at 20 °C. These values were compared with composite modulus values calculated using the storage modulus of the EMA elastomer and the modulus of silica, given as 70 GPa[221]. The calculated modulus values for both series of materials were greater than the lower limit calculated values and less than the upper limit calculated values. The greatest difference between experimental and calculated modulus values occurred in the EMA19 series of materials. The experimental and calculated modulus values for the EMA9-based and EMA19-based materials are displayed in Figures 96 and 97.

Figure 96 Modulus versus silica volume fraction of EMA9 elastomer and EMA9Si composites: Experimental \( E' \) values (-○-); Upper limit calculated \( E' \) values (-□-), Lower limit calculated \( E' \) values (-△-)

160
Figure 97 Modulus versus silica volume fraction of EMA9 elastomer and EMA9Si composites: Experimental $E'$ values (−●−); Upper limit calculated $E'$ values (−□−), Lower limit calculated $E'$ values (−△−)

**Elastic moduli obtained from df-TM, sf-TM, and mf-TM**

The elastic moduli obtained from stress-strain analysis (df-TM), creep analysis (sf-TM) and single frequency mf-TM are listed in Table 25. In stress-strain and creep analysis the elastic modulus is equated to the ratio of the instantaneous strain response with applied stress, while in mf-TM, the elastic modulus is equal to the storage modulus. This storage modulus in Table 25 was taken at 20 °C since this was the temperature (i.e. SLC) at which the stress-strain and creep analyses were performed. Each of the moduli was observed to increase with increasing silica volume fraction (except for the creep elastic modulus of the EMA19 elastomer and EMA19Si composites due to reasons mentioned previously). This increase in modulus increased with increasing silica volume fraction with the largest increase observed between the 10 %.v/v and 20 %.v/v silica filled composites for both weight fraction of methyl acrylate.
Table 25 Elastic modulus values from stress-strain, creep and mf-TM analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress-strain modulus (at 20 °C)</th>
<th>Creep modulus (at 20 °C)</th>
<th>mf-TM 1 Hz modulus (at 20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA9</td>
<td>88</td>
<td>56</td>
<td>311</td>
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<tr>
<td>EMA9Si1</td>
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<tr>
<td>EMA19Si20</td>
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<td>155</td>
<td>1044</td>
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</table>

The mf-TM elastic modulus was the largest followed by the stress-strain modulus then the creep modulus for each of the materials. The storage modulus was observed to be three to four times greater than that of the other two moduli for most materials.

Mastercurves

Mastercurves were constructed from isothermal, multi-frequency modulus data as described in Chapter 3. They were constructed via TTS to predict material responses to analysis frequencies outside instrumental capabilities.

Mastercurves constructed from sinusoidal multi-frequency-modulus data

Figure 98 represents the storage modulus mastercurves for the EMA9 elastomer and EMA9Si composites. The reference temperature was chosen to be 20 °C due to this being the standard laboratory temperature. The resultant frequency range of the mastercurves were approximately $10^{-9} - 10^{17}$ Hz (an increase from the original frequency range of the isothermal multi-frequency data of $10^{-2} - 10^{2}$ Hz) after modulus data had been transposed via the application of shift factors to form a mastercurve. It was observed that with increasing silica content the storage modulus increased. The greatest increase of modulus with increasing frequency (i.e. the steepest gradient) in the mastercurves was at the data that was obtained from temperatures encompassing the $T_g$. There was a reduction in the steepness of the mastercurves with increasing silica volume fraction.
The effect of filler reinforcement was more observable in the lower frequency (i.e. as $\text{Hz} \rightarrow 0$) domain since materials have longer times to respond to applied forces at these frequencies. There were slight increases in modulus with the additions of 1 and 5 % v/v of silica. Greater increases in the storage modulus were observed with the increase from 5 to 10 % v/v, and 10 to 20 % v/v silica. The reinforcing effect of filler was less noticeable due to the material not being able to deform fast enough to applied forces regardless of molecular composition at the highest frequencies (as $\text{Hz} \rightarrow \infty$). No change in modulus was observed between EMA9Si10 and EMA9Si20 indicating the modulus had plateaued (at approximately 7 GPa) at the highest transposed frequencies.

Figure 99 represents the loss modulus mastercurves for the EMA9 elastomer and EMA9Si composites. The loss modulus mastercurves had the greatest change in modulus with increasing frequency for the data immediately encompassing the $T_g$ as with the storage modulus mastercurves. The largest increase in loss modulus was observed with the 10 % v/v and 20 % v/v silica volume fractions, while only slight increases in modulus were observed with the addition of 1 and 5 % v/v silica. The loss modulus of EMA9Si10 and EMA9Si20 plateaued at approximately 400 MPa at the highest transposed frequencies.
An artefact of the loss modulus mastercurves was the frequency interference effects due to resonance. Resonance occurs when the analysis frequency is equal to that of a materials natural frequency. The modulus data obtained at the highest analysis frequencies (50,100 Hz) and low (pre-$T_g$) temperatures exhibited constructive interference. This was observed as the modulus values appearing irregularly large compared with the modulus values at the other analysis frequencies. The EMA9 elastomer and all of the EMA9Si composites exhibited constructive interference, with the effects most pronounced in the highest filled (10, 20 %.v/v) composites. The EMA9 and EMA9Si1 materials exhibited some constructive interference; however more pronounced was destructive interference. The modulus data obtained at 50 and 100 Hz resulted in destructive interference of the modulus values meaning results appeared irregularly smaller compared with data obtained at the other analysis frequencies.

Figure 100 displays the storage modulus mastercurves for the EMA19 elastomer and EMA19Si composites. The greatest increase in modulus with respect to frequency occurred in data from temperatures immediately encompassing and including $T_g$ for each mastercurve. No plateauing in the storage modulus between the materials was observed i.e. the storage modulus increased with increasing silica volume fraction for each addition of silica at the highest transposed frequencies. The EMA19 elastomer possessed higher modulus values than those of EMA19Si1 and EMA19Si5 at frequencies equal to pre-$T_g$ temperatures while the composite EMA19Si20 possessed the greatest modulus values at these frequencies.
Figure 100 Storage modulus mastercurves: EMA19 (-\(\bigcirc\)-); EMA19Si1 (-\(\square\)-); EMA19Si5 (-\(\triangle\)-); EMA19Si10 (-\(\times\)-); EMA19Si20 (-\(\bigtriangleup\)-)

Figure 101 displays the loss modulus mastercurves for the EMA19 elastomer and EMA19Si composites. The mastercurve data of EMA19 elastomer and the EMA19Si composites possessing 0 – 10 %.v/v silica loss possessed a peak in the modulus values obtained from temperatures encompassing and including T\(_g\). The EMA19Si20 composite mastercurve modulus data did not possess a peak and was observed to plateau at these temperatures. The loss modulus values increased with increasing silica volume fraction at the highest transposed frequencies with the largest increase occurring between the increase from 10 to 20 %.v/v silica in the composites. The loss modulus increased with increasing silica volume fraction at low frequencies with the largest increases observed between 5 to 10 %.v/v silica and from 10 to 20 %.v/v silica. All materials exhibited constructive interference in the loss modulus obtained from the 100 Hz analysis frequency at the transposed frequencies equal to pre-T\(_g\) temperatures. No destructive interference was observed except in EMA19Si20 for the loss modulus values obtained from analyses at high temperatures.
Figure 101 Loss modulus mastercurves: EMA19 (-◇-); EMA19Si1 (-□-); EMA19Si5 (-△-); EMA19Si10 (-×-); EMA19Si20 (-○-)

Figure 102 displays the storage modulus mastercurves of EMA9Si5 and EMA19Si5 which represents a comparison between the mastercurves of similar silica volume fraction but differing MA weight fraction. It was observed that EMA9Si5 had slightly greater modulus values in data obtained from frequencies equal to temperatures post T_g (approximately 10^{10} Hz) but had much greater modulus values at frequencies equivalent to pre-T_g temperatures. This meant that the storage modulus values of the EMA19Si5 mastercurve had the greatest change with increasing frequency (as indicated by the steepness of the mastercurve). This was due to the reinforcement provided by the increased crystallinity in the EMA9-based materials being more apparent at low frequencies. These observations were consistent with other comparisons between the unfilled elastomers and materials with similar silica volume fractions but differing methyl acrylate weight fractions, as seen in Appendix 2.4.
Figure 102 Storage modulus versus log(Frequency): EMA9Si5 (-◇-); EMA19Si5 (-□-)

Figure 103 displays the loss modulus mastercurves of EMA9Si5 and EMA19Si5, representing a comparison between the mastercurves with similar silica volume fraction, but differing MA weight fractions. EMA19Si5 possessed a peak in its loss modulus data at the frequency equivalent to $T_g$, while the modulus values of EMA9Si5 plateaued at $T_g$. The value of the EMA19Si5 loss modulus peak was greater than that of EMA9Si5. The EMA9Si5 composite had the largest loss modulus values, except for the constructive interference-resonance modulus values which were larger for EMA19Si5, and the largest modulus values overall for the mastercurves at higher frequencies (equivalent to pre-$T_g$ temperatures). These observations held true for all other comparisons between the elastomers and similarly silica filled materials except for the 20 %v/v silica composites for which the all EMA19Si20 loss modulus values were larger than their EMA9Si20 equivalent. EMA9Si5 possessed the largest loss modulus values at low frequencies (corresponding to pos-$T_g$ temperatures) which was consistent with other comparisons as seen in Appendix 2.4.
Figure 103 Loss modulus versus log(Frequency): EMA9Si5 (-○-); EMA19Si5 (-□-)

Mastercurves created from synthetic multi frequency-modulus data

The dynamic mechanical analyser employed for this research (Perkin Elmer Diamond DMA) is able to apply force in two frequency modes; synthetic and sinusoidal (as described in Chapter 3). The applicability of using frequency-modulus data obtained from synthetic frequency analyses for construction of master curves was investigated with the EMA9 elastomer and EMA9Si composites. The method used for obtaining frequency-modulus data obtained from synthetic frequency analyses and subsequent construction of mastercurves via the $\alpha_T$ shift method was described in Chapter 3. Figure 104 displays the mastercurves from synthetic frequency-modulus data of EMASi5.
This method of obtaining mastercurve data and resultant mastercurves possessed advantages and disadvantages over the mastercurves obtained from sinusoidal frequency-based mastercurves. The advantages of these mastercurves were that the temperature was constant for each series frequency analysis and that a typical frequency sweep temperature program (i.e. temperature increasing at constant rate) could be employed as opposed to a step-wise temperature program (temperature increase after all frequencies have been analysed in sequence). The disadvantages of these mastercurves was that there was poor, if any overlap between the 10 °C increment modulus data (the temperature increments used for $\Delta T$ shift mastercurves) and the inherent limitation of available frequencies for an analysis. This limitation of analysis frequencies was that only 5 frequencies, separated by a factor of 2 between each frequency could be selected. There was no overlap between either the storage or loss modulus data obtained from synthetic frequency analysis as seen in Figure 104. The increment between analysis temperatures would have to be at least halved to counteract this problem which would lead to an excess of data and shift factors. There appeared to be more extreme frequency interference effect with the loss modulus data obtained in the method. Therefore it was decided that this method is not suitable for mastercurve construction. Other mastercurves constructed for the EMA9 elastomer and remaining EMA9Si composites are in Appendix 2.4.
Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami relaxation equations

The Debye (D), Cole-Cole (CC), Cole-Davidson (CD) and Havriliak-Negami (HN) relaxation equations were used to model the EMA elastomer and EMASi composite mastercurves via the method described in the Chapter 3. Values for the infinite and zero modulus ($E_\infty$ and $E_0$ respectively) and the relaxation time ($\tau$) were determined from the modelling of mastercurve data.

The accuracy of modelling mastercurve data with relaxation equations was determined by the Wicket error function (see Equation 57). The closer the resultant error value is to zero the more accurately the relaxation equation is modelling the mastercurve data. It was determined that the HN equation most accurately modelled the mastercurve data, followed by the CC, CD and finally D equations from the Wicket error values listed in Table 26. The high accuracy of the HN equation can be attributed to it possessing two shape parameters which allow it to account for changes in both the symmetry and skewness of the mastercurve data.

<table>
<thead>
<tr>
<th>Material</th>
<th>D model</th>
<th>CC model</th>
<th>CD model</th>
<th>HN model</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA9</td>
<td>6.42</td>
<td>0.49</td>
<td>0.56</td>
<td>0.32</td>
</tr>
<tr>
<td>EMA9Si1</td>
<td>3.07</td>
<td>0.65</td>
<td>0.77</td>
<td>0.04</td>
</tr>
<tr>
<td>EMA9Si5</td>
<td>2.30</td>
<td>1.09</td>
<td>0.77</td>
<td>0.09</td>
</tr>
<tr>
<td>EMA9Si10</td>
<td>3.06</td>
<td>0.34</td>
<td>0.55</td>
<td>0.07</td>
</tr>
<tr>
<td>EMA9Si20</td>
<td>8.70</td>
<td>0.48</td>
<td>1.11</td>
<td>0.35</td>
</tr>
<tr>
<td>EMA19</td>
<td>11.65</td>
<td>4.24</td>
<td>9.96</td>
<td>0.21</td>
</tr>
<tr>
<td>EMA19Si1</td>
<td>10.08</td>
<td>4.06</td>
<td>6.41</td>
<td>0.26</td>
</tr>
<tr>
<td>EMA19Si5</td>
<td>15.53</td>
<td>2.84</td>
<td>8.88</td>
<td>0.35</td>
</tr>
<tr>
<td>EMA19Si10</td>
<td>14.80</td>
<td>1.12</td>
<td>3.56</td>
<td>0.18</td>
</tr>
<tr>
<td>EMA19Si20</td>
<td>8.18</td>
<td>0.58</td>
<td>1.31</td>
<td>0.18</td>
</tr>
</tbody>
</table>

All relaxation equations were observed to more accurately model the EMA9 elastomer and the EMA9Si composites compared with their EMA19 and EMA19Si counterparts. Generally the 1, 5 and 10 %v/v silica filled composites were the best modelled by the relaxation equations for the EMA9 series of materials. The accuracy of the relaxation equations ability to model mastercurve data increased overall with increasing silica volume fractions for the EMA19 series of materials.

An example of the modelling of mastercurve data with the four relaxation equations represented on a Cole-Cole is shown in Figure 105. It was observed that the D equation takes on a symmetrical semi-circular shape. The CD equation is a skewed curve which accurately modelled the large storage and loss modulus data, but cannot account for the asymmetry of the mastercurve. The CC equation accurately models the breadth (asymmetry) of the
mastercurve but cannot model the skewness. The HN equation is able to account for both the skewness in the symmetry in the mastercurve data allowing for it to most accurately model the mastercurve. These observations were similar for the modelling of other EMA-based materials represented on a Cole-Cole plot, as seen in Appendix 2.5.

![Cole-Cole plot of EMA9Si1 mastercurve](image)

*Figure 105 Cole-Cole plot of EMA9Si1 mastercurve (-■-), modelled with: Debye (-□-); Cole-Cole (-△-); Cole-Davidson (-x-); Havriliak-Negami (-O-) models*

The parameters resulting from applying the relaxation equations are listed in Table 27. The relaxation time from each relaxation equation was observed to increase with increasing silica content for both series of materials. This was attributed to the silica particles inhibiting molecular and segmental rotation via physical crosslinks. The relaxation times were overall longest for the EMA9 elastomer and EMA9Si composites compared with their EMA19 counterparts due to the greater crystallinity in the EMA9-based materials.

The infinite and zero moduli were observed to overall increase with increasing silica content for each relaxation equation. The increase in $E_\infty$ between the 10 and 20 %v/v silica filled composites was generally the smallest increase with increasing silica volume fraction since the composites were approaching their plateau, $E_\infty$ values due to the previously mentioned reasons (i.e. filler effects are less noticeable as frequency approaches infinity). The infinite modulus was observed to be slightly larger for the EMA19 elastomer and EMA19Si composites while the zero modulus was largest for the EMA9 elastomer and EMA9Si composites (due to the effect of increased crystallinity being more apparent in the low frequency region) for the D, CC and HN relaxation equations. The $E_\infty$ and $E_0$ moduli were
largest for the EMA9 elastomer and EMA9Si obtained from modelling with the CD relaxation equation.

Table 27: Modelling parameters from applying relaxation models to created mastercurves

<table>
<thead>
<tr>
<th>Material</th>
<th>D model</th>
<th>CC model</th>
<th>CD model</th>
<th>HN model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_\infty$, $E_0$, $\tau$</td>
<td>$E_\infty$, $E_0$, $\tau$, $a$</td>
<td>$E_\infty$, $E_0$, $\tau$, $b$</td>
<td>$E_\infty$, $E_0$, $\tau$, $a$, $b$</td>
</tr>
<tr>
<td></td>
<td>GPa, GPa, s $\times 10^{-9}$</td>
<td>GPa, GPa, s $\times 10^{-9}$</td>
<td>GPa, GPa, s $\times 10^{-5}$</td>
<td>GPa, GPa, s $\times 10^{-7}$</td>
</tr>
<tr>
<td>EMA9</td>
<td>2.55, 0.46, 1.00</td>
<td>3.92, 0.02, 0.02, 0.94</td>
<td>4.93, 0.51, 0.09, 0.04</td>
<td>5.08, 0.03, 0.09, 0.16,0.42</td>
</tr>
<tr>
<td>EMA9Si1</td>
<td>4.20, 0.74, 1.00</td>
<td>5.91, 0.03, 1.00, 0.91</td>
<td>8.46, 0.84, 0.19, 0.03</td>
<td>7.88, 0.06, 0.90, 0.15,0.38</td>
</tr>
<tr>
<td>EMA9Si5</td>
<td>5.04, 0.81, 10.00</td>
<td>6.86, 0.07, 1.00, 0.89</td>
<td>10.10, 0.99, 1.06, 0.02</td>
<td>8.95, 0.08, 1.04, 0.15,0.39</td>
</tr>
<tr>
<td>EMA9Si10</td>
<td>5.87, 0.85, 100.00</td>
<td>7.37, 0.14, 19.00, 0.90</td>
<td>13.50, 1.23, 106.00, 0.01</td>
<td>10.30, 0.17, 24.90, 0.14,0.36</td>
</tr>
<tr>
<td>EMA9Si20</td>
<td>6.06, 1.37, 656000.00</td>
<td>7.59, 0.51, 3.19, 0.01</td>
<td>15.30, 1.57, 1060.00, 0.008</td>
<td>142.00, 0.13,0.35, 10.60, 0.59</td>
</tr>
<tr>
<td>EMA19</td>
<td>4.65, 0.14, 50.00</td>
<td>7.85, 0.01, 0.01, 0.88</td>
<td>4.93, 0.05, 0.01, 0.17</td>
<td>12.20, 0.04, 0.0005, 0.18,0.34</td>
</tr>
<tr>
<td>EMA19Si1</td>
<td>4.65, 0.14, 50.00</td>
<td>5.99, 0.02, 2.39, 0.87</td>
<td>4.37, 0.05, 0.01, 0.15</td>
<td>11.00, 0.03, 0.0005, 0.16,0.36</td>
</tr>
<tr>
<td>EMA19Si5</td>
<td>5.00, 0.14, 500.00</td>
<td>7.18, 0.05, 2.39, 0.84</td>
<td>6.46, 0.08, 0.1, 0.14</td>
<td>11.40, 0.05, 0.001, 0.17,0.48</td>
</tr>
<tr>
<td>EMA19Si10</td>
<td>6.00, 0.19, 500000.00</td>
<td>8.14, 0.02, 2.39, 0.83</td>
<td>6.86, 0.02, 1.10, 0.14</td>
<td>11.90, 0.15, 0.001, 0.15,0.52</td>
</tr>
<tr>
<td>EMA19Si20</td>
<td>8.60, 0.56, 500000.00</td>
<td>10.90, 0.39, 15.70, 0.90</td>
<td>20.90, 0.56, 30.10, 0.02</td>
<td>15.50, 0.21, 0.53, 0.11,0.45</td>
</tr>
</tbody>
</table>

The CC, CD and HN relaxation equations have the shape parameters $\alpha$, $\beta$, $\alpha$ and $\beta$ respectively. The $\alpha$ parameter values determined from modelling with the CC equation decreased with increasing silica volume fraction for the EMA9-based materials. The EMA19-based materials followed a similar trend except the EMA19Si20 composite had the greatest $\alpha$ value. The $\beta$ parameter of the CD equation was observed to decrease with increasing silica volume fraction for both EMA9 and EMA19 series of materials. The $\alpha$ and $\beta$ parameters of the HN equation were observed to decrease with increasing silica volume fraction for the EMA9 series of materials. The $\alpha$ values overall decreased with increasing filler volume fraction but the $\beta$ increased with increases in silica volume fractions except for 20 % v/v whereupon it decreased for the EMA19 series of materials.

The $\alpha$ of the CC relaxation equation was observed to be largest for the EMA9 elastomer and EMA9Si composites while the $\beta$ parameter of the CD relaxation was largest for the EMA19 elastomer and EMA19Si composites. The $\alpha$ parameter was overall largest for the EMA19
elastomer and EMA19Si composites while the $\beta$ parameter was overall largest for the EMA9 elastomer and EMA19Si composites for the HN equation.

**Super-mastercurves constructed from elastomer and composite mastercurves**

The mastercurves of the EMA9 and EMA19 series of materials were formed by altering the frequency values of the modulus-frequency data. Subsequently each of these series of mastercurves was shifted in their frequency values in a similar fashion forming a single curve termed a *super-mastercurve*. These time-temperature-composition super-mastercurves were previously created by Gower and Shanks to display the effects of molecular composition of pressure sensitive adhesive on their peel strength[222].

The shift factors employed for creating super-mastercurves were termed $a_c$, with the $c$ representing concentration. The monomer composition shift factors represent the correlation of the effect of silica on modulus with respect to frequency. Figure 106 represents the EMA9-based materials storage modulus super-mastercurve. The super-mastercurve data had a frequency range of $10^{-11} – 10^{20}$ Hz and displayed feathering at low frequencies due to the higher filled (10 and 20 $\%$ v/v silica) composites. There was precision (i.e. similar data values) in the modulus data at the highest transposed frequencies with only the data from the EMA9 mastercurve deviating. The data from the mastercurves displayed the most precision in the data of the mastercurve obtained at temperatures including and encompassing the $T_g$.

![Figure 106 EMA9Si storage modulus super-mastercurve](image)

Figure 107 represents the EMA9-based materials loss modulus super-mastercurves. The modulus values from the EMA9Si20 mastercurve caused feathering in the super-mastercurve.
at low frequencies. Some feathering in the modulus data was observed at the highest frequencies. This was due to the resonance of the modulus data obtained at low (pre-$T_g$) temperatures and analysed at high (100 and 50 Hz) frequencies. The modulus data was precise for the data obtained at temperatures including and encompassing the $T_g$.

![Figure 107 EMA9Si loss modulus super-mastercurve](image)

**Figure 107 EMA9Si loss modulus super-mastercurve**

Figure 108 represents the EMA19-based materials storage modulus super-mastercurve. Feathering was observed at low frequencies in the modulus data from the EMA19Si10 and EMA19Si20 mastercurves. The modulus data at high frequencies was observed to be precise. The modulus data obtained at temperatures including and encompassing the $T_g$ was precise for all the mastercurves except for data from the EMA19 and EMA19Si20 mastercurves.
Figure 108 EMA19Si storage modulus super-mastercurve

Figure 101 represents the EMA19Si loss modulus super-mastercurve. Feathering was observed at low frequencies originating from all the transposed mastercurve data; however it was most prevalent in the EMA19Si10 and EMA19Si20 mastercurve. Feathering was observed in data from all of the mastercurves at the highest frequencies.

Figure 109 EMA19Si loss modulus super-mastercurve

Mastercurves created from applying Havriliak-Negami relaxation equation to modulus data

The previous method employed for the creation of mastercurves involves shifting frequency-modulus data in the frequency domain to form a single curve. These shifts were determined
by eye to give the congruency in the modulus data. Another method of constructing mastercurves involves the use of the Havriliak-Negami (HN) relaxation equation. This method has been described in detail in Chapter 3.

Figure 110 represents the storage and loss modulus mastercurves of EMA9Si5 constructed, from the manual shift and HN methods. The mastercurves were similar in the transition frequencies ($10^{-2} – 10^{2}$ Hz, the original analysis frequencies); however they differed in the frequency extremes (as frequency approached zero and infinity). The HN method was observed to possess higher and lower frequency extremes than obtained from the manual method.

![Figure 110 Modulus versus log(Frequency): EMA9Si5 E’ mastercurve manual shift method(-○-); EMA9Si5 E’ mastercurve HN method (-●-); EMA9Si5 E” mastercurve manual shift method(-▲-); EMA9Si5 E” mastercurve HN method (-△-)](image)

Figure 111 represents the storage and loss modulus mastercurves of EMA19Si5 constructed from the manual shift and HN methods. The mastercurves created from the HN shift method were shifted positively in the frequency range for reasons that will be discussed in the next section. There was less overlap in data of the HN mastercurves compared with the manual shift mastercurves at the zero and infinite frequency extremes, as seen in the EMA9Si5 mastercurves. These results were consistent with the other EMA9-based and EMA19-based materials as seen in Appendix 2.6.
These two methods of mastercurve construction have a number of advantages and disadvantages. The advantages of the HN method are that there is mathematical basis behind the derivation of shift factors (the ratio between the relaxation times of analysis and the reference temperature) as opposed to shifting by eye. The HN method accounts for vertical shifts (due to density changes) by being able to simulate data at temperatures not analysed. Vertical shifts of modulus data must sometimes be employed resulting in a second series of shift factors in the manual shift method.

The disadvantages of the HN method are that the function may not accurately account for modulus data at the zero and infinite frequency extremes and that the reference temperature must be equivalent to the $T_g$. This is because the data at $T_g$ will almost certainly have the largest difference in modulus between lowest and highest original analysis frequencies, which when this data is modelled will create the highest and lowest $E_\infty$ and $E_0$ values respectively. If the actual modulus data is greater or smaller than the $E_\infty$ and $E_0$ parameters values in the high and low frequency domains, the shift factors will not be able to be calculated via the HN method. If the $E_\infty$ and $E_0$ values are higher than the actual modulus values in the plateau and terminal regions this has no adverse effect on the calculation of shift factors. This accounts for why HN method derived mastercurves were shifted positively in their frequency value compared with the manual shift factor mastercurves in Figure 111. The reference temperature for the manual shifted mastercurves was chosen to be the normal operating temperature of the material, 20 °C (SLC). The HN method used a reference temperature of -20 °C; the
temperature at which there was the greatest difference in modulus data from low and high frequency analysis and an analysis temperature to the $T_g$. If the HN method reference temperature was chosen to be 20 °C then the shift factors were not able to be defined for the modulus data approaching the zero and infinite frequency domains. This problem was not encountered when constructing HN method mastercurves for the EMA9 elastomer and EMA9Si composites as these materials were more rigid than the EMA19Si composites and did not possess a large decrease in modulus at $T_g$, allowing for the reference temperature to be designated 20 °C.

**Conclusion**

The EMA elastomers and EMASi composites possessed a single step mass loss decomposition occurred with an onset above 400 °C over a temperature range of approximately 20 °C. The addition of 20 %.v/v of silica thermally reinforced the EMA9 and EMA19 materials by approximately 20 °C attributed to the silica resulting in a decreased rate of volatiles loss at a particular temperature. The EMA9-based materials possessed a higher volume fraction remaining at the conclusion of TGA them possessing a greater amount of polyethylene compared with EMA19.

Young’s moduli of both the EMA9 and EMA19 series of materials were observed to increase with increasing silica volume fraction since the filler effects predominated at lower strains. The unfilled elastomers and 1.5, and 10 %.v/v silica filled EMASi composites of both series of materials possessed yielding before fracturing or slippage. The EMA9Si20 and EMA19Si20 composites fractured before yielding occurred. The strength of both materials was observed to increase with increasing silica volume fraction. The toughness was slightly increased at the lower silica volume fractions (1 and 5 %.v/v silica) while the materials with higher silica volume fractions (10 and 20 %.v/v silica) had reduced toughness due to brittleness. The EMA9-based materials possessed Young’s moduli double, or triple that of the EMA19-based materials and greater yield stresses indicating that the EMA9-based materials were the strongest due to increased crystallinity. The EMA19-based materials extended to longer strains than their EMA9 counterparts indicating that the EMA19-based materials were tougher due to the higher methyl acrylate weight fraction.

The highest silica volume fraction EMA composites (the 10 %.v/v SiO$_2$ and 20 %.v/v SiO$_2$ composites) had the greatest resistance to creep as observed in creep analysis data. The 10 %.v/v SiO$_2$ and 20 %.v/v SiO$_2$ filled EMASi composites exhibited less curvature in the viscoelastic and viscous creep data indicating shorter times and a smaller magnitude of
viscoelastic and viscous deformation. All materials displayed some instantaneous (elastic) recovery before time dependant (viscoelastic) recovery, represented by the curvature in time-strain recovery data. The 10 %v/v and 20 %v/v silica filled composites had little curvature in their recovery data indicating reduced viscoelastic recovery as expected due to these composites displaying less viscoelastic deformation in the creep phase. The inclusion of silica into the elastomer resulted in faster retardation and relaxation times from these observations. The EMA9 elastomer and EMA9Si composites were observed to have a reduced maximum creep and minimum recovery strain values with increasing silica volume fraction. The EMA19-based materials did not follow a similar pattern with regard to strain values and silica volume fraction. This result was attributed to interactions between the EMA and silica particles with the silica inhibiting nucleation of polyethylene crystals within the EMA19Si composites. However the composites EMA19Si10 and EMA19Si20 had the second lowest and lowest creep strain values respectively indicating that at these silica volume fractions, silica is the dominating reinforcing effect. The EMA9 elastomer and EMA9Si composites were observed to creep less than their EMA19Si counterparts due to the increased crystallinity in the EMA9-based materials. The curvature in the creep and recovery time-strain data was more pronounced in the EMA19 elastomer and EMA19Si composites compared with the EMA9-based materials due to the increased methyl acrylate weight fraction.

The elastic modulus ($E_1$) consistently increased with silica content for the EMA9-based materials from modelling of creep data with 4-element model. An increasing modulus trend was less consistent for the EMA19-based materials. The elastic modulus values of EMA9 elastomer and each silica volume fraction were overall larger that their EMA19-based counterparts indicating that greater crystallinity resulted in increased resistance to elastic deformation. The time dependant uncoiling of molecules was observed to occur at overall lower strains ($E_2$) and longer times ($\eta_2$) with increasing silica volume fraction for the EMA9 and EMA19 series of materials. The $E_2$ and $\eta_2$ values of the EMA9 elastomer and each EMA9Si composite were larger that their EMA19-based counterparts for the elastomers and each silica volume fraction due to the increased crystallinity in the EMA9-based materials and increased methyl acrylate weight fraction in the EMA19-based materials. The irreversible flow ($\eta_3$) was observed to occur at overall increasingly longer times with increasing silica volume fraction for the EMA9 and EMA19 series of materials. The $\eta_3$ values of the EMA9 elastomer and EMA9Si composites were greater than their EMA19 counterparts for each silica volume fraction due to the increased crystallinity in the EMA9-based materials and increased methyl acrylate weight fraction in the EMA19-based materials. The retardation
times were observed to decrease with increasing silica volume fraction for both the EMA9 and EMA19 series of materials.

The resistance to viscoelastic recovery of the EMA9 and EMA19 series of materials calculated from modelling with the KWW equation were observed to overall decrease with increasing silica volume fraction. The resistance to recovery of the EMA19 elastomer and EMA19Si composites were observed to be larger than their EMA9 series counterparts due to the plasticising effect of the increased methyl acrylate weight fraction. There was an overall slight decrease observed in the $\beta$ shape parameter values for both the EMA9 and EMA19 series of materials and were largest for the EMA19 series of materials, indicating they had the least constraints to the operation of relaxation modes. The relaxation times of the EMA19 series of materials were longer than their EMA9 counterparts for the unfilled elastomers and at each silica volume fraction. The relaxation time was observed to overall decrease with increasing silica volume fraction for the EMA9 and EMA19 series of materials.

The storage modulus obtained from mf-TM was observed to consistently increase with each increase to silica volume fraction at all temperatures for both EMA9-based and EMA19-based materials indicating that the resistance to elastic deformation increased with increasing silica content. There appeared to be a transition in the temperature range of approximately 10 °C – 55 °C which may be similar to the polyethylene crystal-crystal transition and there was no apparent increase to the temperature of failure. The loss modulus was observed to consistently increase with increasing silica volume fraction for both EMA9-based and EMA19-based materials indicating that absorption of energy and conversion to heat increased with increasing silica content. The $\tan \delta$ values of all EMA-based materials were observed to decrease with increasing silica content indicating that silica contributed mainly to the viscoelastic modulus. The EMA9 and the EMA9Si exhibited a single broad peak from approximately -28 – 56 °C while the EMA19-based materials exhibited a broad peak over the temperature range of approximately -40 °C – 20 °C, after which the $\tan \delta$ values of all EMA-based materials were constant until the onset of failure when they rapidly increased. The EMA9-based materials possessed greater storage and loss modulus values at all post-$T_g$ analysis temperatures, and higher glass transition temperatures than their EMA19-based counterparts due to the increased crystallinity in EMA9. The EMA19-based materials possessed the greatest $\tan \delta$ damping due to their increased methyl acrylate weight fraction.

Mastercurves formed from multi-frequency mf-TM data possessed frequency ranges of approximately $10^{-9} – 10^{17}$ Hz, increased from the original analysis frequency range of $10^{2} – 10^{7}$ Hz. It was observed for both series of EMA materials that with increasing silica content
the storage modulus increased. The greatest increase of modulus occurred in the data obtained from temperatures encompassing the $T_g$. There was a reduction in the steepness of the mastercurves with increasing silica volume fraction. The effect of the silica filler reinforcement was more observable in the lower frequency with the greatest increase in the storage modulus observed with the increase in silica volume fraction from 5 to 10 %v/v, and 10 to 20 %v/v silica. The storage modulus was observed to plateau at the highest frequencies in the two highest silica filled composites for both series of materials. The greatest change in modulus with increasing frequency in the loss modulus mastercurves of both series of materials occurred in data immediately encompassing the $T_g$. The largest increase in loss modulus was observed with the increases to 10 %v/v at the lowest transposed frequencies while the modulus values of the 10 and 20 %v/v silica filled composites plateaued at the highest transposed frequencies for both series of materials. The EMA9-based materials possessed slightly greater modulus values in the plateau region of the mastercurve but had much greater modulus values at the lowest transposed frequencies. This was due to the reinforcement provided by the increased crystallinity in the EMA9-based materials being more apparent at low frequencies. The EMA9-based materials had the largest loss modulus values at all transposed frequencies except for the peak in data equivalent to the data obtained at $T_g$.

Mastercurves constructed from synthetic frequency data were observed to have the exact same temperature for each modulus value from each analysis frequency. The disadvantages of these mastercurves was that there was poor, if any overlap between the data obtained with the desired temperature increment and the inherent limitation that only 5 frequencies, separated by a factor of 2 can be selected at a time.

The accuracy of modelling mastercurve data with the D, CC, CD and HN relaxation equations was determined by the Wicket error function. The HN equation modelled the mastercurve data most accurately, followed by the CC, CD and finally D equations. The high accuracy of the HN equation was attributed to it possessing two shape parameters which allowed it to account for changes in both the symmetry and skewness of the mastercurve data. All relaxation equations were observed to most accurately model the EMA9-based materials. The relaxation time from each relaxation equation was observed to increase with increasing silica content for both series of materials. This was attributed to the silica particles inhibiting molecular and segmental rotation via physical crosslinks. The relaxation times were overall longest for the EMA9-based materials due to their greater crystallinity. The infinite and zero moduli were observed to overall increase with increasing silica content for each relaxation
equation. The increase in $E_\infty$ between the 10 and 20 %.v/v silica filled composites was the smallest increase since the composites were approaching their plateau. The infinite modulus was observed to be slightly larger for the EMA19 elastomer and EMA19Si composites while the zero modulus was largest for the EMA9 elastomer and EMA9Si composites for the D, CC and HN relaxation equations. The $E_\infty$ and $E_0$ moduli were largest for the EMA9 elastomer and EMA9Si obtained from modelling with the CD relaxation equation. The $\alpha$ of the CC relaxation equation was observed to be largest for the EMA9 elastomer and EMA9Si composites while the $\beta$ parameter of the CD relaxation was largest for the EMA19 elastomer and EMA19Si composites. The $\alpha$ parameter was overall largest for the EMA19 elastomer and EMA19Si composites while the $\beta$ parameter was overall largest for the EMA9 elastomer and EMA19Si composites for the HN equation.

Super-mastercurves were formed with shift factors termed $a_C$, with the $c$ representing concentration. These shift factors represented the correlation of the effect of silica on modulus with respect to frequency. The super-mastercurve data had a frequency range of $10^{-11} – 10^{20}$ Hz and displayed feathering at low frequencies. There was consistency in the storage modulus super-mastercurve data for both series of materials at the highest transposed frequencies with only the data from the EMA9 master curve deviating. Both loss modulus super-mastercurves had feathering at the lowest transposed frequencies caused by mastercurve data from the 20 %.v/v silica filled composites.

Mastercurves were created employing the HN equation instead manually shifting modulus data. These mastercurves possessed similar in the transition frequencies ($10^{-2} – 10^{2}$ Hz, the original analysis frequencies); however they had higher and lower frequency extremes. The EMA9 mastercurves created from the HN shift method were shifted positively in the frequency scale. There was less overlap in data of the HN mastercurves compared with the manual shift mastercurves at the zero and infinite frequency extremes. The advantages of the HN method were that there was mathematical basis behind the derivation of shift factors and accounts for vertical shifts by simulating data. The disadvantages of the HN method are that the equation may not accurately account for modulus data at the zero and infinite frequency extremes and that the reference temperature must be equivalent to the $T_g$ since this is data where there is the greatest difference between highest and lowest analysis frequencies and will best able to model the plateau and terminal region modulus data.
Chapter 6 Thermomechanical properties of thermoplastic polyurethane–silica nanocomposites

Introduction

Polyurethanes are synthesised from a polyol and a diisocyanate forming a block elastomer composed of hard and soft phases. The molecular composition of the polyol and isocyanate will determine the physical properties such as $T_g$, melt properties (if crystalline segments are present) and hardness. Polyurethanes are reinforced by internal physical crosslinking of the hard phase via H-bonding. Changing the molecular structure of the components of the polyurethane will alter its H-bonding properties. Another method of crosslinking is by physical crosslinks with the addition of filler such as silica. The filler is able to bond to either the hard or soft segments, or both which may result in differing properties.

The objective of this study was to prepare polyurethane–silica nanocomposites with varying polyurethane molecular constituents and silica volume fraction and analyse their thermal and thermomechanical properties to study the contributions of the differing thermoplastic polyurethane and silica volume fraction had on these properties.

Experimental

Preparation of polyurethane–silica films

Composites were prepared with hydrophilic nano-particulate silica (Aerosil 380) and two thermoplastic polyurethanes; an ether and an ester-based elastomer. The nanocomposites were prepared by solution dispersion and pressing into sheets according to the method described in Chapter 3. The compositions and naming scheme for the composites is shown in Table 28. Thermogravimetry (TGA) was performed on the nanocomposites using samples of approximately 2 mg. TGA was used to confirm the actual silica composition and to identify any TPU thermal stability conferred by the silica filler. The detailed TGA method for analysis and data processing is described in Chapter 3.
Table 28 Polyurethane–silica nanocomposite formulation designation and composition

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Polyurethane component</th>
<th>Silica volume fraction %,v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>Ether</td>
<td>0</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>Ether</td>
<td>1</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>Ether</td>
<td>5</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>Ether</td>
<td>10</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>Ether</td>
<td>20</td>
</tr>
<tr>
<td>PEs</td>
<td>Ester</td>
<td>0</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>Ester</td>
<td>1</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>Ester</td>
<td>5</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>Ester</td>
<td>10</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>Ester</td>
<td>20</td>
</tr>
</tbody>
</table>

Composite characterisation

Stress-strain analysis (dynamic force thermomechanometry (df-TM)) was performed in tensile mode using rectangular specimens of length × width × thickness 25 × 10 × 0.5 mm. Creep and recovery analysis (static force thermomechanometry (sf-TM)) was performed in tensile mode using rectangular specimens of length × width × thickness 8.5 × 10 × 0.5 mm. Single and multi-frequency modulated force thermomechanometry (mf-TM) were performed in tensile mode using a heating rate of 2 °C•min⁻¹ and a stepwise isothermal temperature program for multiple frequencies. Details of these methods are described in Chapter 3.

Results and discussion

Contribution of silica filler composition and polyurethane type to thermal stability

TGA was performed on the TPU elastomers and TPU-silica nanocomposites to confirm silica composition and assess any contribution to thermal stability from the silica or ether/ester content. The TGA data for PEt and the PEtSi composites is shown in Figure 112. Each composite experienced two observable mass loss inflections corresponding to the thermal degradation of the urethane and the respective soft phase[223]. The first degradation temperature was associated with the degradation of the hard urethane phase (usually at temperatures > 200 °C) while the second degradation temperature is associated with the decomposition of the soft phase[224]. The onset temperature of decomposition increased with increasing silica volume fraction. The elastomer and all composites displayed negligible mass loss at post-500 °C temperatures, even under an oxygen enriched atmosphere at the highest analysis temperatures.
Figure 112 Filler composition and thermal stability: PEt (-\triangleleft-); PEtSi1 (-\Box-); PEtSi5 (-\triangle-); PEtSi10 (-\times-); PEtSi20 (-\lozenge-)

Figure 113 represents the weight loss derivative data obtained from thermogravimetry of PEt series of materials. The data of each material had two troughs representing the degradation of the hard and soft phases of the TPU.

Table 29 lists the values of the minimums of the derivative weight troughs and the temperatures at which they occurred from the data in Figure 106. The temperature at which the first trough occurs increased 42 °C between the PEt and PEtSi20 while the temperature at
which the second trough occurs increased by 19 °C with the addition of 20 %,v/v of silica. The derivative weight values of both troughs were observed to increase by a total of 9 mg.min⁻¹ between the unfilled elastomer and 20 %,v/v silica filled composite. The first derivative weight trough value was observed to be less than the value of the second derivative weight trough for each of the PE-based materials. These observations may indicate that the silica may be distributed more in the hard phase, or more strongly bonded to the hard phase resulting in greatest thermal retardation of the degradation of the urethane phase though there was thermal protection of the ether phase. The rate at which degradation occurred for both troughs was equally affected by increasing silica volume fraction i.e. the rates were reduced by 9 mg.min⁻¹.

Table 29 Minima of the derivative weight troughs and the temperatures of minima

<table>
<thead>
<tr>
<th>Composite</th>
<th>Temperature at 1st trough °C</th>
<th>Derivative weight at 1st trough mg.min⁻¹</th>
<th>Temperature at 2nd trough °C</th>
<th>Derivative weight at 2nd trough mg.min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>345</td>
<td>-18</td>
<td>422</td>
<td>-20</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>360</td>
<td>-16</td>
<td>431</td>
<td>-22</td>
</tr>
<tr>
<td>PEt9Si5</td>
<td>376</td>
<td>-16</td>
<td>432</td>
<td>-19</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>387</td>
<td>-13</td>
<td>440</td>
<td>-16</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>388</td>
<td>-9</td>
<td>441</td>
<td>-11</td>
</tr>
</tbody>
</table>

The TGA data for PEs and the PEsSi composites is shown in Figure 114. Two mass loss inflections corresponding to the decomposition of the urethane and ester phases were observed. The onset temperature of decomposition increased with increasing silica volume fraction. The PEs-based materials displayed negligible mass loss at post -500 °C temperatures, even under an ambient atmosphere (i.e. containing oxygen).
Figure 114 Filler composition and thermal stability: PEs (¬-); PEsSi1 (¬¬-); PEsSi5 (¬△-); PEsSi10 (¬×-); PEsSi20 (¬○-)

Figure 115 represents the weight loss derivative data obtained from thermogravimetry of PEs series of materials. The troughs in the data corresponded to the temperatures at which mass loss was occurring at the fastest rate. All data series were observed to possess either two peaks, or a peak and one shoulder except for PEs and PEsSi1 which possessed an additional shoulder. The values of the weight derivative data were entirely negative (apart from noise) due to this data being a measure of weight loss.

Figure 115 Derivative weight versus temperature: PEs (¬¬-); PEsSi1 (¬¬-); PEsSi5 (¬¬-); PEsSi10 (¬¬-); PEsSi20 (¬¬-)

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Table 30 lists the values of the minima of the derivative weight loss troughs and the temperatures at which they occurred, for the PEs elastomer and PEsSi composites as seen in Figure 115. The temperature at which the first trough occurs was observed to overall increase by 13 °C with increasing silica volume fraction. The weight derivative data of the first troughs/shoulders were observed to decrease with increasing silica volume fraction. The temperature at which the second trough (only PEs possessed a shoulder at these temperatures) in the derivative weight data occurred was observed to consistently increase with increasing silica volume fraction. The derivative weight values at these troughs initially increase with the addition of 1 % v/v of silica, but decreased with subsequent additions of silica. The derivative weight data of the PEs elastomer and PEsSi1 possessed a third shoulder. The temperature at which these shoulders occurred increased by 6 °C with the addition of 1 % v/v of silica, however the derivative weight data were approximately the same for both shoulders. This third shoulder was not observed in the derivative weight data of the other composites since the second trough of these composites was broad enough to encompass the temperatures at which a third shoulder may have been expected to occur.

### Table 30 Temperatures of minimum trough data of the weight derivative data for PEsSi composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature at 1&lt;sup&gt;st&lt;/sup&gt; trough °C</th>
<th>Derivative weight at 1&lt;sup&gt;st&lt;/sup&gt; trough mg.min&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Temperature at 2&lt;sup&gt;nd&lt;/sup&gt; trough °C</th>
<th>Derivative weight at 2&lt;sup&gt;nd&lt;/sup&gt; trough mg.min&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Temperature at 3&lt;sup&gt;rd&lt;/sup&gt; trough °C</th>
<th>Derivative weight at 3&lt;sup&gt;rd&lt;/sup&gt; trough mg.min&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEs</td>
<td>371</td>
<td>-21</td>
<td>398</td>
<td>-13</td>
<td>464</td>
<td>-2</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>372</td>
<td>-16</td>
<td>408</td>
<td>-20</td>
<td>470</td>
<td>-2</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>384</td>
<td>-12</td>
<td>420</td>
<td>-19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>377</td>
<td>-10</td>
<td>428</td>
<td>-18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>384</td>
<td>-6</td>
<td>444</td>
<td>-12</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The decomposition of each material was taken at the temperature (T<sub>0.5</sub>) for 50 %-w/w mass loss. Figure 116 shows the decomposition temperature plotted against the filler volume fraction (Φ). The T<sub>0.5</sub> of both series of materials was observed to increase with increasing silica volume fraction. The PEt-based materials possessed a higher degradation temperature for the unfilled elastomers and the 1 % v/v filled composites, while the PEs-based composites had higher degradation temperatures for all other silica concentrations. Logarithmic curves modelled each data set to give Equations 68 and 69 for PEt-based and PEs based materials respectively.
\[ T_{0.5} = 15 \cdot \ln(\Phi) + 394 \quad \text{Equation 68} \]
\[ T_{0.5} = 18 \cdot \ln(\Phi) + 393 \quad \text{Equation 69} \]

The \( T_{0.5} \) of the PEt-based materials degradation temperature were raised by 69 °C with the addition of 20 %.v/v silica while the PEs-based materials were observed to have their degradation \( T_{0.5} \) raised by 75 °C between the unfilled elastomer and the 20 %.v/v filled composite.

![Figure 116](image)

**Figure 116** Temperature at 50 %.wt loss versus silica concentration: PEt elastomer and PEtSi composites (-•-); PEs elastomer and PEsSi composites (-■■-); solid lines represent logarithmic lines of best fit

Composites were prepared to have desired filler volume fractions. Table 31 lists the final weight fractions (i.e. the remaining weight fractions at the completion of a thermogravimetric analysis) of the TPU materials converted to volume fraction from the TGA weight fraction output. The actual volume fractions remaining were close to the desired volume fractions of silica with the greatest difference being 1 %.v/v (occurring in PEsSi20). The differences between desired and remaining volume fraction of silica were attributed to experimental uncertainty.
Table 31 Final mass reaming after TGA converted to volume fraction

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume fraction remaining after TGA %, v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.0</td>
</tr>
<tr>
<td>PETSi1</td>
<td>0.9</td>
</tr>
<tr>
<td>PETSi5</td>
<td>5.7</td>
</tr>
<tr>
<td>PETSi10</td>
<td>10.5</td>
</tr>
<tr>
<td>PETSi20</td>
<td>20.8</td>
</tr>
<tr>
<td>PEs</td>
<td>0.1</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>1.0</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>5.5</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>10.9</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Direct comparisons between materials with differing polyurethane components but similar silica volume fractions were graphed. Figure 117 represents the filler composition and thermal stability of PETSi5 and PEsSi5. The temperature at the onset of thermal decomposition was approximately the same for these composites. PETSi5 and PEsSi5 were observed to thermally degrade at approximately the same rate (as observed in their similar derivative weight trough values) though PEsSi5 underwent decomposition at slightly higher temperatures. These observations were consistent in figures of the comparisons between the elastomers and other similarly silica filled materials as seen in Appendix 3.1.

![Figure 117 Filler composition and thermal stability: PETSi5 (-•-); PEsSi5 (-△-)](image)

**Stress-strain response with TPU and silica composition**

Dynamic force thermomechanometry, as tensile stress-strain analysis, was employed to characterise the effect of varying TPU composition and silica content on physical crosslink
strength in each material. Figure 118 represents stress-strain analysis of the PET-based materials. Each material possessed an initial elastic deformation followed by a combination of viscoelastic and viscous deformation; although PETSi20 fractured almost immediately after the onset of viscoelastic and viscous deformation. All other materials slipped from the clamps before material fracture occurred due to thinning of the test specimen. The toughness was observed to decrease with increasing silica volume fraction. The Young’s modulus of each PET-based material was calculated from the elastic deformation portion of total deformation. An overall increase in Young’s modulus with increasing silica volume fraction was observed in the PET-series of materials. The modulus values are listed in Table 40 in the comparison of moduli section.

Figure 118 Stress-strain data: PET (-○-); PETSi1 (-□-); PETSi5 (-△-); PETSi10 (-×-); PETSi20 (-◇-)

Figure 119 represents stress-strain analysis of the PEs-based materials. The PEs elastomer and all PEsSi composites possessed an initial elastic deformation followed by a combination viscoelastic and viscous deformation. The stress at yielding was observed to increase with increasing silica volume fraction. Each of the PEs-based materials fractured at the completion of analysis. The toughness was observed to decrease with increasing silica volume fraction. Young’s modulus was observed to consistently increase with increasing silica volume fraction for the PET-series of materials. The modulus values are listed in Table 40 in the comparison of moduli section.
Comparisons were made between the stress-strain analyses of the PEt-based and PEs-based materials to observe the effect of differing TPU composition. Figure 120 displays the stress-strain data of PEtSi5 and PEsSi5. PEtSi5 and PEsSi5 required similar stress for strain extension during elastic deformation. PEsSi5 required a greater stress than PEtSi5 for further strain extension during viscoelastic and viscous deformation. PEtSi5 was observed to be tougher (indicated by its greater strain extension) than PEsSi5. These observations were consistent for comparisons between stress-strain data of the TPU elastomers and similarly silica filled nanocomposites, as seen in the comparison in Appendix 3.3.
Thermoplastic polyurethane–silica composite composition and creep and recovery response

Static force thermomechanometry, as tensile creep and recovery analysis was employed to characterise the effect of varying TPU composition and silica content on physical crosslink strength for each material. Figures 121 and 122 represent the data obtained from creep and recovery analysis with an applied force of 4000 mN of the PEt series and PEs series of materials respectively. All materials displayed elastic creep deformation followed by viscoelastic (represented by the non-linear time-strain data values) and viscous deformation upon application of force. The TPU-based materials with 10 %.v/v and 20 %.v/v SiO₂ were observed to have greatest resistance to creep when compared with the elastomers and composites with the other silica volume fractions. This was indicated by these composites having a small initial elastic strain extension. The 10 %.v/v and 20 %.v/v SiO₂ filled TPUSi composites exhibited less curvature in the viscoelastic creep data compared with the unfilled elastomers and other composites; greater curvature in time-strain data indicates longer times for viscoelastic deformation. These results indicated that the composites with highest silica volume fractions were time-dependently deforming less during the creep time than the other materials. The maximum strain during creep analysis was observed to slightly increase over subsequent analysis cycles for both series of materials with the greatest increase observed in the unfilled elastomers.

Figure 120 Stress-strain data: PEtSi5 (▲-▲-); PEsSi5 (△-△-)

Chapter 6 Thermoplastic polyurethane composition, silica and the thermal properties of polyurethane - silica nanocomposites
The recovery analysis strain data of all TPU-based materials were observed to possess an initial instantaneous recovery (equated to elastic recovery) followed by non-linear time dependant recovery (equated to viscoelastic recovery). The 10 %\text{v/v} and 20 %\text{v/v} silica filled composites had little curvature in their recovery data indicating that there was little viscoelastic deformation to recover. All materials were observed to possess some unrecovered strain (equated to viscous deformation). The magnitude of permanent deformation decreased with increasing silica volume fraction. The amount of permanent strain was observed to slightly increase over subsequent analysis cycles with the unfilled elastomers possessing the greatest increase. It was observed in comparisons between the 4000 mN creep and recovery analyses of the PET-based and PEs-based materials indicated that the PEs-based materials crept less (as indicated by lower strain values) than their PET counterparts. The curvature in both the creep and recovery analyses was observed to be greater in the PET-based materials.
Chapter 6 Thermoplastic polyurethane composition, silica and the thermal properties of polyurethane - silica nanocomposites

Figure 122 Creep and recovery 4000 mN analysis data: PE{(-○-)}; PESi1 (-□-); PESSi5 (-△-); PESi10 (-×-); PESi20 (-●-); Solid lines indicate modelling by the Maxwell-Voigt (creep phase) and KWW (recovery phase) functions

Figures 123 and 124 represent the data obtained from creep and recovery analysis with an applied force of 5000 mN of the PEt series and PEs series of materials respectively. All materials displayed elastic creep deformation followed by viscoelastic and viscous deformation upon application of force. The TPUSi composites with 10%v/v and 20%v/v SiO$_2$ were observed to have greatest resistance to creep when compared with the elastomers and composites with the other silica volume fractions. This was indicated by these composites having a small initial elastic strain extension. The 10%v/v and 20%v/v SiO$_2$ filled TPUSi composites exhibited less curvature in the viscoelastic creep data compared with the unfilled elastomers and other composites; greater curvature in time-strain data indicates longer times for viscoelastic deformation. These results indicated that the composites with highest silica volume fractions were time-dependently and permanently deforming less during the creep time than the other materials. The maximum strain during creep analysis was observed to slightly increase over subsequent analysis cycles for both series of materials with the greatest increase observed in the unfilled elastomers.
Figure 123 Creep and recovery 5000 mN analysis data: PEt (-○-); PEtSi1 (-□-); PEtSi5 (-△-); PEtSi10 (-×-); PEtSi20 (-○-); Solid lines indicate modelling by the Maxwell-Voigt (creep phase) and KWW (recovery phase) functions

The recovery analysis strain data of all TPU-based materials analysed with 5000 mN were observed to possess an initial instantaneous recovery (equated to elastic recovery) followed by non-linear time dependant recovery (equated to viscoelastic recovery). The 10 % v/v and 20 % v/v silica filled composites had little curvature in their recovery data indicating that there was little viscoelastic deformation to recover. All materials were observed to possess some unrecovered strain (equated to viscous deformation). The magnitude of permanent deformation decreased with increasing silica volume fraction. The amount of permanent was observed to slightly increase over subsequent analysis cycles with the unfilled elastomers possessing the greatest increase. It was observed in comparisons between the 4000 mN creep and recovery analyses of the PEt-based and PEs-based materials indicated that the PEs-based materials crept less (as indicated by lower strain values) than their PEt counterparts. The curvature in both the creep and recovery analyses was observed to be greater in the PEt-based materials.
When comparing the creep and recovery analyses of the PEt-based and PEs-based materials analysed with 5000 mN, the PEs-based materials were observed to have smaller maximum creep strain values than their PEt-based counterpart for the unfilled elastomers and each silica volume fraction. The curvature in both the creep and recovery analyses was observed to be greater in the PEt-based materials.

Comparisons were made between the creep and recovery analysis strain data of the same materials conducted with different applied forces. The materials analysed with 5000 mN force possessed greater strain values over both creep and recovery analyses. The strain data of the materials obtained from analyses performed at 5000 mN possessed the longest time for viscoelastic deformation (indicated by curvature in the time dependant deformation region of creep analysis); however, analyses performed at 4000 mN possessed the longest times for viscoelastic recovery in recovery analysis.

**Creep and recovery models**

The 4-element model and Kohlrausch-Williams-Watts (KWW) equation were employed to model creep and recovery data, respectively to determine moduli and relaxation properties. Tables 32 and 33 list the 4-element model parameter values obtained from modelling the 4000 mN creep analysis data of the PEt and PEs series of materials respectively. All of the parameters $E_1$, $E_2$, $\eta_2$ and $\eta_3$ were observed to increase with increasing silica volume fraction. This indicated that there was a greater resistance to elastic deformation ($E_1$), the time
dependant uncoiling of molecules was occurring at increasingly lower strains ($E_2$) and longer times ($\eta_2$) and irreversible flow ($\eta_3$) was observed to occur at increasingly longer times with increasing silica volume fraction. The retardation times were observed to slightly decrease with the addition of and each increase in silica volume fraction. Overall the $E_1$ and $\eta_3$ parameter values were observed to decrease over subsequent analysis cycles while the $E_2$ and $\eta_2$ parameters were observed to increase while the retardation times remained constant for the both series of materials over subsequent analysis cycles.

**Table 32 4-element model parameters obtained from modelling 4000 mN creep analysis data of PET and PETSi composites**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO$_2$ volume fraction %,v/v</th>
<th>$E_1$ MPa</th>
<th>$E_2$ MPa</th>
<th>$\eta_2$ MPa.s</th>
<th>$\eta_3$ GPa.s</th>
<th>$\tau$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>129.0</td>
<td>22.10</td>
<td>7.730</td>
<td>0.73</td>
<td>0.45</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>153.0</td>
<td>32.20</td>
<td>13.90</td>
<td>0.76</td>
<td>0.43</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>173.0</td>
<td>31.70</td>
<td>12.70</td>
<td>1.07</td>
<td>0.40</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>201.0</td>
<td>79.50</td>
<td>22.50</td>
<td>1.92</td>
<td>0.28</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>217.0</td>
<td>239.0</td>
<td>67.80</td>
<td>2.10</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>69.40</td>
<td>25.90</td>
<td>9.070</td>
<td>0.69</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>94.00</td>
<td>31.80</td>
<td>13.80</td>
<td>0.67</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>164.0</td>
<td>31.20</td>
<td>12.50</td>
<td>0.94</td>
<td>0.40</td>
</tr>
<tr>
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<td>24.30</td>
<td>0.90</td>
<td>0.28</td>
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<td>216.0</td>
<td>61.10</td>
<td>1.01</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
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<td>35.60</td>
<td>26.50</td>
<td>92.70</td>
<td>0.64</td>
<td>0.45</td>
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<td>1</td>
<td>38.60</td>
<td>60.20</td>
<td>26.10</td>
<td>0.72</td>
<td>0.43</td>
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<td>80.20</td>
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<td>0.90</td>
<td>0.40</td>
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<td>0.61</td>
<td>0.45</td>
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<td>75.90</td>
<td>33.60</td>
<td>14.60</td>
<td>0.62</td>
<td>0.43</td>
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<td>4</td>
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<td>67.90</td>
<td>0.95</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Comparing the model parameter values obtained from modelling the PET-based and PEs-based materials creep data it was observed that of the $E_1$, $E_2$, $\eta_2$ and $\eta_3$ parameter values were overall greatest for the PET-based materials. This indicated that the ether component bestowed greater resistance to elastic deformation, longer time dependant uncoiling of molecules that occurred at increasingly lower strains and longer times for irreversible flow. The retardation times did not display any significant difference (0.03 s was the greatest difference) between the two series of materials.
Table 33 4-element model parameters obtained from modelling 4000 mN creep analysis data of PEs and PEsSi composites

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO₂ volume fraction</th>
<th>E₁ (MPa)</th>
<th>E₂ (MPa)</th>
<th>η₂ (MPa.s)</th>
<th>η₃ (GPa.s)</th>
<th>τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>59.70</td>
<td>19.70</td>
<td>7.200</td>
<td>0.27</td>
<td>0.42</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>59.50</td>
<td>23.90</td>
<td>7.960</td>
<td>0.34</td>
<td>0.43</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>61.70</td>
<td>49.60</td>
<td>19.00</td>
<td>0.52</td>
<td>0.38</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>75.70</td>
<td>121.0</td>
<td>34.40</td>
<td>0.54</td>
<td>0.28</td>
</tr>
<tr>
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<td>445.0</td>
<td>111.0</td>
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<td>0.25</td>
</tr>
<tr>
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<td>0</td>
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<td>21.60</td>
<td>9.000</td>
<td>0.32</td>
<td>0.42</td>
</tr>
<tr>
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<td>27.10</td>
<td>9.030</td>
<td>0.33</td>
<td>0.43</td>
</tr>
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<td>22.00</td>
<td>0.51</td>
<td>0.38</td>
</tr>
<tr>
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<td>135.0</td>
<td>38.20</td>
<td>0.54</td>
<td>0.28</td>
</tr>
<tr>
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<td>574.0</td>
<td>144.0</td>
<td>6.65</td>
<td>0.25</td>
</tr>
<tr>
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<td>11.10</td>
<td>0.44</td>
<td>0.42</td>
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<td>0.51</td>
<td>0.38</td>
</tr>
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<td>39.10</td>
<td>0.54</td>
<td>0.28</td>
</tr>
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<td>599.0</td>
<td>150.0</td>
<td>6.76</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
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<td>21.50</td>
<td>8.95</td>
<td>0.44</td>
<td>0.42</td>
</tr>
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<td>27.10</td>
<td>9.04</td>
<td>0.42</td>
<td>0.43</td>
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<td>58.30</td>
<td>22.40</td>
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<td>0.38</td>
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<td>603.0</td>
<td>151.0</td>
<td>6.99</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Tables 34 and 35 list the 4-element model parameter values obtained from modelling the 5000 mN creep analysis data of the PEt and PEs series of materials respectively. The E₁, E₂, η₂ and η₃ parameter were observed to increase with increasing silica volume fraction. This indicated that there was a greater resistance to elastic deformation (E₁), the time dependant uncoiling of molecules was occurring at increasingly lower strains (E₂) and longer times (η₂) and irreversible flow (η₃) was observed to occur at increasingly longer times with increasing silica volume fraction. The retardation times were observed to overall slightly decrease with the addition of and each increase in silica volume fraction. Overall the E₁ and η₃ parameter values were observed to decrease over subsequent analysis cycles while the E₂ and η₂ parameters were observed to increase while the retardation times remained constant for the both series of materials over subsequent analysis cycles.
### Table 34 4-element model parameters obtained from modelling 5000 mN creep analysis data of PET and PETSi composites

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO2 volume fraction</th>
<th>E1</th>
<th>E2</th>
<th>η2</th>
<th>η3</th>
<th>τ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%v/v</td>
<td>MPa</td>
<td>MPa</td>
<td>MPa.s</td>
<td>GPa.s</td>
<td>s</td>
</tr>
<tr>
<td>1 0</td>
<td>61.40</td>
<td>61.00</td>
<td>27.60</td>
<td>6.750</td>
<td>0.38</td>
<td>0.43</td>
</tr>
<tr>
<td>1 5</td>
<td>78.00</td>
<td>78.00</td>
<td>27.20</td>
<td>12.30</td>
<td>0.72</td>
<td>0.45</td>
</tr>
<tr>
<td>1 10</td>
<td>87.50</td>
<td>87.50</td>
<td>74.60</td>
<td>19.90</td>
<td>0.77</td>
<td>0.27</td>
</tr>
<tr>
<td>1 20</td>
<td>111.0</td>
<td>265.0</td>
<td>75.20</td>
<td>1.05</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>2 0</td>
<td>37.10</td>
<td>37.10</td>
<td>20.70</td>
<td>8.290</td>
<td>0.37</td>
<td>0.43</td>
</tr>
<tr>
<td>2 5</td>
<td>59.40</td>
<td>59.40</td>
<td>31.50</td>
<td>14.20</td>
<td>0.33</td>
<td>0.45</td>
</tr>
<tr>
<td>2 10</td>
<td>69.90</td>
<td>69.90</td>
<td>32.20</td>
<td>14.50</td>
<td>0.34</td>
<td>0.45</td>
</tr>
<tr>
<td>2 20</td>
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<td>76.40</td>
<td>75.70</td>
<td>20.20</td>
<td>0.76</td>
<td>0.27</td>
</tr>
<tr>
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<td>36.20</td>
<td>20.10</td>
<td>8.020</td>
<td>0.36</td>
<td>0.43</td>
</tr>
<tr>
<td>3 5</td>
<td>40.50</td>
<td>40.50</td>
<td>31.80</td>
<td>14.30</td>
<td>0.48</td>
<td>0.45</td>
</tr>
<tr>
<td>3 10</td>
<td>66.70</td>
<td>66.70</td>
<td>30.50</td>
<td>13.70</td>
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<td>0.45</td>
</tr>
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<td>74.60</td>
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<td>20.00</td>
<td>0.75</td>
<td>0.27</td>
</tr>
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<td>34.60</td>
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<td>7.760</td>
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<td>0.43</td>
</tr>
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<td>55.30</td>
<td>32.00</td>
<td>14.40</td>
<td>0.69</td>
<td>0.45</td>
</tr>
<tr>
<td>4 10</td>
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<td>62.20</td>
<td>30.00</td>
<td>13.50</td>
<td>0.74</td>
<td>0.45</td>
</tr>
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<td>96.70</td>
<td>761.0</td>
<td>216.0</td>
<td>0.86</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Comparing the model parameter values obtained from modelling the PET-based and PEs-based materials 5000 mN creep data it was observed that of the $E_1$, $E_2$, $\eta_2$ and $\eta_3$ parameter values were overall greatest for the PET-based materials for the unfilled elastomer and 1 %v/v silica filled composite; however they were greatest for the PEs-based materials with 5, 10 and 20 %v/v silica. This indicated that the polyether component bestowed greater resistance to elastic deformation and caused greater resistance to time dependant uncoiling of molecules which occurred at longer times. It caused irreversible flow to occur at longer time for pure elastomers and low concentrations of silica. The ester molecule resulted in superior properties at higher silica volume fractions. The retardation times did not display any significant difference between the two series of materials.
The 4-element model parameter values from the creep analyses of the PEt-based materials conducted with 4000 mN and 5000 mN applied force were compared. It was observed that the $E_1$, $E_2$, $\eta_2$, and $\eta_3$ values obtained from the 4000 mN creep analysis were greatest. The largest difference was observed between the $E_1$ and $\eta_3$ parameter values, while the $E_2$ and $\eta_2$ parameter values were more precise. The difference between modulus values with increasing silica volume fractions. There was negligible difference between the retardation times obtained under different analysis forces.

The creep analyses of the PEs-based materials conducted at 4000 and 5000 mN were compared. It was observed that overall the $E_1$, $E_2$, $\eta_2$, and $\eta_3$ parameter values were greatest for the analyses conducted at 4000 mN. The difference between parameter values was observed to increase with increasing silica volume fraction. The retardation was observed to be overall longest for data obtained from 5000 mN creep analyses. These observations were consistent over each subsequent analysis cycle.

The recovery analysis strain data was modelled with the KWW function. Tables 36 and 37 list the KWW parameters obtained from modelling of the recovery data for PEt-based and PEs-based materials respectively, obtained with 4000 mN creep. The relaxation times ($\tau$) of both...
series of materials were observed to decrease with the addition of and increase in silica volume fraction, and increase over subsequent analysis cycles. The distribution factor ($\beta$) was observed to overall decrease with increasing silica volume fraction and decrease during subsequent analysis cycles. This indicated the distribution of relaxations became skewed and possessed more constraints to the operation of relaxation modes with the addition of silica and further analysis cycles. The pre-exponential parameter ($A$) was observed to overall decrease with increasing silica volume fraction, and increase during subsequent analysis cycles for each material indicating silica caused resistance to viscoelastic recovery to decrease but subsequent analysis cycles caused it to increase.

**Table 36 KWW function parameters obtained from modelling 4000 mN creep analysis data of PEt and PEtSi composites**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$\text{SiO}_2$ volume fraction</th>
<th>$\tau$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% v/v</td>
<td>min</td>
<td>mm.mm$^{-1}$</td>
</tr>
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<td>0.134</td>
</tr>
<tr>
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<td>1</td>
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</tr>
<tr>
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<td>0.056</td>
</tr>
<tr>
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<td>10</td>
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</tr>
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</tr>
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<td>5.999</td>
<td>0.141</td>
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<tr>
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<td>1</td>
<td>4.999</td>
<td>0.094</td>
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<td>5</td>
<td>3.199</td>
<td>0.057</td>
</tr>
<tr>
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<td>1.599</td>
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</tr>
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<td>4.999</td>
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</tr>
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<td>3.199</td>
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<td>1.599</td>
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<tr>
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<td>10</td>
<td>1.599</td>
<td>0.039</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.999</td>
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</tr>
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</table>

The KWW function parameter values obtained from modelling 4000 mN recovery data of the PEt series of materials were observed to be greater than the parameter values obtained for the PEs series of materials. This indicated that the polyether had fewer constraints to the operation of relaxation modes and caused greater resistance to viscoelastic recovery with increasingly longer relaxation times.
Table 37 KWW function parameters obtained from modelling 4000 mN creep analysis data of PEs and PEsSi composites

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO$_2$ volume fraction</th>
<th>$\tau$ (min)</th>
<th>$\beta$</th>
<th>A (mm.mm$^{-1}$)</th>
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</thead>
<tbody>
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</tr>
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<td>1</td>
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<td>0.019</td>
<td>0.121</td>
</tr>
<tr>
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<td>5</td>
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<td>0.094</td>
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<td>2</td>
<td>1</td>
<td>4.200</td>
<td>0.019</td>
<td>0.122</td>
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<td>2</td>
<td>5</td>
<td>3.099</td>
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<td>2.299</td>
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<tr>
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<tr>
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<td>1</td>
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<td>0.124</td>
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<td>0.014</td>
<td>0.095</td>
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<td>10</td>
<td>2.299</td>
<td>0.009</td>
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<tr>
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<td>0.125</td>
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<td>20</td>
<td>1.299</td>
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<td>0.004</td>
</tr>
</tbody>
</table>

Tables 38 and 39 list the KWW parameters obtained from the modelling of the recovery data PEt-based and PEs-based materials respectively, obtained with 5000 mN creep. The relaxation times ($\tau$) of both series of materials were observed to decrease with the addition of and increase in silica volume fraction, and increase over subsequent analysis cycles. The distribution factor ($\beta$) was observed to overall decrease with increasing silica volume fraction, and decrease during subsequent analysis cycles indicating more constraints to the operation of relaxation modes with increasing silica and analysis cycles. The pre-exponential parameter (A) was observed to overall decrease with increasing silica volume fraction, and increase during subsequent analysis cycles for each material indicating silica caused resistance to viscoelastic recovery to decrease but subsequent analysis cycles caused it to increase.
Table 38 KWW function parameters obtained from modelling 5000 mN creep analysis data of PEt and PEtSi composites

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO₂ volume fraction</th>
<th>τ (min)</th>
<th>β</th>
<th>A (mm.mm⁻¹)</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5.300</td>
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<td>1</td>
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</tr>
<tr>
<td>1</td>
<td>5</td>
<td>4.526</td>
<td>0.032</td>
<td>0.096</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>3.625</td>
<td>0.009</td>
<td>0.061</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>2.426</td>
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<td>4.999</td>
<td>0.038</td>
<td>0.097</td>
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<tr>
<td>2</td>
<td>5</td>
<td>4.526</td>
<td>0.033</td>
<td>0.101</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>3.625</td>
<td>0.017</td>
<td>0.064</td>
</tr>
<tr>
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<td>20</td>
<td>2.426</td>
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<td>0.026</td>
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<td>5</td>
<td>4.526</td>
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<td>10</td>
<td>3.625</td>
<td>0.018</td>
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<td>0.009</td>
<td>0.027</td>
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<td>0.065</td>
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<tr>
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<td>0.008</td>
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</table>

The τ values obtained from modelling 5000 mN recovery data of the PEt series of materials were observed to be longer than the parameter values obtained for the PEs series of materials for the unfilled elastomers and each silica volume fraction. The β and A values were greatest for the PEt-based materials for the unfilled elastomer and 1 %.v/v silica, and greatest for the PEs-based materials with 5, 10 and 20 %.v/v silica. This indicated that the polyether had fewer constraints to the operation of relaxation modes and greater resistance to viscoelastic recovery for the elastomers and 1 %.v/v silica filled composites. However the polyester had fewer constraints to the operation of relaxation modes and greater resistance to viscoelastic recovery at the higher silica volume fractions.
<table>
<thead>
<tr>
<th>Cycle</th>
<th>SiO$_2$ volume fraction %, v/v</th>
<th>$\tau$ Min</th>
<th>$\beta$</th>
<th>A/mm.mm$^{-1}$</th>
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<td>0.055</td>
</tr>
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<td>10</td>
<td>2.499</td>
<td>0.014</td>
<td>0.054</td>
</tr>
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<td>20</td>
<td>1.299</td>
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<td>0.018</td>
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<td>0.024</td>
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<tr>
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<td>2.499</td>
<td>0.015</td>
<td>0.056</td>
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<td>0.018</td>
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<td>0.033</td>
<td>0.061</td>
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<td>3</td>
<td>10</td>
<td>2.499</td>
<td>0.011</td>
<td>0.056</td>
</tr>
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<td>20</td>
<td>1.299</td>
<td>0.012</td>
<td>0.018</td>
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<td>0.032</td>
<td>0.063</td>
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<tr>
<td>4</td>
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<td>2.499</td>
<td>0.025</td>
<td>0.056</td>
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<tr>
<td>4</td>
<td>20</td>
<td>1.299</td>
<td>0.009</td>
<td>0.018</td>
</tr>
</tbody>
</table>

The KWW parameters of PEt series of materials at 4000 mN and 5000 mN were compared. The analyses performed at 5000 mN possessed overall shorter relaxation times for the elastomer, but longer for the silica-filled composites. The distribution factor was observed to be overall larger for analyses conducted with 4000 mN applied force meaning the greatest analysis force caused fewer constraints to the operation of relaxation modes. The pre-exponential parameter was observed to be overall greatest for the analyses performed at 5000 mN indicating this analysis force had the greatest resistance to viscoelastic recovery. The KWW parameters of PEs series of materials at 4000 mN and 5000 mN were compared. It was observed that there was negligible difference between the relaxation times calculated from the analyses at the two applied forces. The $\beta$ and A parameters were overall greatest for the values calculated from the 5000 mN analyses indicating that at this analysis force the materials had fewer constraints to the operation of relaxation modes and more resistance to viscoelastic recovery.
Material glass transitions and damping properties with TPU composition and silica content

Modulated force thermomechanometry (mf-TM) employing a single frequency (1 Hz) was used to characterise the contributions of TPU compositions and filler on glass transition temperature and damping. Figure 125 represents the storage modulus data obtained from analysis of the PEt elastomer and PEtSi composites. The storage modulus was observed to consistently increase with each increase in silica volume fraction at all temperatures for the PEt-based materials. The storage modulus values of all materials were constant from the initial analysis temperature to approximately -40 °C upon which they continually decreased until the final analysis temperature. The PEt, PEtSi1 and PEtSi5 materials were observed to have a temperature of failure at approximately 160 °C. The PEtSi10 and PEtSi20 composites did not fail at this temperature; this was the temperature at which the analysis concluded.

![Figure 125 Storage modulus versus temperature: PEt (○); PEtSi1 (□); PEtSi5 (△); PEtSi10 (×); PEtSi20 (○)](image)

Figure 125 represents storage modulus values of the PEt-based materials obtained at 20 °C. The storage modulus was observed to increase with increasing silica volume fraction. Slight increases in the storage modulus were observed with the addition of 1 and 5 %.v/v silica. The largest increase in modulus occurred between the 10 and 20 %.v/v silica filled composites. These observations indicate that the presence of silica inhibits elasticity and that the increase from 10 to 20 %.v/v silica results in the greatest inhibition.
Figure 126 Storage modulus versus silica volume fraction at 20 °C of PEt elastomer and PEtSi composites

Figure 127 represents the loss modulus data for the PEt elastomer and PEtSi composites. The loss modulus values of all materials were observed to increase from the initial analysis temperature until peaking at $T_g$, after which they decreased until the final analysis temperature. All of the PEt-based materials loss modulus values were observed to peak at $T_g$ then continually decrease at post-$T_g$ temperatures until temperature of failure. The loss modulus values of PEtSi10 were observed to be lower than those of PEtSi1 and PEtSi5 at temperatures above 25 °C.
Chapter 6 Thermoplastic polyurethane composition, silica and the thermal properties of polyurethane - silica nanocomposites

Figure 127 Loss modulus versus temperature: PEt (-○-); PEtSi1 (-□-); PEtSi5 (-△-); PEtSi10 (-×-); PEtSi20 (-□-)

Table 40 lists the $T_g$s of the PEt-based composites (equivalent to the temperature at which $E''_{\text{max}}$ occurs). It was observed that the $T_g$ did not overall change with the addition of silica except for the addition of 1% v/v silica for which there was a 5 °C decrease in $T_g$.

Table 40 Glass transition temperature and $E''$ of PEt and PEtSi composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ °C</th>
<th>Loss modulus, $E''$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>-40</td>
<td>415.0</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>-45</td>
<td>456.1</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>-41</td>
<td>631.6</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>-40</td>
<td>634.8</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>-40</td>
<td>559.9</td>
</tr>
</tbody>
</table>

Figure 128 represents loss modulus values of the PEt-based materials obtained at 20 °C. It was observed that the loss modulus increased with increasing silica volume fraction. Slight increases in the loss modulus were observed with the addition of 1, 5 and 10% v/v silica and the largest increase in modulus occurred between the 10 and 20% v/v silica filled composites. This indicated that the presence of silica in any of the designated volume fractions increased the absorption of energy and conversion to heat however 20% v/v of silica resulted in the greatest increase.
Figure 128 Loss modulus versus silica volume fraction at 20 °C of PET elastomer and PETSi composites

Figure 129 represents the tan δ data of PET and the PETSi composites. The tan δ values were observed to decrease with increasing silica content. The materials possessed constant tan δ values from the initial analysis temperature then exhibited a single peak at approximately -30°C, after which their tan δ values were constant until the onset of failure where the tan δ values rapidly increased.

Figure 129 Tan δ versus temperature: PET (-◊-); PETSi1 (-□-); PETSi5 (-Δ-); PETSi10 (-×-); PETSi20 (-○-)
Figure 130 represents the maximum tan \( \delta \) values obtained for the PEt series of materials. It was observed that the tan \( \delta_{\text{max}} \) values consistently reduced with increasing silica volume fraction. This indicated that the silica was mainly affecting the elasticity and was increasingly inhibiting energy dispersion with the increasing presence of physical crosslinks at the highest silica volume fractions.

![Graph](image)

**Figure 130 Tan \( \delta_{\text{max}} \) versus silica volume fraction of PEt elastomer and PEtSi composites**

Figure 131 represents the storage modulus data obtained from analysis of the PEs elastomer and PEsSi composites. The storage modulus was observed to consistently increase with each increase in silica volume fraction at all temperatures for the PEs-based materials. The storage modulus values of all materials were constant from the initial analysis temperature to approximately -40 °C upon which they continually decreased until the final analysis temperature. The PEs, PEsSi1 and PEsSi5 materials were observed to have a temperature of failure at approximately 160 °C. The PEtSi10 and PEtSi20 composites did not fail at this temperature; this was the temperature at which the analysis concluded.
Figure 131 Storage modulus versus temperature: PEs (◇); PEsSi1 (□); PEsSi5 (△); PEsSi10 (×); PEtSi20 (○)

Figure 132 represents storage modulus values of the PEs-based materials obtained at 20 °C. The storage modulus was observed to increase with increasing silica volume fraction. The largest increase in modulus occurred between the 10 and 20 %,v/v silica filled composites. These observations indicate that the presence of silica inhibited elasticity and that the increase from 10 to 20 %,v/v silica resulted in the greatest inhibition.

Figure 132 Storage modulus versus silica volume fraction at 20 °C of PEt elastomer and PEtSi composites
Figure 133 represents the loss modulus data for the PEs elastomer and PEsSi composites. The loss modulus values of all materials were observed to increase from the initial analysis temperature until peaking at $T_g$, after which they decreased until the final analysis temperature. All of the PEs-based materials loss modulus values were observed to peak at $T_g$ then continually decrease at post-$T_g$ temperatures until temperature of failure or completion of analysis. The loss modulus values of PEsSi10 were observed to be lower than those of PEsSi5 at temperatures above 25 °C.

Table 41 lists the $T_g$s of the PEs-based composites. It was observed that the $T_g$ decreased slightly with the addition of silica. It was observed to decrease by 4 °C with the addition of 20 % v/v silica.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ °C</th>
<th>Loss modulus, $E''$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEs</td>
<td>-36</td>
<td>446.1</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>-36</td>
<td>491.0</td>
</tr>
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<td>PEsSi5</td>
<td>-38</td>
<td>625.3</td>
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<td>PEsSi20</td>
<td>-40</td>
<td>639.8</td>
</tr>
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</table>

Figure 134 represents loss modulus values of the PEs-based materials obtained at 20 °C. It was observed that the loss modulus overall increased with increasing silica volume fraction. The loss modulus values of the 5 and 10 % v/v silica filled were approximately equal. These
observations indicated that the 20 %.v/v silica filled composite resulted in the greatest increase in absorption of energy and conversion to heat.

![Figure 134 Loss modulus versus silica volume fraction at 20 °C of PET elastomer and PETSi composites](image)

Figure 134 Loss modulus versus silica volume fraction at 20 °C of PET elastomer and PETSi composites

Figure 135 represents the tan δ data of PEs and the PEsSi composites. The tan δ values were observed to decrease with increasing silica content. The materials possessed constant tan δ values from the initial analysis temperature then exhibited a single peak at approximately -30°C, after which their tan δ values were constant until the onset of failure where the tan δ values rapidly increased.
Figure 135 Tan δ versus temperature: PEs (-○-); PEsSi1 (-□-); PEsSi5 (-△-); PEsSi10 (-×-); PEsSi20 (-○-)

Figure 136 represents the maximum tan δ values obtained for the PET series of materials. It was observed that the tan δ_max values consistently reduced with increasing silica volume fraction. This indicated that the silica was mainly affecting the elasticity and was increasingly inhibiting energy dispersion with the presence of physical crosslinks.

Figure 136 Tan δ_max versus silica volume fraction of PET elastomer and PETSi composites

Figure 137 displays the storage modulus data of PETSi5 and PESi5. The storage modulus of PETSi composite was greatest at pre-T_g temperatures, while at post-T_g temperatures the PESi
composite was greatest. These observations were consistent with other comparisons between the unfilled elastomers and materials with similar silica volume fractions except for the 10 and 20 %,v/v silica filled composites where the PEsSi composites possessed the greater modulus values at all analysis temperatures. These observations indicated that presence of polyether caused the greatest inhibition to elasticity in the unfilled elastomers and 1 and 5 %,v/v silica filled materials at pre-T_g temperatures. However the presence of polyester resulted in the greatest resistance to elasticity in the 10 and 20 %,v/v silica filled composites at pre-T_g temperatures and for all materials at post T_g temperatures. Comparison figures for the unfilled elastomers and other similarly silica filled materials can be found in Appendix 3.3.

**Figure 137 Storage modulus versus temperature: PEtSi5 (-\(\triangle\)-); PEsSi5 (-\(\blacktriangle\)-)**

Figure 138 displays the loss modulus data of PEtSi5 and PEsSi5. The PEtSi5 composite possessed the greatest modulus values at the pre-T_g temperatures and similar modulus value at T_g. This indicated that PEsSi5 composite modulus values increased the most at the onset of T_g. PEsSi5 was observed to have the greatest modulus values at post-T_g temperatures until the final analysis temperatures. These observations were consistent for comparisons between the elastomers and other similarly silica filled composites. This indicated that presence of polyether caused the greatest energy dispersion for all materials at pre-T_g temperatures. However the presence of polyester resulted in the greatest energy dispersion at post T_g temperatures for all TPU-based materials. Comparison figures for the unfilled elastomers and other similarly silica filled materials can be found in Appendix 3.3.
Figure 138 Loss modulus versus temperature: PEtSi5 (-△-); PEsSi5 (-▲-)

Figure 139 displays the tan δ data of PEtSi5 and PEsSi5. The PEtSi5 composite had the greatest tan δ value at most of the analysed temperatures and possessed a slightly broader peak in its tan δ data. These observation were consistent for comparisons between the unfilled elastomers and other similarly silica filled materials. These results indicated that the presence of polyester mainly affected the elasticity and was increasingly inhibiting energy dispersion compared with polyether. Comparison figures for other materials with similar silica volume fractions can be found in Appendix 3.3.

Figure 139 Tan δ versus temperature: PEtSi5 (-△-); PEsSi5 (-▲-)
Theoretical single frequency mf-TM modulus values

The single frequency mf-TM experimental storage modulus values of the TPU-based materials were compared with modulus values calculated from the rule of mixture equations (Equations 66 and 67 on page 158).

The experimental moduli of the unfilled elastomers and composites were taken to be the storage moduli at 20 °C. These values were compared with composite modulus values calculated using the storage modulus of the TPU elastomers and the modulus of silica, given as 70 GPa. The calculated modulus values for both series of materials were greater than the experimental values. The greatest difference between experimental and calculated modulus values occurred in the PET series of materials. The experimental and calculated modulus values for the PET-based and PEs-based materials are displayed in Figures 140 and 141.

Figure 140 Modulus versus silica volume fraction of PET elastomer and PETSi composites: Experimental $E'$ values (●); Upper limit calculated $E'$ values (■), Lower limit calculated $E'$ values (▲)
Elastic moduli obtained from stress-strain, creep and mf-TM

The elastic moduli obtained from stress-strain analysis (df-TM), creep analysis (sf-TM) and single frequency mf-TM are listed in Table 42. Each of the modulus values were observed to increase with increasing silica volume fraction. The largest increase for each type of modulus occurred between the increase from 10 %.v/v to 20 %.v/v silica. The storage modulus was largest overall followed by the stress-strain modulus then creep analysis modulus for the elastomers and each silica volume fraction.

Table 42 Elastic modulus values from stress-strain, creep and recovery and mf-TM

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress-strain modulus (at 20 °C) MPa</th>
<th>Creep modulus (at 20 °C, 5000 mN) MPa</th>
<th>mf-TM storage modulus (at 20 °C) MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>11.9</td>
<td>61.4</td>
<td>109.9</td>
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<td>240.1</td>
<td>168.0</td>
<td>1321.2</td>
</tr>
</tbody>
</table>
Mastercurves created with Havriliak-Negami relaxation equation

Mastercurves were constructed from the isothermal multi-frequency mf-TM data of all PEt and PEs-based materials via the HN shift method as described in Chapter 3. Figure 142 represents the storage modulus mastercurves constructed for the PEt elastomer and PEtSi composites. Slight increases in modulus values with the additions of 1, 5 and 10 %v/v of silica to the PEt elastomer were observed at the highest transposed frequencies. The modulus values of PEtSi10 and PEtSi20 were observed to be approximately equal indicating that the material response had plateaued at 10 %v/v silica at these frequencies. The effect of filler was more observable at slower frequencies. Slight increases in modulus values with the additions of 1 and 5 %v/v of silica to the PEt elastomer were observed. The largest increase in modulus values were observed between the PEtSi10 and PEtSi20 composites. Feathering was observed in the modulus data at low frequencies of all the PEt-based materials; however the extent of feathering was reduced with increasing silica volume fraction.

![Mastercurves](image)

Figure 142 Storage modulus mastercurves: PEt (○-○); PEtSi1 (□-□); PEtSi5 (△-△); PEtSi10 (×-×); PEtSi20 (○-○)

Figure 143 represents the loss modulus mastercurves for the PEt elastomer and PEtSi composites. All loss modulus mastercurves possessed a peak in the loss modulus data; corresponding to \( T_g \) and occurring at the analysis frequencies of the original isothermal mf-TM. All of the filled (1, 5, 10 and 20 %v/v of silica) composites plateaued at approximately the same modulus values at the highest frequencies transposed. The modulus data obtained at the highest analysis frequencies (50,100 Hz) at low (pre-\( T_g \)) temperatures exhibited constructive interference. This was observed as the modulus values appearing irregularly
large compared with the modulus values at the other analysis frequencies. The PEt elastomer and all of the PEtSi composites exhibited constructive interference, with the effects most pronounced in the highest filled (10, 20 %,v/v) composites. The PEt elastomer and 1, 5 and 10 %,v/v silica filled composites had similar loss modulus values at low frequencies indicating these volume fractions of silica had only a small reinforcing effect on the loss modulus. The increase in silica volume fraction from 10 %,v/v to 20 %,v/v resulted in the largest increase in modulus values.

![Graph of Figure 143 Loss modulus mastercurves: PEt (-○-); PEtSi1 (-□-); PEtSi5 (-△-); PEtSi10 (-×-); PEtSi20 (-◇-)](image)

Figure 144 represents the storage modulus mastercurves constructed for the PEt elastomer and PEtSi composites. Slight increases in modulus values with the additions of 1, 5 and 10 %,v/v of silica to the PEt elastomer were observed at the highest transposed frequencies. The modulus values of PEtSi10 and PEtSi20 were observed to be approximately equal indicating that the material response had plateaued at 10 %,v/v silica at these frequencies. The effect of filler was more observable at lower frequencies. The modulus values increased with increasing silica volume fraction. The largest increase in modulus values were observed between the PEtSi10 and PEtSi20 composites.
Figure 144 Storage modulus mastercurves: PEs (-○-); PEsSi1 (-□-); PEsSi5 (-△-); PEsSi10 (-×-); PEsSi20 (-○-)

Figure 145 represents the loss modulus mastercurves for the PEs elastomer and PEsSi composites. All of the mastercurves possessed a peak in the loss modulus data; corresponding to $T_g$ and occurring at the analysis frequencies of the original isothermal mf-TM. The unfilled elastomer, and 1 and 5 % v/v silica filled composites possessed similar modulus values at high frequencies. The 10 % v/v to 20 % v/v silica filled composites modulus values were observed to be moderately larger at these frequencies. The modulus data obtained at the highest analysis frequencies (50, 100 Hz) at low (pre-$T_g$) temperatures exhibited constructive interference. This was observed as the modulus values appearing irregularly large compared with the modulus values at the other analysis frequencies. The PEs elastomer and all of the PEsSi composites exhibited constructive interference, with the effects most pronounced in the highest filled (10, 20 % v/v) composites. The loss modulus values of the PEs-based materials at lower frequencies were observed to be increase with increasing silica volume fraction.
Figure 145 Loss modulus mastercurves: PEs (-○-); PEsSi1 (-□-); PEsSi5 (-△-); PEsSi10 (-×-); PEsSi20 (-○-)

Figure 146 displays the storage modulus mastercurves of PEsSi5 and PEsSi5 which represents a comparison between the mastercurves of similar silica volume fraction but differing TPU composition. The storage modulus values of these two composites were approximately equal at the highest transposed frequencies. The PEsSi5 modulus values were largest at the transition frequencies (frequencies equal to the original isothermal mf-TM frequencies) and lowest transposed frequencies. These observations were consistent with other comparisons between the unfilled elastomers and TPU materials with similar silica volume fractions as seen in Appendix 3.4.
Figure 146 Storage modulus mastercurves: PEtSi5 (-○-); PEsSi5 (-□-)

Figure 147 displays the loss modulus mastercurves of PEtSi5 and PEsSi5 which represents a comparison between the mastercurves of similar silica volume fraction but differing TPU composition. The loss values of these two composites were approximately equal at the highest transposed frequencies. PEsSi5 possessed the slightly larger modulus at the transition frequencies and moderately larger at the lowest transposed frequencies. These observations were overall consistent with other comparisons between the unfilled elastomers and TPU materials with similar silica volume fractions as seen in Appendix 3.4.

Figure 147 Loss modulus mastercurves: PEtSi5 (-○-); PEsSi5 (-□-)
Mastercurve shift factor models

Shift factor models were employed to model the shift factor values obtained from the creation of mastercurves from mf-TM analysis of the TPU-based materials. The three selected models were the Williams-Landel-Ferry (WLF – Equation 21) model, the Vogel-Fulcher-Tammann-Hesse (VFTH – Equation 22) model and the V’ant Hoff arctan based model (Equation 25) as described in Chapter 2.

Table 43 lists the sum of least squares error values obtained from modelling the shift factor data of each PEt and PEs-based material with the shift factor models. It was observed that overall the WLF model modelled the shift factor data best, followed by the arctan model then the VFTH model.

<table>
<thead>
<tr>
<th>Material</th>
<th>WLF error</th>
<th>VFTH error</th>
<th>V’ant Hoff error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>16</td>
<td>128</td>
<td>27</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>21</td>
<td>158</td>
<td>145</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>23</td>
<td>353</td>
<td>211</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>14</td>
<td>167</td>
<td>56</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>12</td>
<td>437</td>
<td>23</td>
</tr>
<tr>
<td>PEs</td>
<td>32</td>
<td>279</td>
<td>47</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>22</td>
<td>404</td>
<td>118</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>25</td>
<td>647</td>
<td>53</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>15</td>
<td>347</td>
<td>74</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>15</td>
<td>736</td>
<td>46</td>
</tr>
</tbody>
</table>

Figure 148 represents a WLF model model to the shift factors for the mastercurve of the PEtSi5 composite.
Figure 148 Experimentally derived and calculated shift factor values for PETSi5: WLF function calculated shift factors (- ▲ -); experimentally derived values ( -△ -)

The WLF model was observed to most accurately model shift factor data in the region just after $T_g$. It should be noted that the theory of the WLF model states that this model is only suitable for modelling shift factors over the domain $T_r - T_r + 100 \, ^\circ C$. For this research the reference temperature was taken to be the $T_g$. Table 44 lists the resultant $C_1$ and $C_2$ material parameters obtained from the WLF modelling of shift factors. In both the PET and PEs-based series of materials the 20 % v/v silica filled composites possessed the largest $C_1$ and $C_2$ values. It was observed that both material parameters either increased or decreased in value together in relation to other material parameters. Overall, the material parameter values were generally lower for the PETSi composites than their PEsSi counterparts.

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>12.4</td>
<td>100.3</td>
</tr>
<tr>
<td>PETSi1</td>
<td>11.0</td>
<td>79.7</td>
</tr>
<tr>
<td>PETSi5</td>
<td>12.8</td>
<td>86.3</td>
</tr>
<tr>
<td>PETSi10</td>
<td>12.2</td>
<td>98.5</td>
</tr>
<tr>
<td>PETSi20</td>
<td>21.7</td>
<td>138.9</td>
</tr>
<tr>
<td>PEs</td>
<td>15.9</td>
<td>100.1</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>23.8</td>
<td>157.6</td>
</tr>
<tr>
<td>20PEsSi5</td>
<td>21.6</td>
<td>137.9</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>15.0</td>
<td>106.7</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>30.1</td>
<td>153.2</td>
</tr>
</tbody>
</table>
Figure 149 represents the VFTH modelling of shift factors obtained from the construction of the PEtSi5 mastercurve. The VFTH model data has an inflexible logarithmic shape (similar to that of the KWW function) where only the asymptotes can be altered. This inflexibility inhibits the VFTH model from accurately modelling the varying difference between shift factor values at pre and post-\(T_g\) temperatures.

![Figure 149 Experimentally derived and calculated shift factor values for PEtSi5: VFTH function calculated shift factors (-▲-); experimentally derived values (-△-)](image)

Table 45 lists the \(\tau_0\) and B material parameters obtained from the modelling with the VFTH model to shift factors used to construct mastercurves. There was no apparent correlation between increasing silica volume fraction and the change in the material parameter values.

**Table 45 VFTH parameters obtained from modelling mastercurve shift factors with the VFTH function**

<table>
<thead>
<tr>
<th>Material</th>
<th>(\tau_0 \times 10^{-14})</th>
<th>B</th>
<th>(T_0) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>2000</td>
<td>1140</td>
<td>170</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>38</td>
<td>1568</td>
<td>170</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>0.2</td>
<td>1659</td>
<td>170</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>6790</td>
<td>1208</td>
<td>170</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>8</td>
<td>1261</td>
<td>170</td>
</tr>
<tr>
<td>PEs</td>
<td>1000</td>
<td>1114</td>
<td>170</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>1</td>
<td>1146</td>
<td>170</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>0.01</td>
<td>1332</td>
<td>170</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>193</td>
<td>1205</td>
<td>170</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>0.001</td>
<td>1605</td>
<td>170</td>
</tr>
</tbody>
</table>
Figure 137 represents the modelling with arctan model of the shift factors derived from the construction of the PEtSi5 mastercurve. It appeared that the arctan model was able to best model with either a great or small change in shift factor values at temperatures encompassing \( T_g \) (as exhibited by unfilled elastomers and highest silica filled composites respectively). The advantage of this model was that it was able to model the inflection-like shape that the shift factors from these mastercurves possess.

Table 46 lists the A and C material parameters obtained from modelling shift factor data values with the arctan model. The A and C parameter values were observed to overall decrease with increasing silica volume fraction for the PEt-based materials. The C parameter values were observed to overall decrease with increasing silica volume fraction; however the A parameter values remained approximately constant with increasing silica volume fraction for the PEs-based materials.
### Table 46 V’ant Hoff parameters obtained from modelling the mastercurve shift factors with the V’ant Hoff function

<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>C</th>
<th>T_g °C</th>
<th>T_0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>-0.47</td>
<td>0.004</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>-0.99</td>
<td>0.013</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>-0.65</td>
<td>0.004</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>-0.42</td>
<td>0.003</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>-0.25</td>
<td>0.001</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>-0.28</td>
<td>0.001</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>-0.30</td>
<td>0.001</td>
<td>-38</td>
<td>-30</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>-0.32</td>
<td>0.001</td>
<td>-38</td>
<td>-30</td>
</tr>
</tbody>
</table>

### Havriliak-Negami relaxation equation parameters derived from mastercurve construction and parameters derived from subsequent modelling

The HN relaxation equation was employed to construct mastercurves for TPU-based materials resulting in a series of the HN material parameters (E_∞, E_0, α, β and τ) for each material, as described in Chapter 3. These parameters are listed in Table 47.

### Table 47 HN equation parameters obtained from modelling mf-TM reference temperature data

<table>
<thead>
<tr>
<th>Material</th>
<th>E_∞ GPa</th>
<th>E_0 GPa</th>
<th>α</th>
<th>β</th>
<th>τ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>5.90</td>
<td>0.02</td>
<td>0.26</td>
<td>0.31</td>
<td>0.014</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>6.20</td>
<td>0.03</td>
<td>0.24</td>
<td>0.27</td>
<td>0.033</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>7.72</td>
<td>0.04</td>
<td>0.23</td>
<td>0.26</td>
<td>0.063</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>10.10</td>
<td>0.05</td>
<td>0.22</td>
<td>0.24</td>
<td>1.215</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>15.20</td>
<td>0.14</td>
<td>0.11</td>
<td>0.23</td>
<td>5.240</td>
</tr>
<tr>
<td>PEt</td>
<td>5.90</td>
<td>0.02</td>
<td>0.31</td>
<td>0.41</td>
<td>0.025</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>6.30</td>
<td>0.04</td>
<td>0.29</td>
<td>0.42</td>
<td>0.035</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>6.40</td>
<td>0.07</td>
<td>0.25</td>
<td>0.44</td>
<td>0.105</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>6.80</td>
<td>0.11</td>
<td>0.21</td>
<td>0.45</td>
<td>1.656</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>8.90</td>
<td>0.50</td>
<td>0.12</td>
<td>0.62</td>
<td>10.656</td>
</tr>
</tbody>
</table>

These values were used with the HN equation to model the reference temperature modulus data, and modulus data at other temperatures although with differing relaxation times to create mastercurves. Since the E_∞, E_0, α and β material parameters were optimised for modelling the modulus data at the reference temperature these parameters may not result in the best modelling of the entire mastercurve. Therefore after the mastercurves were constructed they were remodelled with the HN relaxation equation to obtain best modelling HN parameters. Table 48 lists the Wicket error values derived from these re-modellings. All of the TPU-based
mastercurves were best modelled by the re-modelling HN parameters rather than the parameters used to model the reference temperature data. The HN equation overall modelled the PEt-based materials better than their PEs-based counterparts.

Table 48 Wicket errors from re-modelling mastercurves with HN equation

<table>
<thead>
<tr>
<th>Material</th>
<th>HN Wicket error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>0.264</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>0.286</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>0.377</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>0.725</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>0.228</td>
</tr>
<tr>
<td>PEs</td>
<td>0.040</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>0.458</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>0.544</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>0.308</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>0.228</td>
</tr>
</tbody>
</table>

Table 49 lists the HN parameters derived from the remodelling of the mastercurve data with the relaxation equation. It was observed that with increasing silica volume fraction, the zero and infinite moduli increased for both the PEt and PEs series of materials, except for the infinite modulus which was identical for the PEtSi10 and PEtSi20 composites, and the PEsSi10 and PEsSi20 composites. This indicated that at 10% v/v silica the HN equation modelled infinite modulus had plateaued. The infinite modulus was observed to be largest for all the PEs-based materials. The zero modulus was overall largest for the PEs-based nanocomposites. The α and β shape parameters were observed to decrease with increasing silica content for both series of materials except for the β values of the 20% v/v silica filled nanocomposites which increased to greater than the β values of the unfilled elastomers. The shape parameter values were similar between the two series of materials. The relaxation time was observed to increase with increasing silica volume fraction. The largest increase was observed between the PEsSi10 and PEsSi20 nanocomposites. The PEt-based materials possessed the overall longest relaxation times.
Table 49: HN equation parameters obtained from subsequent modelling of polyurethane-silica mastercurves

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_\infty$ (GPa)</th>
<th>$E_0$ (GPa)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\tau_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt</td>
<td>5.60</td>
<td>0.05</td>
<td>0.34</td>
<td>0.41</td>
<td>0.021</td>
</tr>
<tr>
<td>PEtSi1</td>
<td>5.91</td>
<td>0.06</td>
<td>0.33</td>
<td>0.39</td>
<td>0.091</td>
</tr>
<tr>
<td>PEtSi5</td>
<td>6.91</td>
<td>0.06</td>
<td>0.30</td>
<td>0.38</td>
<td>0.131</td>
</tr>
<tr>
<td>PEtSi10</td>
<td>9.08</td>
<td>0.10</td>
<td>0.27</td>
<td>0.37</td>
<td>0.287</td>
</tr>
<tr>
<td>PEtSi20</td>
<td>9.08</td>
<td>0.31</td>
<td>0.14</td>
<td>0.54</td>
<td>0.887</td>
</tr>
<tr>
<td>PEs</td>
<td>6.21</td>
<td>0.04</td>
<td>0.34</td>
<td>0.42</td>
<td>0.030</td>
</tr>
<tr>
<td>PEsSi1</td>
<td>6.55</td>
<td>0.05</td>
<td>0.30</td>
<td>0.40</td>
<td>0.068</td>
</tr>
<tr>
<td>PEsSi5</td>
<td>8.06</td>
<td>0.12</td>
<td>0.29</td>
<td>0.33</td>
<td>0.127</td>
</tr>
<tr>
<td>PEsSi10</td>
<td>12.20</td>
<td>0.20</td>
<td>0.21</td>
<td>0.33</td>
<td>0.197</td>
</tr>
<tr>
<td>PEsSi20</td>
<td>12.20</td>
<td>0.43</td>
<td>0.11</td>
<td>0.54</td>
<td>1.411</td>
</tr>
</tbody>
</table>

Comparisons between the HN parameters used to construct mastercurves (as seen in Table 47) and the HN parameters derived from subsequent modelling of mastercurves (as seen in Table 49) were made. The $E_\infty$ and $\tau$ parameter values obtained for the PEt-based were the largest while the $E_0$, $\alpha$ and $\beta$ parameter values were largest for the remodelled HN equation parameters. The relaxation time was longest for the mastercurve construction parameters, while the $E_\infty$, $E_0$, $\alpha$ and $\beta$ parameters were largest for the subsequent re-modelling HN equation parameters for the PEs-based materials.

Figure 151 represents a comparison between the HN created mastercurve data and the data derived from the remodelling of the HN relaxation equation to the mastercurves over the same frequencies as the mastercurve data, for PEtSi5. The HN equation was observed to model the storage modulus mastercurve data most accurately. The HN equation accurately modelled the transition region (equal to the original analysis frequencies) of the loss modulus mastercurve data but did not accurately model the low and high frequency modulus values. The HN equation predicted that the loss modulus values would sharply decrease at both the low and high frequencies, however actually the modulus values decreased less at reduced rate at low frequencies and plateaued at high frequencies. These observations held true for all materials, both PEt and PEs-based. However the HN equation appeared to more accurately model the loss modulus data with increasing silica volume fraction. Other comparison figures can be seen in Appendix 3.5.
Super-mastercurves constructed from polyurethane–based mastercurves

Super-mastercurves were constructed from their respective elastomer and TPUSi composite mastercurves for each of the PEt-based and PEs-based materials. They were constructed by shifting mastercurve data via $a_c$ shift factors, where $c$ represented concentration. The 5 % v/v silica filled mastercurve was used as the reference curve for each series of materials as they possessed the median modulus data values. Figure 152 represents the PEt-based material storage modulus super-mastercurve. This super-mastercurve extended over a frequency range of $10^{-11} - 10^{20}$ Hz. There was good continuity between the data at high frequencies. All data was displayed precision low frequencies except data from the 20 % v/v silica filled composite mastercurve.
Figure 152 PEt elastomer and PEtSi composite storage modulus super-mastercurve

Figure 153 represents the PEt-based materials loss modulus super-mastercurve. There was good precision between the super-mastercurve data at high frequencies. Feathering was observed at low frequencies from mastercurve data originating from the pure elastomer, 1 and 5 % v/v silica filled composites. This resulted in the super-mastercurve data possessing a wide band of values at low frequencies as opposed to a single continuous data series.

Figure 153 PEt elastomer and PEtSi composite loss modulus super-mastercurve

Figure 154 represents the PEs-based materials storage modulus super-mastercurve. Slight feathering was observed in the super-mastercurve at low frequencies, due to the pure
elastomer, 1, 5 and 10 %v/v silica filled materials. The storage modulus data values from PESi20 at low frequencies were observed to be much greater than those of the other mastercurves and they did not form a continuous data series after the application of shift factors. There was precision between the respective mastercurve data at high frequencies with the modulus values of the PESi10 and PESi20 being the plateau modulus values.

![Figure 154 PEs elastomer and PESi composite storage modulus super-mastercurve](image)

Figure 154 represents the PESi loss modulus super-mastercurve. Feathering was observed at both low and high frequencies. All of the respective mastercurve modulus data were observed to feather at low frequencies. The pure elastomer, 1, 5 and 10 %v/v silica filled composite mastercurve data was observed to have precision at high frequencies, however the PESi20 mastercurve modulus data was greater than that of the other four materials.
Conclusion

The TPU-based materials were observed to possess two mass loss inflections in their TGA data corresponding to degradation of the hard and soft phases. The onset temperature of decomposition of all TPU-based materials increased with increasing silica volume fraction and possessed negligible mass loss at post-500 °C temperatures. The onset temperature of decomposition was similar between the elastomers and composites with similar silica volume fractions. The derivative weight data indicated that the silica may be distributed more in the hard phase, or more strongly bonded to the hard phase. The $T_{0.5}$ of both series of materials was observed to increase with increasing silica volume fraction. The PEt-based materials possessed a higher degradation temperature for the unfilled elastomers and the 1 % v/v filled composites, while the PEs-based composites had higher degradation temperatures for all other silica concentrations. The $T_{0.5}$ of the PEt-based materials it was raised by a total of 69 °C while for the PEs-based materials it was raised by 75 °C with the addition of 20 % v/v silica.

Stress-strain analysis revealed each TPU-based material possessed an initial elastic deformation followed by a combination of viscoelastic and viscous deformation. The toughness was observed to decrease with increasing silica volume fraction. The stress at yielding was observed to increase with increasing silica volume fraction. An overall increase in Young’s modulus was observed with increasing silica volume fraction. The PEt and PEs-based materials possessed similar stress for strain extension during elastic deformation. The PEs-based materials required a greater stress than PEt-based materials after yielding. PEt-based materials were observed to be the toughest.
Creep and recovery analysis revealed all materials displayed elastic creep deformation followed by viscoelastic and viscous deformation. The TPUSi composites with 10 \%v/v and 20 \%v/v SiO\textsubscript{2} were observed to have greatest resistance to creep when compared with the elastomers and composites with the other silica volume fractions. This was indicated by these composites having a small initial elastic strain extension. The 10 \%v/v and 20 \%v/v SiO\textsubscript{2} filled composites exhibited less curvature in the viscoelastic data compared with the unfilled elastomers and other composites indicating that the composites with highest silica volume fractions were time-dependently deforming less during the creep time than the other materials. The recovery analysis strain data of all TPU-based materials were observed to possess an initial instantaneous recovery followed by non-linear time dependant recovery. The 10 \%v/v and 20 \%v/v silica filled composites had little curvature in their recovery data indicating that there was little viscoelastic deformation to recover. All materials were observed to possess some unrecovered strain and magnitude of permanent deformation decreased with increasing silica volume fraction. It was observed in comparisons between the 4000 mN creep and recovery analyses of the Pet-based and PEs-based materials indicated that the PEs-based materials crept less (as indicated by lower strain values) than their Pet counterparts. The curvature in both the creep and recovery analyses was observed to be greater in the Pet-based materials. The 5000 mN analysis data of the PEs-based materials were observed to have smaller maximum creep strain values than their Pet-based counterparts. The curvature in both the creep and recovery analyses was observed to be greater in the Pet-based materials. Comparisons were made between the creep and recovery analysis strain data of the same materials conducted with different applied forces revealed that the materials analysed with 5000 mN force possessed greater strain values over both creep and recovery analyses. The strain data of the materials obtained from analyses performed at 5000 mN possessed the longest time for viscoelastic deformation, however analyses performed at 4000 mN possessed the longest times for viscoelastic recovery in recovery analysis.

The 4-element model parameters $E_1$, $E_2$, $\eta_2$, and $\eta_3$ obtained from modelling creep analysis data of all TPU-based materials were observed to increase with increasing silica volume fraction. This indicated that there was a greater resistance to elastic deformation, the time dependant uncoiling of molecules was occurring at increasingly lower strains and longer times, and longer times for irreversible with increasing silica volume fraction. The retardation times were observed to slightly decrease with increasing silica volume fraction.

Comparing the model parameter values obtained from modelling 4000 mN creep data the Pet-based and PEs-based materials creep data it was observed that of the $E_1$, $E_2$, $\eta_2$ and $\eta_3$
parameter values were overall greatest for the PEt-based materials. This indicated that the ether component bestowed greater resistance to elastic deformation, longer time dependant uncoiling of molecules that occurred at increasingly lower strains, and longer times for irreversible flow. The retardation times did not display any significant difference. Comparing the model parameter values obtained from modelling the PEt-based and PEs-based materials 5000 mN creep data it was observed that all parameter values were greatest for the PEt-based materials for the unfilled elastomer and 1 \%v/v silica filled composite; however they were greatest for the PEs-based materials with 5, 10 and 20 \%v/v silica indicating the ester molecule resulted in superior properties at higher silica volume fractions. The retardation times did not display any significant difference between the two series of materials. The 4-element model parameter values from the creep analyses of the PEt-based and PEs-based materials conducted with 4000 and 5000 mN applied force were compared. It was observed that the parameter values obtained from the 4000 mN creep analysis were greatest. There was negligible difference between the retardation times obtained under different analysis forces.

The 4000 mN recovery analysis strain data was modelled with the KWW function and parameters were obtained for the PEt-based and PEs-based materials. The relaxation times of both series of materials were observed to decrease with increasing silica volume fraction. The distribution factor was observed to overall decrease with increasing silica volume fraction indicating the distribution of relaxations became skewed and possessed more constraints to the operation of relaxation modes with the addition of silica. The pre-exponential parameter was observed to overall decrease with increasing silica volume fraction indicating silica caused resistance to viscoelastic recovery to decrease. The KWW function parameter values obtained from modelling 4000 mN recovery data of the PEt series of materials were observed to be greater than their PEs series counterparts. This indicated that polyether had fewer constraints to the operation of relaxation modes and caused greater resistance to viscoelastic recovery with increasingly longer relaxation times.

The 5000 mN recovery analysis strain data was modelled with the KWW function and parameters were obtained for the PEt-based and PEs-based materials. The relaxation times of both series of materials were observed to decrease with increasing silica volume fraction. The distribution factor was observed to overall decrease with increasing silica volume fraction. The pre-exponential parameter was observed to overall decrease with increasing silica volume fraction. The \( \tau \) values obtained from modelling 5000 mN recovery data of the PEt series of materials were observed to be longer than their PEs series counterparts. The \( \beta \) and A values
were greatest for the PEt-based materials for the unfilled elastomer and 1 %.v/v silica, and
greatest for the PEs-based materials with 5, 10 and 20 %.v/v silica.

The KWW parameters of PEt series of materials at 4000 mN and 5000 mN were compared.
The analyses performed at 5000 mN possessed shorter relaxation times for the elastomer, but
longer for the silica-filled composites. The distribution factor was observed to be overall
larger for analyses conducted with 4000 mN applied force meaning the greatest analysis force
caused fewer constraints to the operation of relaxation modes. The pre-exponential parameter
was observed to be overall greatest for the analyses performed at 5000 mN indicating this
analysis force had the greatest resistance to viscoelastic recovery. The KWW parameters of
PEs series of materials at 4000 mN and 5000 mN were compared. It was observed that there
was negligible difference between the relaxation times calculated and the $\beta$ and A parameters
were overall greatest for the values calculated from the 5000 mN analyses.

Modulated force thermomechanometry was conducted on all TPU-based materials. The
storage modulus was observed to consistently increase with each increase in silica volume
fraction at all temperatures for the PEt-based PEs-based materials indicating the presence of
silica inhibits elasticity. The storage modulus values of all materials were constant from the
initial analysis temperature until approximately -40 °C upon which they continually decreased
until the final analysis temperature. The unfilled elastomers, and the 1 and 5 %.v/v silica filled
composites were observed to have a temperature of failure at approximately 160 °C. The
storage modulus values of the PEt-based materials were greater than the PEs-based materials
at pre-$T_g$ temperatures. The modulus values of the PEs-based materials were greatest at post-
$T_g$ temperatures. This indicated that the polyether caused the greatest inhibition to elasticity in
the unfilled elastomers at pre-$T_g$ temperatures; however polyester resulted in the greatest
resistance to elasticity at post-$T_g$.

The loss modulus values of all TPU-based materials were observed to increase from the initial
analysis temperature until peaking at $T_g$, after which they decreased until the final analysis
temperature. The loss modulus values were observed to increase with increasing silica volume
fraction accept at temperatures above 30 °C where the 10 and 20 %.v/v silica filled
composites had lower loss modulus values than the 5 %.v/v silica filled composites. This
indicated that the presence of silica in any of the designated volume fractions increased the
absorption of energy and conversion to heat accept at post-30 °C temperatures where the
higher silica volume fractions inhibited conversion to heat. The $T_g$ did not overall change with
increasing silica volume fraction for the PEt-based materials while the $T_g$ of PEs decreased by
4 °C at the highest silica volume fraction. The PEt-based materials possessed the greatest
modulus values at the pre-$T_g$ temperatures. The PEs-based materials had the greatest modulus values at post-$T_g$ temperatures until the final analysis temperatures. These observations indicated that polyether caused the greatest energy dispersion for all materials at pre-$T_g$ temperatures the polyester caused greater energy dispersion at post-$T_g$ temperatures.

The tan δ data of all TPU-based materials were observed to decrease with increasing silica volume fraction. All materials possessed constant tan δ values from the initial analysis temperature then exhibited a single peak at approximately -30 °C, after which their tan δ values were constant until the onset of failure where the values rapidly increased. The PEt-based materials possessed the greatest tan δ values at nearly all the analysed temperatures. This indicated that the presence of polyester mainly affected the elasticity and was increasingly inhibiting energy dispersion compared with polyether.

Mastercurves were constructed from the isothermal multi-frequency mf-TM data of all TPU-based materials via the HN shift method. Slight increases in modulus values were observed with the additions of 1, 5 and 10 %v/v of silica to elastomers at the highest transposed frequencies. The modulus values of 10 and 20 %v/v silica filled composites were observed to be approximately equal indicating that the material response had plateaued at 10 %v/v silica at these frequencies. Slight increases in modulus values with the additions of 1 and 5 %v/v of silica to the elastomers were observed at the lowest transposed frequencies. The largest increase in modulus values were observed between the 10 and 20 %v/v silica filled composites at low frequencies. The storage modulus mastercurve values of the PEt-based and PEs-based materials were approximately equal at the highest transposed frequencies. The PEs-based materials had the greatest modulus values in the transition and lowest transposed frequency regions.

All loss modulus mastercurves possessed a peak in the loss modulus data corresponding to $T_g$. Each of the silica filled composites plateaued at approximately the same modulus values at the highest frequencies transposed. The modulus data obtained at the highest analysis frequencies at low temperatures exhibited constructive interference with the effects most pronounced in the highest filled composites. The increase in silica volume fraction from 10 %v/v to 20 %v/v resulted in the largest increase in modulus values at the lowest transposed frequencies. The loss modulus mastercurve values of the series of materials were approximately equal at the highest transposed frequencies. The PEs-based materials possessed the slightly larger modulus at the transition frequencies and moderately larger at the lowest transposed frequencies.
Three shift factor models (WLF, VFTH and arctan based model) were employed to model the shift factor values obtained from the creation of mastercurves. The WLF model was observed to most accurately model shift factor data in the region just after $T_g$. The 20 %.v/v silica filled composites possessed the largest $C_1$ and $C_2$ values for both series of materials. It was observed that both material parameters either increased or decreased in value together in relation to other material parameters. The material parameter values were overall lower for the PET-based materials. This inflexibility of the VFTH model inhibited it from accurately modelling the varying difference between shift factor values at pre and post-$T_g$ temperatures. There was no apparent correlation between increasing silica volume fraction and the change in the VFTH material parameter values. The arctan model was able to best model with either a great or small change in shift factor values at temperatures encompassing $T_g$. The advantage of this model was that it was able to model the inflection-like shape that the shift factors that these mastercurves possess. The A and C parameter values were observed to overall decrease with increasing silica volume fraction for the PET-based materials while the C parameter decreased and the A parameter values remained constant for the PEs-based materials.

The HN relaxation equation was employed to construct mastercurves for TPU-based materials resulting in a series of the HN material parameters for each material. These parameters may not have resulted in the best modelling of the mastercurves so they were remodelled with the HN relaxation equation. The parameters from re-modelling were observed to more accurately model mastercurves that the parameters used to construct the mastercurves.

It was observed that with increasing silica volume fraction, the zero and infinite moduli increased for both the PET and PEs series of materials except for the 10 and 20 %.v/v silica composites which possessed similar plateau modulus values. The plateau and zero moduli were observed to be overall largest for the PEs-based materials. The $\alpha$ and $\beta$ shape parameters were observed to decrease with increasing silica content for both series of materials, except for the $\beta$ values of the 20 %.v/v silica filled nanocomposites which increased. The shape parameter values were observed to be similar between the two series of materials. The relaxation time was observed to increase with increasing silica volume fraction. The PEs-based materials possessed the overall longest relaxation times.

Super-mastercurves were constructed for both series of materials. The 5 %.v/v silica filled mastercurves were used as the reference curves for both series of materials. The super-mastercurves extended over a frequency range of $10^{-11} – 10^{20}$ Hz. There was high precision between the super mastercurve storage modulus data at high frequencies. Storage modulus data was precise at low frequencies except for the data from the 20 %.v/v silica filled
composite mastercurves. There was good precision in the super-mastercurve loss modulus data at high frequencies. Feathering was observed at low frequencies originating from mastercurve data from the pure elastomer, 1 and 5 % v/v silica filled composites. This resulted in the super-mastercurve data possessing a wide band of values at low frequencies as opposed to a single continuous data series.
Chapter 7 Comparison of analysis results

Introduction

This chapter will compare and evaluate data obtained under similar analysis conditions for the three material groups i.e. EPDM-based, EMA-based and TPU-based materials. The material groups are each elastomeric possessing different kinds of reinforcement including chemical crosslinks, crystalline physical cohesion and hard-soft phase separated polymers. The property types were each measured with the same instruments under similar conditions, except where stated otherwise. Analysis and modelling were performed to quantify the transitions and relaxations revealed for each material.

Discussion

Dynamic force thermomechanometry – Stress-Strain analysis

Table 50 lists the Young’s modulus values obtained from stress-strain analysis of the EMA-based and TPU-based materials. The EPDM-based were not included in this comparison because their stress-strain analyses were conducted with a different instrument and instrumental parameters.

The EMA9-based materials possessed the greatest modulus, followed by EMA19, PEs and PET series of materials for the unfilled elastomers and each silica volume fraction. The Young’s modulus values of the two series of TPU materials displayed a smaller difference than the difference between the values of two series of EMA materials. This indicated that the reinforcement of the elastomer provided by crystalline polyethylene segments in both series of EMA materials resulted in a greater resistance to elastic deformation than the resistance provided by the H-bonding in the hard segments of the two series of TPU materials.
Table 50 Young’s modulus from stress-strain analysis of EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction %, v/v</th>
<th>EMA9 materials MPa</th>
<th>EMA19 materials MPa</th>
<th>PEt materials MPa</th>
<th>PEs materials MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.8</td>
<td>28.2</td>
<td>11.9</td>
<td>16.2</td>
</tr>
<tr>
<td>1</td>
<td>96.4</td>
<td>38.6</td>
<td>28.1</td>
<td>28.2</td>
</tr>
<tr>
<td>5</td>
<td>135.9</td>
<td>54.9</td>
<td>26.2</td>
<td>37.0</td>
</tr>
<tr>
<td>10</td>
<td>210.3</td>
<td>87.2</td>
<td>84.4</td>
<td>85.9</td>
</tr>
<tr>
<td>20</td>
<td>593.7</td>
<td>255.2</td>
<td>144.5</td>
<td>240.1</td>
</tr>
</tbody>
</table>

Static force thermomechanometry – Creep and recovery analysis

Creep analysis model parameters

Comparisons were made between the 4-element model parameters derived from modelling the first cycles of the creep analysis performed with 5000 mN of force for the EMA-based and TPU-based materials. The parameters derived from modelling creep data of the EPDM-alumina were not included as they were obtained under different analysis parameters.

Table 51 lists the elastic, $E_1$ modulus for the EMA-based and TPU-based materials obtained from the first cycle of creep analysis. The EMA9-based materials had the overall largest moduli values. All composites displayed the largest increase in modulus between the 10 and 20 %, v/v filled composites. These results indicated that instantaneous molecular uncoiling was most limited by the crystalline segments in EMA9, while the reduced amount of crystalline segments in EMA19 produced similar limitations as the H-bonding in the hard segments of PEs.

Table 51 $E_1$ modulus from modelling creep data with the 4-element model for all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction %, v/v</th>
<th>EMA9 materials MPa</th>
<th>EMA19 materials MPa</th>
<th>PEt materials MPa</th>
<th>PEs materials MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>56.8</td>
<td>47.3</td>
<td>61.4</td>
<td>37.8</td>
</tr>
<tr>
<td>1</td>
<td>59.4</td>
<td>63.2</td>
<td>61.0</td>
<td>55.6</td>
</tr>
<tr>
<td>5</td>
<td>114.2</td>
<td>38.8</td>
<td>78.0</td>
<td>61.2</td>
</tr>
<tr>
<td>10</td>
<td>221.7</td>
<td>45.2</td>
<td>87.5</td>
<td>69.5</td>
</tr>
<tr>
<td>20</td>
<td>494.4</td>
<td>155.7</td>
<td>111.0</td>
<td>168.0</td>
</tr>
</tbody>
</table>

Table 52 lists the $E_2$ and $\eta_2$ parameter values of the EMA-based and TPU-based materials obtained from modelling the first cycle of 5000 mN creep analysis. The EMA9-based materials possessed the largest $E_2$ and $\eta_2$ values for the unfilled elastomers and each silica volume fraction except at the 20 %, v/v silica volume fraction, where PEtSi20 had a larger $\eta_2$. 

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value and PEsSi20 has larger \( E_2 \) and \( \eta_2 \) value. The largest increase in parameter values occurred between the 10 and 20 % v/v filled composites for all series of materials. These results indicated the crystalline segments in EMA9 caused it to overall have the most inhibitions to time dependant molecular uncoiling that occurred over the longest times. The crystallinity in EMA19 and H-bonding in PEs resulted in similar relaxation times and limitations to time-dependant molecular uncoiling.

Table 52 \( E_2 \) and \( \eta_2 \) moduli parameters from modelling creep data with the 4-element model for all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO(_2) volume fraction % v/v</th>
<th>EMA9 materials</th>
<th>EMA19 materials</th>
<th>PEt materials</th>
<th>PEs materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_2 ) MPa</td>
<td>( \eta_2 ) MPa.s(^{-1})</td>
<td>( E_2 ) MPa</td>
<td>( \eta_2 ) MPa.s(^{-1})</td>
</tr>
<tr>
<td>0</td>
<td>59.8</td>
<td>13.0</td>
<td>27.8</td>
<td>10.2</td>
</tr>
<tr>
<td>1</td>
<td>72.8</td>
<td>24.3</td>
<td>19.9</td>
<td>69.6</td>
</tr>
<tr>
<td>5</td>
<td>121.0</td>
<td>40.3</td>
<td>25.9</td>
<td>11.2</td>
</tr>
<tr>
<td>10</td>
<td>116.0</td>
<td>36.6</td>
<td>38.0</td>
<td>12.7</td>
</tr>
<tr>
<td>20</td>
<td>280.0</td>
<td>74.7</td>
<td>155.0</td>
<td>49.2</td>
</tr>
</tbody>
</table>

Table 53 lists the \( \eta_3 \) parameter values of the EMA-based and TPU-based materials obtained from modelling the first cycle of 5000 mN creep analysis. The EMA9-based materials overall possessed the greatest parameters values for each concentration of silica. All materials were observed to have an increase in \( \eta_3 \) with increasing silica volume fraction. The largest increase in modulus occurred between the 10 and 20 % v/v filled composites. These results indicated that the crystallinity in EMA9 resulted in it having the longest time for permanent deformation, whilst the crystallinity in EMA19 and H-bonding in PEs resulted in similar times for permanent deformation.

Table 53 \( \eta_3 \) parameter from modelling creep data with the 4-element model for all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO(_2) volume fraction % v/v</th>
<th>EMA9 materials GPa.s(^{-1})</th>
<th>EMA19 materials GPa.s(^{-1})</th>
<th>PEt materials GPa.s(^{-1})</th>
<th>PEs materials GPa.s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.59</td>
<td>0.43</td>
<td>0.31</td>
<td>0.38</td>
</tr>
<tr>
<td>1</td>
<td>0.73</td>
<td>0.58</td>
<td>0.46</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>0.32</td>
<td>1.27</td>
<td>0.72</td>
</tr>
<tr>
<td>10</td>
<td>1.14</td>
<td>0.42</td>
<td>1.51</td>
<td>0.77</td>
</tr>
<tr>
<td>20</td>
<td>3.03</td>
<td>1.52</td>
<td>1.73</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Table 54 lists the $\tau$, retardation time values of the EMA-based and TPU-based materials obtained from modelling the first cycle of 5000 mN creep analysis. The retardation times of all materials were observed to be overall reduced with increasing silica volume fraction. The TPU-based materials possessed longer retardation times for the unfilled elastomers and 1 %.v/v silica filled composites. The EMA-based materials had longer times for all other silica concentrations. The TPU-based materials were observed to have greatest reduction in retardation time overall (between the 0 and 20 %.v/v filled composites).

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction %.v/v</th>
<th>EMA9 materials min</th>
<th>EMA19 materials min</th>
<th>PEt materials min</th>
<th>PEs materials min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.34</td>
<td>0.37</td>
<td>0.52</td>
<td>0.40</td>
</tr>
<tr>
<td>1</td>
<td>0.33</td>
<td>0.35</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>0.33</td>
<td>0.33</td>
<td>0.25</td>
<td>0.45</td>
</tr>
<tr>
<td>10</td>
<td>0.32</td>
<td>0.33</td>
<td>0.30</td>
<td>0.27</td>
</tr>
<tr>
<td>20</td>
<td>0.26</td>
<td>0.32</td>
<td>0.28</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Recovery analysis model parameters

Comparisons were made between the KWW model parameters derived from modelling the first cycles of the recovery analysis performed with 5000 mN of force of the EMA-based and TPU-based materials. The parameters derived from modelling recovery data of the EPDM-alumina were not included as they were obtained under different analysis parameters.

Table 55 lists the pre-exponential coefficient, A of the EMA-based and TPU-based materials obtained from modelling the first cycle of 5000 mN creep analysis. The A coefficient was observed to overall decrease with increasing silica volume fraction for all series of materials. The EMA19-based materials possessed the highest values, followed by the PEt-based, PEs-based and finally the EMA9-based materials; however there was little difference between their values. This implied that the resistance to viscoelastic recovery was similar between all materials.
Table 55 A pre-exponential factors from modelling creep data with the 4-element model for all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction %.v/v</th>
<th>EMA9 materials mm.mm$^{-1}$</th>
<th>EMA19 materials mm.mm$^{-1}$</th>
<th>PEt materials mm.mm$^{-1}$</th>
<th>PEs materials mm.mm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.099</td>
<td>0.141</td>
<td>0.134</td>
<td>0.091</td>
</tr>
<tr>
<td>1</td>
<td>0.064</td>
<td>0.081</td>
<td>0.092</td>
<td>0.121</td>
</tr>
<tr>
<td>5</td>
<td>0.033</td>
<td>0.160</td>
<td>0.056</td>
<td>0.094</td>
</tr>
<tr>
<td>10</td>
<td>0.024</td>
<td>0.093</td>
<td>0.036</td>
<td>0.053</td>
</tr>
<tr>
<td>20</td>
<td>0.013</td>
<td>0.033</td>
<td>0.024</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 56 lists the relaxation time, $\tau$, of the EMA-based and TPU-based materials obtained from modelling the first cycle of 5000 mN creep analysis. The relaxation times of all series of materials were observed to decrease with increasing silica volume fraction. The TPU-based materials were observed to have greatest reduction in relaxation time overall (between the 0 and 20 %.v/v filled composites).

Table 56 $\tau$ relaxation time from modelling creep data with the 4-element model for all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction %.v/v</th>
<th>EMA9 materials min</th>
<th>EMA19 materials min</th>
<th>PEt materials min</th>
<th>PEs materials min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.000</td>
<td>5.000</td>
<td>5.999</td>
<td>4.999</td>
</tr>
<tr>
<td>1</td>
<td>5.000</td>
<td>5.000</td>
<td>4.999</td>
<td>4.200</td>
</tr>
<tr>
<td>5</td>
<td>5.000</td>
<td>5.000</td>
<td>3.199</td>
<td>3.099</td>
</tr>
<tr>
<td>10</td>
<td>5.000</td>
<td>5.000</td>
<td>1.599</td>
<td>2.299</td>
</tr>
<tr>
<td>20</td>
<td>4.999</td>
<td>5.000</td>
<td>0.999</td>
<td>1.299</td>
</tr>
</tbody>
</table>

Table 57 lists the distribution factor, $\beta$, of the EMA-based and TPU-based materials obtained from the first cycle of 5000 mN creep analysis. The $\beta$ values were observed to overall decrease with increasing silica volume fraction for each series of materials. The distribution factors were observed to be of a similar magnitude between the elastomers and each silica-filled composite indicating that all materials possessed similar constraints to the release of relaxation modes.
Chapter 7 Comparison of analysis results

Table 57 β shape parameter from modelling creep data with the 4-element model for EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction</th>
<th>EMA9 materials</th>
<th>EMA19 materials</th>
<th>PEt materials</th>
<th>PEs materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.020</td>
<td>0.035</td>
<td>0.045</td>
<td>0.035</td>
</tr>
<tr>
<td>1</td>
<td>0.028</td>
<td>0.053</td>
<td>0.017</td>
<td>0.019</td>
</tr>
<tr>
<td>5</td>
<td>0.029</td>
<td>0.024</td>
<td>0.050</td>
<td>0.017</td>
</tr>
<tr>
<td>10</td>
<td>0.012</td>
<td>0.030</td>
<td>0.005</td>
<td>0.012</td>
</tr>
<tr>
<td>20</td>
<td>0.017</td>
<td>0.033</td>
<td>0.005</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Modulated force thermomechanometry

Single frequency analysis

Comparisons were made between the storage modulus of all (EDPM-based, EMA-based, TPU-based) materials as they were all analysed under the same instrumental parameters.

Table 58 lists the storage moduli obtained at 20 °C from 1 Hz mf-TM for each series of materials. The EPDM-based materials possessed the lowest storage modulus values with the xE modulus being ten times smaller than of any other material. The EMA9-based materials possessed the greatest modulus values for the unfilled elastomers and each concentration of silica. The EMA19-based material modulus values were greater than those of the TPU-based materials for the unfilled elastomers and 1 and 5 % v/v silica volume fractions silica concentrations. These results indicated that the crystallinity in EMA9 resulted in the greatest resistance to elastic deformation while the H-bonding in the TPU materials and crystallinity in the EMA19 material possessed similar resistances.

Table 58 E’ values obtained from mf-TM analysis of EPDM-based, EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction</th>
<th>EMA9 series GPa</th>
<th>EMA19 series GPa</th>
<th>PEt series GPa</th>
<th>PEs series GPa</th>
<th>xE GPa</th>
<th>xE-SDS GPa</th>
<th>xE-SDS-PS GPa</th>
<th>xE-UT GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.311</td>
<td>0.114</td>
<td>0.110</td>
<td>0.051</td>
<td>0.004</td>
<td>0.019</td>
<td>0.011</td>
<td>0.027</td>
</tr>
<tr>
<td>1</td>
<td>0.367</td>
<td>0.123</td>
<td>0.140</td>
<td>0.079</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.599</td>
<td>0.251</td>
<td>0.185</td>
<td>0.233</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.778</td>
<td>0.341</td>
<td>0.418</td>
<td>0.499</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.121</td>
<td>1.044</td>
<td>1.129</td>
<td>1.321</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HN relaxation equation parameters

Comparisons were made between the five parameters of the HN relaxation equation derived from the modelling of mastercurve data of the EMA-based and TPU-based materials. The HN
parameters derived for the EDPM-based materials were not included as they were derived from modelling single frequency data.

Table 59 lists the $E_\infty$ and $E_0$ modulus HN parameters obtained from modelling EMA-based and TPU-based material mastercurve data. The $E_\infty$ parameter values were overall greatest for the EMA-based materials than TPU-based counterparts with the EMA19 series of materials possessing the greatest values. The $E_0$ parameter values were overall greater for the EMA-based materials with the EMA9-series of materials possessing the greatest values. The $E_\infty$ parameter values of the TPU-based materials were observed to plateau for the 10 and 20 %v/v silica filled composites whereas the values of the TPU-based materials increase between these silica volume fractions.

<table>
<thead>
<tr>
<th>SiO$_2$ volume fraction</th>
<th>EMA9 materials</th>
<th>EMA19 materials</th>
<th>PEt materials</th>
<th>PE$_s$ materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_\infty$ GPa</td>
<td>$E_0$ GPa</td>
<td>$E_\infty$ GPa</td>
<td>$E_0$ GPa</td>
</tr>
<tr>
<td>0</td>
<td>5.08</td>
<td>0.03</td>
<td>12.20</td>
<td>0.04</td>
</tr>
<tr>
<td>1</td>
<td>7.88</td>
<td>0.06</td>
<td>11.00</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>8.95</td>
<td>0.08</td>
<td>11.40</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>10.30</td>
<td>0.17</td>
<td>11.90</td>
<td>0.15</td>
</tr>
<tr>
<td>20</td>
<td>10.60</td>
<td>0.59</td>
<td>15.50</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 60 lists the $\alpha$ and $\beta$, shape HN parameters obtained from modelling EMA-based and TPU-based material mastercurve data. The $\alpha$ parameter values for all series of materials were observed to decrease with increasing silica volume fraction and were overall largest for the TPU-based materials. The $\beta$ parameter values were observed to overall decrease with increasing silica volume fraction for all series of materials except for the PE$_s$ series of materials which had an increase with the addition of 20 %v/v of silica.
Table 60 α and β HN parameters obtained from mf-TM analysis of all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO₂ volume fraction %, v/v</th>
<th>EMA9 materials</th>
<th>EMA19 materials</th>
<th>PEₜ materials</th>
<th>PEₘ materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>β</td>
<td>α</td>
<td>β</td>
<td>α</td>
</tr>
<tr>
<td>0</td>
<td>0.16</td>
<td>0.42</td>
<td>0.18</td>
<td>0.34</td>
</tr>
<tr>
<td>1</td>
<td>0.15</td>
<td>0.38</td>
<td>0.16</td>
<td>0.36</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>0.39</td>
<td>0.17</td>
<td>0.48</td>
</tr>
<tr>
<td>10</td>
<td>0.14</td>
<td>0.36</td>
<td>0.15</td>
<td>0.52</td>
</tr>
<tr>
<td>20</td>
<td>0.13</td>
<td>0.35</td>
<td>0.11</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table 61 lists the τ relaxation time HN parameters obtained from modelling EMA-based and TPU-based material mastercurve data. The EMA9-based materials relaxation times were the overall longest, followed by the EMA19-based, PEₘ-based then PEₜ-based materials. The largest increase in relaxation time occurred with the increase in silica volume fraction from 10 to 20 %, v/v. The greatest difference in relaxation time between the unfilled elastomer and 20 %, v/v silica filled occurred in the EMA series of materials.

Table 61 τ HN parameter obtained from mf-TM analysis of all EMA-based and TPU-based materials

<table>
<thead>
<tr>
<th>SiO₂ volume fraction %, v/v</th>
<th>EMA9 materials</th>
<th>EMA19 materials</th>
<th>PEₜ materials</th>
<th>PEₘ materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ s × 10⁻⁹</td>
<td>τ s × 10⁻⁹</td>
<td>τ s × 10⁻⁹</td>
<td>τ s × 10⁻⁹</td>
<td>τ s × 10⁻⁹</td>
</tr>
<tr>
<td>0</td>
<td>9.000</td>
<td>0.050</td>
<td>0.0210</td>
<td>0.0300</td>
</tr>
<tr>
<td>1</td>
<td>90.00</td>
<td>0.050</td>
<td>0.0911</td>
<td>0.0683</td>
</tr>
<tr>
<td>5</td>
<td>104.0</td>
<td>0.100</td>
<td>0.1311</td>
<td>0.1273</td>
</tr>
<tr>
<td>10</td>
<td>2490.0</td>
<td>1.000</td>
<td>0.2867</td>
<td>0.1965</td>
</tr>
<tr>
<td>20</td>
<td>14200.0</td>
<td>53.00</td>
<td>0.8867</td>
<td>1.4110</td>
</tr>
</tbody>
</table>

Conclusion

Data obtained under similar analysis conditions for the three material groups (EPDM-based, EMA-based and TPU-based materials) was compared and evaluated. The EMA9-based materials possessed the greatest Young’s modulus, followed by EMA19, PEₘ and PEₜ series of materials for the unfilled elastomers and each silica volume fraction. This indicated that the reinforcement of the elastomer provided by crystalline polyethylene segments in both series
of EMA materials resulted in a greater resistance to elastic deformation than the resistance provided by the H-bonding in the hard segments of the two series of TPU materials.

The EMA9-based materials had the overall largest $E_1$ moduli values obtained from modelling creep data with the 4-element model. These results indicated that instantaneous molecular uncoiling was most limited by the crystalline segments in EMA9, while the reduced amount of crystalline segments in EMA19 produced similar limitations as the H-bonding in the hard segments of PEs. The EMA9-based materials possessed the overall largest $E_2$ and $\eta_2$ values for the unfilled elastomers and each silica volume fraction. The crystalline segments in EMA9 caused it to have the most inhibitions to time dependant molecular uncoiling that occurred over the longest times. The crystallinity in EMA19 and H-bonding in PEs resulted in similar relaxation times and limitations to time-dependant molecular uncoiling. The EMA9-based materials overall possessed the greatest $\eta_3$ parameter values for the elastomers and each concentration of silica. All materials were observed to have an increase in $\eta_3$ with increasing silica volume fraction. The crystallinity in EMA9 resulted in it having the longest time for permanent deformation, while the crystallinity in EMA19 and H-bonding in PEs resulted in similar times for permanent deformation. The retardation times of all materials were observed to be overall reduced with increasing silica volume fraction. The TPU-based materials possessed longer retardation times for the unfilled elastomers and 1 %,v/v silica filled composites; for all other silica concentrations, the EMA-based materials had longer times.

Comparisons were made between the KWW model parameters derived from modelling the first cycles of the recovery analysis performed with 5000 mN of force of the EMA-based and TPU-based materials. The A coefficient was observed to overall decrease with increasing silica volume fraction for all series of materials. The EMA19-based materials possessed the highest values, followed by the PEt-based, PEs-based and finally the EMA9-based materials however there was little difference between the values implying that resistance to viscoelastic recovery was similar between the materials. The relaxation times of all series of materials were observed to decrease with increasing silica volume fraction. The TPU-based materials were observed to have greatest reduction in relaxation time overall (between the 0 and 20 %,v/v filled composites). The $\beta$ values were observed to overall decrease with increasing silica volume fraction for each series of materials. The distribution factors were observed to be of a similar magnitude between the elastomers and each silica filled composite indicating all materials possessed similar constraints to the release of relaxation modes.

The EPDM-based materials possessed the lowest storage modulus values with the $x_E$ modulus being ten times smaller than of any other material. The EMA9-based materials
possessed the greatest modulus values for the unfilled elastomers and each concentration of 
silica. The EMA19-based material modulus values were greater than those of the TPU-based 
materials for the unfilled elastomers and 1 and 5 % v/v silica volume fractions silica 
concentrations. These results indicated that the crystallinity in EMA9 resulted in the greatest 
resistance to elastic deformation while the H-bonding in the TPU materials and crystallinity in 
the EMA19 material possessed similar resistances.

Comparisons were made between the five parameters of the HN relaxation equation derived 
from the modelling of mastercurve data of the EMA-based and TPU-based materials. The $E_\infty$ 
parameter values were overall greater for the EMA-based materials than TPU-based 
counterparts with the EMA19 series of materials possessing the greatest values. The $E_0$ 
parameter values were overall greatest for the EMA-based materials with the EMA9-series of 
materials possessing the greatest values. The $\alpha$ parameter values for all series of materials 
were observed to decrease with increasing silica volume fraction. The $\alpha$ parameter values 
were overall largest for the TPU-based materials. The $\beta$ parameter values were observed to 
overall decrease with increasing silica volume fraction for all series of materials except for the 
PEs series of materials, which had an increase with the addition of 20 % v/v of silica. The 
EMA9-based materials relaxation times were the overall longest, followed by the EMA19-
based, PEs-based then PEt-based materials. The greatest difference in relaxation time between 
the unfilled elastomer and 20 % v/v silica filled occurred in the EMA series of materials.
Conclusions

The aim of this research was to modify matrix polymer’s relaxation processes by the inclusion of filler and to characterise the interfacial interaction in between matrix polymer and filler. Greater compatibility between filler and elastomer resulted in better dispersion of filler in an elastomeric matrix, as seen in ESEM micrographs of the EPDM composites. All elastomers were observed to have thermal reinforcement provided by the presence of fillers. Greater compatibility between elastomer and filler resulted in increased thermal stability, as seen in xE-SDS and xE-SDS-PS. Thermal reinforcement was observed to increase with increasing filler volume fraction with the $T_{0.5}$ of EMA9 and EMA19 series increased by approximately 20 °C and the $T_{0.5}$ increased by approximately 70 °C with the addition of 20% v/v of filler. The increased crystallinity in EMA9 provided it with slightly greater thermal reinforcement compared to EMA19 while the polyester in the PEs materials provided it with the greatest thermal reinforcement at higher filler volume fractions. Filler was observed to preferentially to bond to certain regions as evidenced by the increased thermal reinforcement in the hard phase of the TPUs.

The results from stress-strain analysis indicated that greater compatibility between filler and elastomer matrix showed greater reinforcement, however all filler provided some reinforcement. The Young’s moduli and strength of all elastomer based systems were observed to increase with increasing filler volume fraction. The toughness increased with increase filler-elastomer compatibility but decreased with increasing filler volume fraction. Increased crystallinity and decreased MA weight fraction in EMA9-based materials resulted in increased strength but decreased toughness compared EMA19-based materials. The presence of polyester resulted in stronger materials while polyether resulted in tougher materials. Crystallinity at the weight fractions in both the EMA9 and EMA19-based materials resulted in stronger materials compared to the H-bonding in the TPU-based materials and chemical crosslinks in the EPDM-based materials.

The creep and recovery analyses showed that greater compatibility between filler and elastomer, and increased filler volume fraction resulted in more resistance to elastic and viscoelastic deformation, and viscous flow. However the presence of any filler inhibited
deformation to some degree. Increased crystallinity and reduced MA weight fraction in EMA9-based materials resulted in greater resistance to all forms of deformation compared with EMA19-based materials. The polyester in PEs-based materials resulted in greater resistance to elastic and viscoelastic deformation, and viscous flow compared with the polyether in the PEt-based materials.

Modelling of creep analysis data revealed that the presence of any filler resulted in increased resistance to instantaneous and time dependant uncoiling and extension of molecules but greater compatibility results in greater resistance, as seen in the modelling of EPDM-based materials creep data. Increasing filler volume fraction resulted in greater resistance to instantaneous and time dependant uncoiling of molecules, and irreversible flow. The concentration of crystallinity in EMA9 materials provided the most resistance to elastic deformation compared with the crystallinity in the EMA19 materials, and the H-bonding in the PEt and PEs materials. The H-bonding in the PEs and PEt-based materials provided the most resistance to time dependant uncoiling and extension of molecules which took place at increasingly longer times, compared with the resistance provided by the crystallinity in the EMA-based materials. The crystallinity in the EMA9 materials provided the most resistance to irreversible deformation compared with the other series of materials. Calculated retardation times showed negligible difference with differing elastomer and filler content. Materials analysed with a reduced force had greater resistance to all modes of deformation as indicated by their parameter values being greater than those obtained at a higher force.

Modelling of recovery analysis data revealed greater compatibility between filler and elastomer resulted in less resistance to recovery and less constraints to the operation of relaxation modes. Resistance to recovery overall decreased with increasing filler volume fraction. The EMA19 based materials possessed the greatest resistance to viscoelastic recovery due to the plasticising effect of the increased methyl acrylate weight fraction. Increasing filler volume fraction resulted in more constraints to the operation of relaxation modes. The crystallinity and methyl acrylate in the EMA-based materials resulted in the least constraints to the operation of relaxation modes compared with the H-bonding in the TPU-based materials with the EMA19 materials having the least constraints. Relaxation times decreased with increasing filler volume fraction. The crystallinity in the EMA-based materials resulted in longer times than the H-bonding in the TPU-based materials. Parameter values obtained from analyses conducted with reduced analysis force indicated that a lower analysis force results in less resistance to viscoelastic recovery, longer relaxation times and fewer constraints to the operation of relaxation modes.
Modulated force thermomechanometry characterised the elasticity and damping properties of materials. The storage modulus was observed to increase with increasing filler volume fraction; however increased compatibility between filler and elastomer resulted in reduced $E'$ values. The temperature of failure increased with compatibility and increasing filler volume fraction. It appeared that increased filler volume fraction was more efficient at increasing temperature of failure than compatibility as seen from the mf-TM data of xE-UT and xE-SDS-PS. Increased crystallinity and reduced MA weight fraction in EMA9-based materials resulted in greater resistance to elastic deformation, while the polyester in PEs-based materials resulted in greater resistance to elastic deformation in comparisons with their respective material counterparts. The crystallinity in EMA9-based materials resulted in the greatest modulus values while the H-bonding in PEs and PET-based materials resulted in slightly greater modulus values than the values provided resultant from the crystallinity in EMA19-based materials. The loss modulus was observed to increase with increasing filler volume fraction; however increased compatibility between filler and elastomer resulted in lower loss of energy. The EMA9 and PET-based materials possessed greater energy dispersion at pre-$T_g$ temperatures, while EMA9 and PEs-based materials possessed greater energy dispersion at post-$T_g$ temperatures in comparisons between the respective systems. The $\tan \delta$ values decreased with the addition of any filler and increasing filler volume fraction; however increased compatibility between filler and elastomer reduced the $\tan \delta$ by a lesser amount. The EMA19-based materials possessed the greatest damping compared with EMA9-based materials due to their increased methyl acrylate weight fraction and reduced crystallinity. The polyether in PET-based materials possessed the greatest damping compared with materials with a polyester component.

Mastercurves were constructed from the isothermal multi-frequency mf-TM data for the EMA and TPU series of materials. Two methods of obtaining frequency-modulus data were trialled; sinusoidal frequency sweeps and synthetic frequency sweeps. Mastercurves constructed from synthetic frequency data were observed to have poor, if any overlap between the data obtained with the desired temperature increment and the inherent limitation that only 5 frequencies, separated by a factor of 2 could be selected for each analysis. Therefore the sinusoidal method was chosen for obtaining data. Two methods for constructing mastercurves were trialled; manual shift method and the HN relaxation equation method. The HN mastercurves possessed less overlap in data compared with the manual shift mastercurves at the zero and infinite frequency extremes. The advantages of the HN method were that there was mathematical basis behind the derivation of shift factors and this method accounts for vertical shifts by simulating data. The disadvantages of the HN method were that the equation may not
accurately account for modulus data at the zero and infinite frequency extremes and the reference temperature must be equivalent to the $T_g$.

The mastercurves possessed frequency ranges of approximately $10^9 – 10^{17}$ Hz, increased from the original analysis frequency range of $10^2 – 10^5$ Hz. The storage modulus mastercurve data values increased with increasing filler volume fraction for all materials. The greatest increase in modulus with increasing frequency occurred in the transition frequencies (frequencies equal to the original analysis frequencies). The increase in modulus with increasing frequency decreased with increasing filler volume fraction. The storage modulus values plateaued at the highest frequencies for the 10 and 20 %.v/v filled nanocomposites. This indicated that resistance to elasticity at these frequencies plateaued at 10 %.v/v filler.

The increased crystallinity in the EMA9-based materials provided slight enhanced reinforcement in the plateau frequency region and greater reinforcement in the terminal frequency region. The storage modulus mastercurve values of the PEt-based and PEs-based materials were approximately equal at the highest transposed frequencies; however materials with polyester had greater resistance to elasticity in the lowest transposed frequency regions.

The loss modulus mastercurves of both EMA and TPU-based materials possessed a peak in the loss modulus data corresponding to $T_g$. Each of the filled composites plateaued at approximately the same modulus values at the highest transposed frequencies. The modulus data obtained at the highest analysis frequencies and at low temperatures exhibited constructive interference with the effects most pronounced in the highest filled composites.

Three shift factor models (WLF, VFTH and arctan based model) were employed to model the shift factor values obtained from the creation of TPU-based materials mastercurves. The WLF model was observed to most accurately model shift factor data in the region just after $T_g$. Both material parameters either increased or decreased in value together in relation to other material parameters. The inflexibility of the VFTH model inhibited it from accurately modelling the varying difference between shift factor values at pre and post-$T_g$ temperatures. There was no apparent correlation between increasing filler volume fraction and the change in the VFTH material parameter values. The arctan model was able to best model with either a great or small change in shift factor values at temperatures encompassing $T_g$. The advantage
of this model was that it was able to model the inflection-like shape that the shift factors that these mastercurves possess.

Mastercurve data of EMA-based materials was modelled with four relaxation equations; the Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami equations. The accuracy of these relaxation equations modelling mastercurve was determined with the Wicket error function. The HN equation modelled the mastercurve data most accurately, followed by the CC, CD and finally D equations. The greater accuracy of the HN equation was attributed to it possessing two shape parameters allowing it to account for changes in the symmetry and skewness of the mastercurve data. The relaxation equations most accurately modelled the EMA9-based materials. The HN relaxation equation was employed to construct mastercurves for TPU-based materials resulting in a series of the HN material parameters for each material. These parameters did not result in the best modelling of the mastercurves, so mastercurve data was remodelled with the HN relaxation equation. The parameters from re-modelling were observed to more accurately model mastercurves than the parameters used to construct the mastercurves as evidenced by Wicket error values.

It was observed that with increasing filler volume fraction, the zero and infinite moduli increased for both the EMA and TPU series of materials. The plateau (infinite) modulus values of the 10 and 20 \%\(\text{v/v}\) filler nanocomposites possessed similar \(E_\infty\) values, indicating that modulus values plateaued at 10 \%\(\text{v/v}\) filler at the highest transposed frequencies. The infinite modulus was observed to be slightly larger for the EMA19-based materials while the zero modulus was largest for the EMA9-based materials since the reinforcing effect of increased crystallinity in EMA9 was more observable at the lowest transposed frequencies. The plateau and zero moduli were observed to be overall largest for the PEs-based materials compared with the values from the PEt series of materials. The EMA19-based materials possessed the overall greatest \(E_\infty\) values compared with the EMA9, PEt and PEs materials, while the crystallinity in the EMA9-based materials resulted in them having the greatest \(E_0\) values. The relaxation time parameter values were observed to increase with increasing filler volume fraction for all series of materials. The EMA9-based materials were observed to have the longest relaxation times followed by the EMA19, PEs and PEt series of materials indicating that crystallinity caused the longest times compared with H-bonding. The \(\alpha\) and \(\beta\) shape parameters were observed to overall decrease with increasing filler content for all materials, except for the \(\beta\) values of the EMA19 series of materials which accounted for highest filled nanocomposites loss modulus values being smaller than those of the lowest
filled nanocomposites. The $\alpha$ values were similar between all series of materials while the $\beta$ values were largest for the TPU-based materials.

Mastercurves were not constructed for the EPDM-based materials as these materials could not be analysed at sufficiently high frequencies without fracturing. Therefore another method was employed to model single frequency mf-TM data utilising the HN relaxation equation. The presence of filler was observed to increase the $E_0$ modulus values. The addition of compatibilized filler resulted in an increase in $E_\infty$ modulus values while uncompatabilzed filler caused a reduction in $E_\infty$. The $\alpha$ shape parameter was observed to decrease with the addition of all fillers with the untreated filler resulting in the greatest reduction. The $\beta$ shape parameter was observed to slightly decrease with the addition compatibilized fillers but increase with the addition of the uncompatabilzed filler. The calculated relaxation times were observed to decrease with decreasing compatibility between filler and elastomer.

Super-mastercurves of the EMA-based and TPU-based materials were formed with shift factors termed $a_c$, with the $c$ representing concentration. These shift factors represented the correlation of the effect of silica on modulus with respect to frequency. The 5 %,v/v filled mastercurves were used as the reference curves for all series of materials. The super-mastercurve data possessed frequency ranges of $10^{-11}$ – $10^{20}$ Hz. Modulus values were observed to be precise at the highest transposed frequencies due to plateauing; however feathering was observed at the lowest transposed frequencies in both storage and loss modulus super-mastercurves.

**Further research**

The crosslinking agent used in the preparation of EPDM composites was dicumyl peroxide, other peroxides and various concentrations could be tested to determine the most efficient crosslinking agent. The filler added to EPDM was alumina with differing surface chemistry. Different polymers could be used when employing admicellar polymerisation with alumina, and different inorganic particulates such as zinc and magnesium oxides or carbonates could be employed as filler.

The silica added to the EMA and TPU elastomers possessed polar surface chemistry. A possible research avenue is the addition of silicas with non-polar chemistry to determine if there will be any contribution to material properties. This would be particularly relevant for use with the EMA since non-polar silicas would bond to polyethylene segments (as opposed to the polar silicas which bonded to the methyl acrylate units). Varying non-polar surface chemistries could be used to determine which is best for interfacial bonding. The non-polar
silicas could be added to the TPUs to determine whether they would preferentially bond to different molecular regions of the TPU and if they have a different effect on material properties. A combination of polar and non-polar silicas could be added to the EMAs and TPUs to determine what effect the simultaneous reinforcement of the different molecular regions in the elastomer would have on material properties.

Modulated force thermomechanical analysis results in an output of the storage modulus, resistance to elastic deformation, and the loss modulus resistance, to reversible time-dependent deformation. If a material being analysed was extended so it is near the onset of yielding (determined from stress-stain analysis) but still in its linear viscoelastic region, then analysed via mf-TM, the resultant storage and loss modulus values may be entirely representative of the resistance to viscoelastic deformation.

The 4-element model was used in this research to model the creep analysis. A potential avenue for the development of a creep model is the Dirac delta function. The Dirac delta function (or unit impulse) is a useful aid in modelling impulses in physical systems such as electrical circuits or mechanically vibrating systems[225]. A general representation of the unit impulse is seen in Equation 70 and Figure 156.

 Equation 70

$$
\delta(t) = \begin{cases} 
\frac{1}{\varepsilon} & \text{if } 0 < t < \varepsilon \\
0, & \text{otherwise}
\end{cases}
$$

Figure 156 Graphical representation of $\delta(t)$
The values of the data in Figure 156 appear similar to that of a force schematic for creep analysis. Since the creep analysis is a sudden impulse (application of constant force) applied to a system (the analysed material) this could provide the basis for using the Dirac delta function in modelling creep data. This author could only find one previous mention of the Dirac delta function in relation to the modelling of creep in the research conducted by Martin Goldstein into *A model for cold flow in amorphous polymer* in 1966[226].

Mastercurves created via the HN method can usually account for vertical (modulus range) discontinuities in data by modelling modulus values at temperatures (corresponding to frequencies via TTS). Another approach that may be taken is to insert vertical shift factors (similar to the $a_v$ shift factors found in the manual shift mastercurve creation method) into the modulus values of the HN mastercurve data. The value of these vertical shifts would be based upon the $E_\infty$ and $E_0$ values in HN parameters obtained from modelling the isothermal data sets.
References

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References


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