FUNCTIONALISED POLYMER NANOCOMPOSITES AND BLENDS

by

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A thesis presented in fulfilment for the Degree of Doctor of Philosophy

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Melbourne, Australia

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STATEMENT OF AUTHENTICITY

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.

The core cross-linked star polymers referred to in Chapters 4 and 5 were synthesised by Tor Kit Goh and Anton Blencowe. The magnetite-functionalised carbon nanotubes utilised in Chapter 9 were prepared by Ing Kong.

The work described in this research project was carried out in the School of Applied Sciences, RMIT University since the official date of commencement of the program.

Signed: ................................................................. Date: 15/09/2011

Steven Spoljaric
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“The world is chiral and clinal: enjoy the symmetry wherever you find it”.

Vladimir Prelog (1906-1998)
PUBLICATIONS

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Refereed conference publications


Conference presentations


Other conference publications

Spoljaric, S., Köpplmayr, T., Genovese, A., Goh, T. K., Blencowe, A., Qiao, G. G. and Shanks, R. A. Structural relaxation of core cross-linked star polymer blends by volumetric and enthalpic analyses, poster presentation at the RMIT University, College of Science, Engineering and
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<tr>
<td>α</td>
<td>Coefficient of linear thermal expansion</td>
<td>FITC Fluorescein isothiocyanate</td>
</tr>
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<td>α&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Temperature shift factor (WLF equation)</td>
<td>FTIR Fourier transform infrared (spectroscopy)</td>
</tr>
<tr>
<td>β</td>
<td>Non-exponential factor</td>
<td>G Gauss</td>
</tr>
<tr>
<td>Δα</td>
<td>Change of volume expansion coefficient</td>
<td>H Enthalpy</td>
</tr>
<tr>
<td>Δh*/R</td>
<td>Relative apparent activation energy</td>
<td>HCl Hydrochloric acid</td>
</tr>
<tr>
<td>ΔT</td>
<td>Temperature change</td>
<td>KWW Kohlrausch-Williams-Watts (function)</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometre</td>
<td>m&lt;sub&gt;f&lt;/sub&gt;-TM Modulated force – thermomechanometry</td>
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<td>η</td>
<td>Viscosity</td>
<td>m&lt;sub&gt;T&lt;/sub&gt;-DSC Modulated temperature – differential scanning calorimetry</td>
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<td>Relaxation/retardation time</td>
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<td>τ&lt;sub&gt;V&lt;/sub&gt;</td>
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<td>MWNT Multi-wall nanotube</td>
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<td>%</td>
<td>Percentage</td>
<td>M Segmental mobility</td>
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<td>%·vol</td>
<td>Volume percent</td>
<td>nm Nanometre</td>
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<td>%·wt</td>
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<td>ATRP</td>
<td>Atom transfer radical polymerisation</td>
<td>PAA Polyallylamine</td>
</tr>
<tr>
<td>B</td>
<td>AGS model constant</td>
<td>PAAc Poly(acrylic acid)</td>
</tr>
<tr>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Calcium carbonate</td>
<td>PAMAM Polyaminodiamine</td>
</tr>
<tr>
<td>CCS</td>
<td>Core cross-linked star (polymer)</td>
<td>PAN Polyacrylonitride</td>
</tr>
<tr>
<td>CI</td>
<td>Colour index</td>
<td>PBA Poly(butyl acrylate)</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
<td>PC Polycarbonate</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
<td>PDMA Poly(dimethylacrylamide)</td>
</tr>
<tr>
<td>D&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Fractal dimension</td>
<td>PDMAEMA Poly(dimethylaminoethyl methacrylate)</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
<td>PEG Poly(ethylene glycol)</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
<td>PEGDMA Poly(ethylene glycol dimethacrylate)</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
<td>PEI Polyethyleneimine</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
<td>PEO Poly(ethylene oxide)</td>
</tr>
<tr>
<td>E’</td>
<td>Storage modulus</td>
<td>PET Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>E”</td>
<td>Loss modulus</td>
<td>PHEA Poly(hydroethyl acrylate)</td>
</tr>
<tr>
<td>f</td>
<td>Fractional free volume</td>
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<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PMP</td>
<td>Poly(4-methyl-1-pentene)</td>
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<td>PNIPAM</td>
<td>Poly(N-isopropylacrylamide)</td>
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<tr>
<td>POSS</td>
<td>Polyhedral oligomeric silsesquioxanes</td>
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<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<td>PVA</td>
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<td>PVP</td>
<td>Poly(vinyl pyrrolidone)</td>
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<tr>
<td>q</td>
<td>Rate of temperature change</td>
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<tr>
<td>Rg</td>
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<td>ROX</td>
<td>6-carboxy-X-rhodamine N-succinimidyl ester</td>
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<tr>
<td>S</td>
<td>Entropy</td>
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<td>Sc</td>
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</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
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<td>SBR</td>
<td>Styrene-butadiene rubber</td>
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<td>SBS</td>
<td>Poly(styrene-b-butadiene-b-styrene)</td>
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<td>SiCl4</td>
<td>Silicon tetrachloride</td>
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<td>SiO2</td>
<td>Silicon dioxide (silica)</td>
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<td>Single-wall nanotube</td>
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<tr>
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<tr>
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<tr>
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<td>Annealing temperature</td>
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</tr>
<tr>
<td>Td</td>
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<td>T'f</td>
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<tr>
<td>Tg</td>
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<tr>
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<td>Melting temperature</td>
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<tr>
<td>Tm&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Temperature at which maximum rate of decomposition occurs</td>
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<td>Thermogravimetric analysis</td>
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<td>TNM</td>
<td>Tool-Narayanaswamy-Moynihan (model)</td>
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<td>Ultraviolet</td>
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<tr>
<td>V</td>
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</tr>
<tr>
<td>V0</td>
<td>Occupied volume</td>
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<tr>
<td>Vf</td>
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<td>WLF</td>
<td>Williams-Landel-Ferry (equation)</td>
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<tr>
<td>x</td>
<td>Non-linearity constant</td>
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SUMMARY

Functionalised polymer composites and blends were prepared with the aim of enhancing the mechanical and thermal properties of the polymer matrix, while maintaining the characteristic property (functionality) of the introduced functional group. This involved the use of nanoparticles with novel architecture (core cross-linked star polymers, POSS-functionalised dendrimers, telechelic POSS) to provide attributes for improving mechanical and thermal stability, in addition to physical aging stability and phase selectivity. Furthermore, nanoparticles were functionalised to provide attributes such as colour (dye-functionalised POSS) and magnetism (magnetite-functionalised carbon nanotubes). These nanoparticles were investigated in amorphous polymer matrices, with structure-property relationships explored.

Core cross-linked star (CCS) polymers consisting of a poly(ethylene glycol dimethacrylate) ‘core’ and polystyrene (PS) or poly(methyl methacrylate) (PMMA) ‘arms’ were blended with linear PS or PMMA. These novel blends were characterised, with an emphasis on glass transition and relaxation properties. The glass transition temperature ($T_g$) of linear PS and PMMA increased with CCS polymer content, while enthalpy ($\Delta H$) relaxation decreased. This was attributed to reduced volume within the blends and CCS polymer ‘arms’ imparting restrictions on segmental motions of polymer chains. Isothermal sub-$T_g$ annealing (physical ageing) increased $T_g$ and $\Delta H$, reaching maximum values at annealing times ($t_a$) of 100 h. This was due to reduced free volume ($V_F$) and mobility. Blends maintained higher $T_g$ and lower $\Delta H$ values than pure, linear polymers for identical $t_a$, indicating that CCS polymers continue to restrict segmental motion during structural relaxation. The coefficient of thermal expansion ($\alpha$) and shrinkage decreased with the addition of CCS polymers, due to restrictions on flow and motions that govern expansion behaviour. Volume relaxation was successfully observed in real time, creating a novel application for modulated temperature – thermomechanometry.

Blending with CCS polymers had minimal influence on the thermal stability of PS, while PMMA exhibited enhanced thermal properties due to CCS polymer ‘arm’ structure. The
radius of gyration ($R_g$) and fractal dimension ($D_f$) decreased with increasing CCS polymer concentration, indicative of constrained and contorted polymer chains. Blends displayed superior tensile modulus and strength values, while becoming less ductile. Restricted molecular motions within the blends resulted in reduced creep deformation and increased permanent strain. Storage ($E'$) and loss ($E''$) moduli increased with CCS polymer content, while dampening ability decreased. Time-temperature superposition revealed an increase in dynamic fragility and apparent activation energy with the addition of CCS polymer, while fractional free volume and the free volume expansion coefficient decreased. The results indicate that CCS polymers within a like-linear polymer blend behave in a similar manner to physical crosslinks.

Building from the linear-CCS polymer blend data, Boltorn hyperbranched aliphatic polyesters were functionalised with polyhedral oligomeric silsesquioxane (POSS) and incorporated into linear thermoplastic polyurethane (TPU). Increasing POSS-functionalised Boltorn concentration led to an increase in agglomerate size and frequency, due to interactions between POSS molecules. The Boltorn dendrimer primarily influenced the morphology of the blends. Blends displayed enhanced thermal stability, due to restrictions on chain vibration imparted by the Boltorn and thermal shielding by POSS. Increasing the blend concentration resulted in higher tensile modulus and strength, while ductility decreased due to increased rigidity. Creep deformation decreased and permanent deformation increased with increased Boltorn content, while $E'$, $E''$ and $T_g$ values all increased. TPU blended with higher generation Boltorn displayed superior thermal and mechanical properties than those containing lower generation dendrimer, due to enhanced interaction and restrictions on TPU chain segments. Both Boltorn and POSS contributed to material properties.

POSS molecules were functionalised with adipoyl and sebacoyl chloride, to prepare novel telechelic (dumbbell-shaped) fillers that were subsequently incorporated into poly(styrene-$b$-butadiene-$b$-styrene) (SBS). Inter-particle interactions resulted in increased agglomerate size with filler concentration. Composite morphology was dependent on the organic substituent groups on POSS that provided affinity for either the polybutadiene or
Summary

polystyrene phase within SBS. Thermal stability was influenced by phase affinity and POSS structure. Tensile properties and permanent strain increased with POSS concentration, while creep deformation decreased. \( E', E'' \) and \( T_g \) values all increased with the addition of POSS. Composites containing isobutylPOSS functionalised with adipoyl chloride exhibited superior mechanical properties due to the rigid structure of the filler and its affinity for the polybutadiene (continuous) phase. Material properties were influenced by filler concentration, phase preference and POSS architecture.

Further functionalisation of POSS was performed by introducing dichlorotriazine reactive dyes. Following incorporation into SBS, aggregation was observed due to inter-POSS and inter-chromophore interactions. Morphology was influenced by phase preference and the volume of polybutadiene or polystyrene for the POSS to disperse throughout. Colour intensity was able to be controlled by altering the functionalised-POSS concentration. Colourimetric properties began to deteriorate at filler concentrations higher than 5 %·wt, with increased colour swirling and fleck formation caused by larger filler diameters. Thermal stability increased with functionalised POSS concentration, with phase preference and chromophore structure contributing to the thermal integrity of the composite. The addition of POSS reduced creep deformation and increased permanent strain, due to restrictions on molecular mobility. Tensile properties, \( E', E'' \) and \( T_g \) values increased up to filler concentrations of 5 %·wt, before deteriorating at higher filler loadings. This was attributed to reduced material density and nanoparticle agglomeration caused by high filler concentrations. Optimum mechanical and colourimetric/optical properties were attained at filler concentrations of 5 %·wt.

Carbon nanotubes (CNTs) were functionalised with magnetite (Fe₃O₄) and incorporated into TPU to prepare novel magnetic elastomer composites. The influence of two different physical blending methods; melt-mixing and solvent dispersion, to disperse the functionalised nanotubes throughout the matrix was analysed. Fe₃O₄ nanoparticles were present on both the surface and inside the CNTs. The addition of functionalised CNTs encouraged phase separation within TPU, increasing the \( R_g \), while \( D_f \) decreased due to the greater number of rod-like scattering objects (nanotubes). Films became more magnetic.
with filler concentration, as interactions between Fe₃O₄ particles increased. Melt-mixing enhanced thermal stability while solution blending compromised it, due to ineffective filler distribution. Increasing filler concentration led to enhanced tensile modulus and strength, while reducing the ductility. Restrictions on TPU chain motions imparted by CNTs resulted in reduced creep deformation and increased permanent strain. E', E" and T⁺ all increased with CNT content, reaching maximum values at concentrations of 10 %·wt. Melt-mixing was more effective at de-agglomerating and distributing functionalised CNTs than solvent dispersion. As a result, melt-mixed composites exhibited more dramatic changes in material properties and displayed superior magnetic, mechanical and thermal properties than their solvent dispersed counterparts.
CHAPTER 1: INTRODUCTION

1.1 Overview

Functionalised nanoparticles are substances with dimensions in the nano-range that have had their surfaces modified via the chemical or physical introduction of a molecular structure that introduces functionality, such as fluorescence, colour, magnetism, dichroism, light-scattering, nucleation (crystals), flame retardancy, etc. This allows nanoparticles to be tailored and optimised towards a specific application. Due to their nano-sized dimensions and diverse range of functional groups that can be introduced, functionalised nanoparticles are becoming important applications of nanotechnology. These versatile materials have begun to attract attention in various industries and applications, including catalysis, medical applications, security and electronics [1-4].

Polymer-nanocomposite technology has become a significant contributor to materials research over the last several decades, due to enhanced material properties and economical benefits these materials provide. Among the range of nanoparticulate fillers incorporated into polymer matrices, functionalised nanoparticles are rapidly gaining attention. The unique synergy achieved by combining the intrinsic strength, hardness and thermal stability of nanoparticles with the specific functionality of introduced surface groups is providing a broad range of materials with novel properties and applications. While a great number of nanoparticle-functional group and polymer-functionalised nanoparticle combinations have been prepared, the potential for new arrangements exists. Incorporation of functionalised nanoparticles into a polymer is arguably the most convenient method of introducing a specific functionality into the matrix; however this must not be at the expense of intrinsic material characteristics, including mechanical properties and thermal stability. Furthermore, the incorporation of functionalised nanoparticles into multi-phase polymers, including co-polymers and elastomers provides new challenges for preparing nanocomposites, due to the influence of phase selectivity and compatibility. These factors are particularly important when physical blending techniques are used to prepare polymer nanocomposites, due to the tendency of nanoparticles to
agglomerate. By addressing these specific aspects, the potential for novel functionalised polymer nanocomposite materials will be promising.

1.2 Rationale
The development of functionalised polymer nanocomposites is an important aspect of materials science, with potential application in a wide range of fields. However, incorporating molecules with functionality into a polymer is often at the expense of the mechanical and thermal properties of the polymer matrix. Poor matrix-filler compatibility leads to filler aggregation, producing composites with inferior properties. Chemical treatment of the functional molecules to encourage compatibility often leads to diminished functionality. By attaching functional molecules to a stable filler substrate before compounding, several issues can be resolved. Utilising a rigid filler substrate can impart mechanical strength and thermal stability into the polymer. Selecting a filler which is compatible with the matrix can encourage dispersion, allowing the functionality to be controlled and enhancing overall material properties. Furthermore, using physical blending techniques that allow for effective filler dispersion and distribution enables a simple and effective method of preparing large quantities of functionalised polymer nanocomposites.

1.3 Aim
To prepare and characterise polymer nanocomposites containing functionalised nanoparticles, where the nanoparticle substrate enhances the mechanical and thermal properties of the polymer matrix, while the bonded functional group displays a characteristic intrinsic property (functionality).

1.4 Objectives
- To functionalise nanoparticles via the introduction of optical, magnetic, hyperbranched or architecture-defining functional groups.
- To prepare functionalised polymer nanocomposites, using solution blending or melt mixing to distribute functionalised-nanoparticles throughout polymer matrices.
• To characterise the specific functionality of the polymer nanocomposites and determine the influence of functionalised-filler concentration on intrinsic polymer properties.

• To determine the influence of core cross-linked star (CCS) polymers on glass transition, structural relaxation and thermal expansion behaviour of linear polymers.

• To characterise the mechanical, thermal, relaxation, optical and morphological properties of functionalised polymer nanocomposites.

1.5 Research questions
This proposed research raises questions that are important for meeting the objectives. The questions that need to be addressed are:

1. Can a molecule with a specific functionality be bonded onto the surface of a nanofiller substrate to prepare a stable functionalised nanoparticle?

2. Can a specific functionality be controlled by altering the functionalised nano-filler concentration within a nanocomposite?

3. How does functionalised nanoparticle concentration and degree of dispersion influence the intrinsic mechanical, thermal and morphological properties of a polymer matrix?

4. What effect does phase selectivity have on functionality and material properties, when a functionalised nano-filler is incorporated into a multi-phase polymer matrix?

5. How does preparation technique influence functionalised polymer nanocomposite properties?

6. What correlations can be drawn between enthalpic and volumetric structural relaxation, by utilising modulated temperature analysis techniques?
1.6 Thesis structure

This thesis contains ten chapters. The structure of the thesis is summarised in Figure 1.1. A general introduction describing the aim and objectives of the project is presented in Chapter 1. Chapter 2 comprises a review of relevant published literature. This includes general aspects of polymer nanocomposites and functionalised nanoparticles, while focusing on the specific polymer matrices and nanoparticles used in this project. A summary of glass transition theories and structural relaxation, including phenomenological models used to describe such behaviour, is included.

Chapter 3 contains specifications of the materials and experimental methods used in this project. Functionalisation of nanoparticles and preparation of functionalised polymer nanocomposites and blends are detailed, as are general characterisation technique parameters. Where appropriate, the specific material dimensions and experimental parameters used for material characterisation are presented in the Results chapters.

Core cross-linked star polymers, consisting of a highly cross-linked poly(ethylene glycol dimethacrylate) ‘core’ and either linear polystyrene (PS) or poly(methyl methacrylate) (PMMA) ‘arms’ were prepared and incorporated into linear PS or PMMA. The influence of CCS polymers on the glass transition, thermal expansion and structural relaxation properties of linear polymer matrices is investigated in Chapter 4. In addition to conventional differential scanning calorimetry (DSC), modulated temperature – differential scanning calorimetry (mT-DSC) and modulated temperature – thermomechanometry (mT-TM) are utilised to resolve data into components that are in-phase (reversing) or out-of-phase (non-reversing) with the modulated temperature program. Chapter 5 details the mechanical, thermal, optical and morphological properties of linear-CCS polymer blends.

Utilising the knowledge gained from how hyperbranched CCS polymers behave in a linear matrix, hyperbranched dendritic polyesters were functionalised with rigid polyhedral oligomeric silsesquioxanes (POSS) to provide additional strength, dimensions and thermal stability. The functionalised hyperbranched macromolecules were subsequently incorporated into thermoplastic polyurethane (TPU). Chapter 6 details the influence of these hyperbranched dendrimers on mechanical, thermal and morphological properties.
In addition to the use as a functional group, POSS were used as substrates, being functionalised with diacyl chlorides to prepare telechelic (‘dumbbell’ shaped) structures and reactive dyes to prepare new novel pigments. Dumbbell-shaped POSS were synthesised by bridging POSS ‘weights’ with adipoyl and sebacoyl chloride ‘bars’ and incorporated into poly(styrene-b-butadiene-b-styrene) (SBS) via solution blending. The influence these telechelic fillers impart on polymer mechanical, thermal, optical and morphological properties is presented in Chapter 7. In addition to the effects of filler concentration, the influence of ‘barbell’ length and phase partition is discussed. SBS composites containing POSS functionalised with dichlorotriazine reactive dyes are discussed in Chapter 8.

Chapter 9 discusses the influence of incorporating magnetite-functionalised carbon nanotubes (CNTs) into TPU. In addition to magnetic properties, the effects of functionalised filler on mechanical and thermal properties are examined. Two methods of physical blending; solvent dispersion and melt mixing, were used to prepare the nanocomposites and their influence on material properties compared.

Chapter 10 presents the conclusions of the thesis and recommendations for future work.
Figure 1.1 Flow chart of thesis structure
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction
Polymer-nanocomposite technology has remained one of the most popular and evolutionary research areas of the last several decades, fuelled by the potential of producing novel materials with a range of enhanced properties. The economic benefits of these materials are significantly promising, since filler concentrations required for property enhancement are generally low (1-5 %-vol) and nanocomposites are compatible with conventional polymer processing techniques [5]. Research in the nanocomposite field has primarily focused on composite reinforcement and mechanical properties; however a range of other potential applications have been investigated, including membrane properties, thermal stability, flammability resistance, electrical/electronic properties and gas barrier properties [6]. Furthermore, fillers can be functionalised by reacting particulates with molecules displaying properties such as fluorescence, magnetism, dichroism etc., creating a new class of materials that can provide unique attributes in addition to mechanical and thermal reinforcement. As a result, functionalised polymer composites have received much attention from various industrial sectors, particularly the automotive, aerospace, construction and medical industries [7, 8].

This literature review is arranged in six main sections. Firstly, a summary of the basic theory and reinforcement mechanisms of polymer nanocomposites is presented (Section 2.2), followed by an overview of functionalised nanoparticles and functionalised polymer nanocomposites (Section 2.3). Section 2.4 presents the properties and applications of thermoplastic elastomers, focusing specifically on thermoplastic polyurethane and poly(styrene-b-butadiene-b-styrene), while Section 2.5 examines the use of polyhedral oligomeric silsesquioxanes and carbon nanotubes as conventional and functionalised nanofillers. Core cross-linked star polymer structure and properties are covered in Section 2.6. Finally, Section 2.7 critically appraises glass transition theories, structural relaxation and observing such behaviour experimentally and via various models.
2.2 Polymer nanocomposites

Polymer nanocomposites are multi-phase materials that consist of two physically distinct components; a continuous (matrix) polymer phase and dispersed (reinforcement/filler) nanoparticulate phase. Unlike conventional composites, where the filler is of the order of microns, polymer nanocomposites are characterised by constituents with at least one of their solid dimensions in the nanometre (1-100 nm) range. These nanoparticulates can be classified in several categories (organic/inorganic, rigid/flexible) although the most common method is based on dimension and physical form. Physical dimensions (in conjunction with chemical structure) determine nanoparticle properties. The classification categories are shown in Figure 2.1.

![Nano-filler categorisation by dimension and physical form](image)

**Figure 2.1** Nano-filler categorisation by dimension and physical form

In the case of nanolayers and nanotubes, the high aspect ratios and nanoscale dimensions these fillers possess lead to polymer nanocomposites displaying several characteristics that distinguish them from traditional filled systems, as identified by Vaia and Wagner [9];

- Low percolation threshold (~0.1-2 %·vol)
- Particle-particle correlation (orientation and position) arising at low volume fractions
- A large number density of particles ($10^6$-$10^8 \, \mu m^{-3}$)
- Extensive interfacial area per volume of particles ($10^3$-$10^4 \, m^2\cdot mL^{-1}$)
- Short inter-particle distances (10-50 nm at concentrations of ~1-8 %·vol)
• Comparable size scales among the nanoparticulates, distance between particles and the relaxation volume of polymer chains

The first two characteristics are typically not observed for spherical nanoparticles, due to their small aspect ratio, although they can be achieved through innovative processing techniques or proto-assembly. Regardless of filler dimensions, one of the key aspects that sets polymer nanocomposites apart from traditional composite materials are the new properties and unique synergisms that can only occur when the length scale of the morphology and critical length associated with a specific property coincide [9]. Enhanced modulus, tensile strength, yield strength, flammability, thermal and electrical conductivity and gas barrier properties have been reported in polymer nanocomposites, often at a fraction of the concentration of traditional micro-sized fillers [10]. These results, in conjunction with increased research and a growing market suggest that polymer nanocomposites offer much potential for the future.

2.2.1 Property enhancement in polymer nanocomposites

The use of additives in polymers, such as fillers, plasticisers, stabilisers and curing agents is a well established practice, since pure polymers are often inadequate for their intended applications. Provided appropriate material and processing conditions are met, significant alterations in polymer matrix properties can be achieved at relatively low filler concentrations, particularly when nano-sized fillers are used. Apart from physical dimensions, concentration and orientation, two other inter-related factors are crucial in determining the extent to which fillers will manipulate or enhance polymer matrix properties;

2.2.1.1 Matrix-filler compatibility

The nature and degree of interactions between the polymer matrix and filler are an important consideration for polymer nanocomposites. This interaction is particularly important at the interface, where the matrix and filler are in close contact with one another and the bulk of property alterations take place. Sanchez et al [11] classified these interfacial interactions into two classes. Class I where only weak bonds (hydrogen bonding, van der Waals or π-π bonds) between the matrix and filler are present and Class II where strong
chemical bonds (covalent or ionic bonds) link the two phases. Complications in polymer-matrix compatibility can arise when the respective components possess different chemical structures and environments. For example, complications would arise when attempting to disperse polar fumed silica throughout a non-polar polyolefin, such as polystyrene or polypropylene. These hindrances can be readily overcome by chemical treatment of the filler surface, encouraging effective interfacial interaction and increasing the number of potential matrix-filler combinations. Furthermore, surface functionalisation allows for fillers to be incorporated into multi-phase polymers, such as block copolymers, selectively dispersing throughout a specific phase of the matrix. By dispersing particulates throughout one phase of the matrix and not the other/s, selective material properties can be tuned and manipulated.

Enhancing the interaction between the polymer and filler subsequently increases the degree of wettability of the filler by the polymer [12]. This can be described as the ability of a polymer to ‘coat’ the filler particles, leading to greater a degree of interaction between the two phases. Although all material properties are influenced by matrix-filler adhesion, mechanical properties are arguably most directly dependent. Rigid fillers act as stress concentrators within polymer composites. Strong interfacial adhesion and wetting enables the polymer chains to effectively transfer stress to the filler when under an applied load, imparting enhanced strength and toughness into the composite. Poorly wetted fillers lead to void formation around the particulates. These void locations are where failures initiate when the material is subjected to stress, leading to reduced strength [13].

2.2.1.2 Filler dispersion and networks
Fillers are generally dispersed throughout a polymer matrix with the aim of achieving a uniform distribution. This even distribution of filler throughout a matrix is believed to provide an even transfer of stress from the matrix to the reinforcement, resulting in enhanced mechanical properties. Materials such as iron oxides require adequate interparticle space, critical particle-size and favourable matrix-filler interactions to maximise intrinsic properties, including superparamagnetism and electromagnetic wave absorption [14-16]. Additional composite properties, including thermal, optical and barrier
properties, are also known to be enhanced by effective filler dispersion. Several methods are available to encourage filler dispersion and prevent cluster formation, the most common being chemical modification of the filler surface [17, 18]. Other techniques available, specifically for composites prepared by physical blending, include ultrasonic disruption and shear during mixing. Furthermore, processing conditions such as pH and temperature can be altered to influence the extent of filler dispersion [19].

Despite various methods of encouraging particle dispersion, the small size and high specific surface area of many nanoparticulates promotes strong filler-filler interaction between the primary particles. This interaction is generally in the form of electrostatic attractions, such as Coulomb and van der Waals forces [20, 21]. Increased interaction between nanoparticles during the filler-manufacturing process or nanocomposite preparation can leave aggregates remaining, small clusters of primary particulates. Aggregates can interact and flocculate to form larger cluster-like structures, referred to as agglomerates. These clusters (referring to both aggregates and agglomerates) are shown to exhibit fractal geometry and form randomly-shaped structures [19, 22]. The relationship between primary particles, aggregates and agglomerates is displayed in Figure 2.2, using precipitated silica as the filler. The two categories of agglomerates were classified by Schafer and Justice [5] according to sonication studies. Clusters that could be broken-down into smaller clusters (‘de-agglomerated’) were designated “soft”, while those which remained intact were labeled “hard”.

![Figure 2.2 Particle clustering in precipitated silica](image)

Particle agglomeration can be encouraged by increasing the filler concentration. Once a critical concentration is obtained, filler agglomerates can continue growing and form a
three-dimensional continuous network throughout the polymer matrix. The network is formed primarily through rigid filler-filler interactions, although polymer chains bridging onto filler particles create flexible contacts that also contribute [23, 24]. As shown in Figure 2.3, Aranguren et al. [25] suggested three types of these filler-polymer-filler interactions that encourage agglomerate and filler-network formation:

(a) direct-bridge: a single polymer chain is adsorbed on two separate aggregates;
(b) primary entanglement: entanglement between two polymer chains adsorbed on separate aggregates;
(c) secondary entanglement: entanglements involving non-adsorbed polymer chains.

![Figure 2.3](image)

*Figure 2.3* Schematic showing three types of these filler-polymer-filler interactions that encourage agglomerate and filler-network formation; (a) direct-bridge, (b) primary entanglement, (c) secondary entanglement, adapted from [25]

Network formation in polymer composites has attracted significant attention over the last several years, particularly for the enhancement in mechanical properties and electrical conductivity that filler networks achieve [23, 24, 26-31]. Enhancement in thermal stability has also been observed in nanocomposites containing filler network structures [32, 33]. Gauthier et al. [34] investigated the non-linear viscoelastic behaviour of silica-filled styrene-butadiene rubber composites. Dynamic mechanical analysis determined an increase in storage modulus (E’) with silica content, suggesting the filler network contributes to modulus enhancement. Composites containing surface-treated silica displayed the lowest E’ values, further supporting the network influence on the modulus.

Gauthier et al. observed that as the amplitude increased a reduction in E’ was observed and continued to decrease as silica content increased. This reduction in modulus of particle-
reinforced elastomers with increasing amplitude is referred to as the Payne effect, first proposed in the 1960’s. Several other studies have observed this phenomenon [35-41]. Payne initially attributed this behaviour to a breakdown and reformation of a filler network. While the exact cause of the Payne effect is still undetermined, it is believed this mechanism works in conjunction with filler-polymer interactions [27, 38]. Additionally, it has been observed that segments of polymer chains can be entrapped within the network, referred to as bound rubber. These segments are protected from deformation and behave as part of the reinforcement [42]. In addition to the filler network and trapped polymer segments, other non strain-dependent components, including matrix strength, interfacial reaction and hydrodynamic effects can contribute to the modulus and strength of the composite [43]. Some of these contributions are show in Figure 2.4.

![Figure 2.4 Modulus contributions as a function of strain [43]](image)

### 2.3 Functionalised nanoparticles

Nanoparticles have constantly attracted interest due to their distinct properties and range of geometries and shapes which they possess. This has led to their application in various areas of chemistry, physics, materials science, medicine and electronics [44-46]. Nano-sized particles exhibit significantly different properties from macro- or even micro-sized particles of the same material, due to the quantum size effect. In order to tailor and optimise the nanoparticles towards a specific application, functionalisation of the particle surface can be performed. This involves introducing a functional group, either chemically
or physically, onto the surface of the nanoparticle. As shown in Figure 2.5 the number of nanoparticle-functional group combinations is almost endless.

Figure 2.5 Functionalised nanoparticles [47]

Nanoparticle functionalisation can provide numerous benefits, including [47]:

- Influencing nanoparticle shape and dimension during the growth stage by stabilizing it in solution,
- Providing functional groups for future derivitisation/reactions,
- Enhancing particle solubility,
- Preparing controllable particles by modifying optical, chemical, electronic and spectroscopic properties,
- Influencing particle assembly and affinity towards specific targets,
- Enhancing surface properties, such as thermal stability, resistance to oxidation, mechanical strength,
- Reducing particle toxicity.

As listed previously, by introducing one or more functional groups to a nanoparticle surface existing properties can be enhanced while overcoming any challenges. An example of this involves the use of liposomes to transport therapeutic drugs. Liposomes are nano-sized (50-100 nm) phospholipid vesicles with excellent circulation, diffusion and penetration properties [3]. While non-functionalised liposomes possess the intrinsic
properties necessary for drug delivery applications, they cannot differentiate between healthy and unhealthy cells or tissues. Furthermore, liposomes are readily eliminated from the blood. Functionalising the liposome surface with ligands or bio-compatible polymers can overcome these deficiencies by improving drug delivery efficiency and specificity and enhancing solubility properties [48, 49].

Table 2.1 Functionalised nanoparticles

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Functional group (see General Abbreviations and Nomenclature for definitions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotubes</td>
<td><strong>Bio-molecules:</strong> Nucleic acids [50], peptides [50], DNA [51], chitosan [52]</td>
</tr>
<tr>
<td></td>
<td><strong>Metals:</strong> Gold [53], iron oxide [53]</td>
</tr>
<tr>
<td></td>
<td><strong>Organic groups:</strong> Triazolinedione [54], dichlorocarbene [55],</td>
</tr>
<tr>
<td></td>
<td>methoxyphenylhydrazine [56], 3,6-diaminotetrazine [57]</td>
</tr>
<tr>
<td></td>
<td><strong>Polymers:</strong> PEG [58], PS [59], PMMA [59, 60]</td>
</tr>
<tr>
<td>Silica</td>
<td><strong>Organic groups:</strong> C18 alkyl chains [61], FITC [62], ROX [62]</td>
</tr>
<tr>
<td>Polyhedral oligomeric silsesquioxanes</td>
<td><strong>Polymers:</strong> PMMA [63, 64], PS [64], PDMA [64], PBA [64]</td>
</tr>
<tr>
<td>Magnetic particles</td>
<td><strong>Catalysts:</strong> Ruthenium-complex catalysts [73, 74]</td>
</tr>
<tr>
<td></td>
<td><strong>Organic groups:</strong> Oleic acid [61], oleylamine [61], silanes [75, 76]</td>
</tr>
<tr>
<td>Liposomes</td>
<td><strong>Polymers:</strong> PLA [77], PDMAEMA [77], PEG [77], PS [78], PAAc [78]</td>
</tr>
<tr>
<td>Metals</td>
<td><strong>Polymers:</strong> PEG [49], PVA [79], PVP [80]</td>
</tr>
<tr>
<td>Metal oxides</td>
<td><strong>Polymers:</strong> PMMA [90], PS, PHEA [92], PAAc [93]</td>
</tr>
<tr>
<td>Quantum dots</td>
<td><strong>Metals:</strong> Cobalt [94], nickel [94]</td>
</tr>
<tr>
<td></td>
<td><strong>Organic groups:</strong> Trioctylphosphine oxide [61], squaraine dye [95],</td>
</tr>
<tr>
<td></td>
<td>methacryloamidocysteine [96]</td>
</tr>
<tr>
<td></td>
<td><strong>Polymers:</strong> PNIPAM [97], P3HT [98], PS [99], PS-co-PMMA [99]</td>
</tr>
</tbody>
</table>

Table 2.1 lists a cross-section of the functionalised nanoparticles already synthesised. The field is rapidly growing, fuelled by the ongoing interest in nanotechnology and large number of areas which require exploration. Similarly, the range of applications continues to expand, with functionalised nanoparticles attracting interest in various industries and applications, including catalysis, medical applications, security and electronics [1-4].
2.3.1 Functionalised polymer nanocomposites

As mentioned previously, the ongoing preparation of novel functionalised nanoparticles provides much potential for a range of applications. One particular use involves incorporating functionalised nanoparticles into a polymer matrix, resulting in a functionalised polymer nanocomposite. Conventional fillers, such as carbon nanotubes, silica, clay, etc, provide one or more generic attributes (enhanced mechanical strength, thermal stability). Functionalised nanoparticles can provide a synergic result, combining the stability of the nano-filler with the specific functionality of the introduced functional group.

Table 2.2 Functionalised polymer nanocomposites

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Functional group</th>
<th>Polymer matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotubes</td>
<td><em>Organic groups:</em> Carboxylic acid [100, 101], amine [102], thionyl chloride [103]</td>
<td>P3HT [100], PA [101], PEI [102], PAA [102], PMMA [103], P3OT [104, 105], Silver paste [106], Epoxy resin [107], PTP [108], PAN [109]</td>
</tr>
<tr>
<td></td>
<td><em>Dyes:</em> Naphthalocyanine [104], N-(1-pyrenyl)maleimide [105]</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Metals:</em> Silver [106], nickel [106, 107], gold [108]</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Metal oxides:</em> Titanium dioxide [109]</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td><em>Organic groups:</em> Aminosilane [110-112]</td>
<td>SBR [110], PAMAM [111], epoxy resin [112], PMMA [113], PP [114]</td>
</tr>
<tr>
<td></td>
<td><em>Polymers:</em> PMMA [113, 114], PP [114], PS [114], PEA [114], PBA [114]</td>
<td></td>
</tr>
<tr>
<td>Polyhedral</td>
<td><em>Organic groups:</em> 2,2-bis(4-hydroxyphenyl)propane [115], aminopropyl [116]</td>
<td>PEO [115], PET [116], PP [117]</td>
</tr>
<tr>
<td>oligomeric</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silsesquioxanes</td>
<td><em>Metals:</em> aluminium [117], zinc [117]</td>
<td></td>
</tr>
<tr>
<td>Silver nanoparticles</td>
<td><em>Organic groups:</em> Diacids [118]</td>
<td>Epoxy resin [118]</td>
</tr>
</tbody>
</table>

Table 2.2 summarises current interest in exploiting functionalised nanoparticles and this is expected to increase due to the possible combination and application of this novel technology. A wide range of functionalised nano-particles have been incorporated into different polymer matrices, including thermoplastics, thermosets, elastomers and block copolymers. Functionalised composites have the potential to be utilised in a variety of fields, including packaging, sensing, security, optics and electrical applications. A recent example involves the investigation of polymer-cadmium selenide (CdSe) nanocomposites for use in photovoltaic devices [119]. The CdSe nanorods were functionalised with alkane
ligands, allowing the nanoparticles to align in the direction of an applied electric field and phase separate from the polymer matrix. Several examples of polymer nanocomposites containing functionalised polyhedral oligomeric silsesquioxanes (POSS) and carbon nanotubes (CNTs) are discussed in Sections 2.4.1.1 and 2.4.2.1, respectively.

2.4 Nano-sized particulate fillers

2.4.1 Polyhedral oligomeric silsesquioxanes

POSS (empirical formula RSiO$_{1.5}$) are a hybrid organic-inorganic class of molecule, consisting of a rigid inorganic core made up of silicon atoms linked by oxygen atoms, with organic ‘R’ substituents attached at the corners of the silica cage. As shown in Figure 2.6 the molecular architecture of POSS can take on many forms. Their name is derived from the non-integer (one and one-half or *sesqui*) ratio between the silicon and oxygen atoms and the organic substituents [120]. The central core is ceramic in nature, providing thermal stability and rigidity, while the organic groups compatibilise the molecule, allowing it to dissolve in polymers, solvents or coatings [121]. First synthesised in 1946 by Scott [122], POSS have been utilised in a variety of applications, including aerospace coatings, dental adhesive and high temperature lubricants and catalysts [123, 124].

![POSS Structures](image)

**Figure 2.6** Various POSS structures, adapted from [125, 126]
The structure of the POSS molecule is dependent on the preparation method. POSS can be synthesised using a number of different reactions [127], which Li et al [126] classified into two types; (i) reactions that create new Si-O-Si bonds as the polyhedral cage takes shape, (ii) reactions that leave the Si-O-Si skeleton intact while manipulating substituents at the silicon atom. Generally, the synthesis of POSS begins with the hydrolysis and condensation of alkyl trichlorosilane monomers [128]. As shown in Equation 2.1, chlorosilanes are hydrolysed to silanols which then undergo acid- or base-catalysed condensation to form siloxane bonds [129].

\[ RCl_3 + 3H_2O \rightarrow RSi(OH)_3 + 3HCl \]  
hydrolysis

\[ RSi(OH)_3 \xrightarrow{\text{Catalyst}} 3RSiO_{3/2} + 1.5H_2O \]  
condensation

\[ RSi(OH)_3 + RCl_3 \xrightarrow{\text{Catalyst}} RSiO_{3/2} + 3HCl \]  
condensation

The trisilanolPOSS can be easily capped with an appropriate silane coupling agent, preparing a fully condensed POSS structure. The entire process is summarised in Figure 2.7.

![Figure 2.7 Synthesis of condensed POSS via condensation, adopted from [129]](image)

2.4.1.1 Functionalised POSS-polymer nanocomposites

It is only during the last 10-15 years that POSS have been receiving serious attention as filler in composite materials, due to their unique structure and properties and the ongoing interest in nanotechnology (the entire molecule being 1-3 nm in size). The incorporation of POSS into polymer matrices can enhance many properties, including modulus, elongation at break, glass transition temperature (T_g), thermal stability, corrosion resistance and permeability. POSS has been compounded with a number of polymers, including PS [130-
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132], PMMA [133, 134], polypropylene (PP) [135], polycarbonate (PC) [136] and polyurethane (PU) [137]. Specialty POSS molecules, such as the trisilanolPOSS partial cage (refer Figure 2.5) allow for the introduction of various functional groups through bonding directly onto the ceramic silicone core. The resulting product is a hybrid molecule which combines the strength and thermal stability of POSS and specific functionality of the reactive group. Consequently, various POSS molecules have been functionalised with a range of compounds and materials, including organic groups [138], metals [139], fluorescent emitters [140, 141] and magnetic groups [142, 143]. The compatibilising ‘R’ groups on the POSS provide potential for these hybrid materials to act as fillers in polymer compounds.

Fine et al [117] prepared composites of PP and POSS functionalised with zinc and aluminium, as shown in Figure 2.8. The metal species were incorporated into the POSS structure due to the enhancement in thermal stability, with aluminium- and zinc-POSS displaying maximum degradation temperatures ($T_d$) of 342 and 490 °C, respectively, both significantly higher than octaisobutyl POSS ($T_d = 265 °C$). Incorporation of the functionalised filler significantly improved the thermal stability of PP, with filler loadings of 3 %·wt increasing $T_d$ from 315 °C (pure PP) to 347 (zinc-POSS) and 349 °C (aluminium-POSS). Increasing the POSS concentration to 10 %·wt further raised the $T_d$ to 382 and 378 °C for zinc- and aluminium-functionalised POSS, respectively. The metal-functionalised fillers also delayed the onset of thermal degradation.

![Figure 2.8](image)

(a) Aluminium-POSS, (b) Zinc-POSS; R = i-C$_4$H$_9$ [117]
Apart from exhibiting a specific property or trait, functionalisation can be utilised to encourage dispersion or interaction within a polymer or solvent. Song et al [142] prepared magnetically-functionalised POSS which can readily copolymerise with monomers to form polymer nanocomposites. POSS was functionalised with ferrocene and C=C bonds using a Wittig reaction and incorporated into linear PS via bulk free radical polymerisation. The functionalised POSS exhibited paramagnetism and soft magnetic properties at room temperature. Incorporation of POSS into PS enhanced tensile strength, impact strength and storage modulus, indicating the hybrid filler reinforced the PS matrix. Glass transition temperature and thermal stability were also observed to increase, with the optimal POSS concentration being 3 %·wt.

Another method of functionalisation involves manipulating the architecture, shape and structure of the filler/particulate. POSS molecules with various architectures and molecular shapes have been prepared, including pendant [144], bead [145], tadpole [146] and star [71, 72] structures. Several of these shape-functionalised POSS have been grafted onto polymer chains to prepare nanocomposites [147-150] with noticeable enhancements in glass transition temperature, thermal stability and mechanical properties.

One particular form of POSS architecture beginning to receive attention within recent years is telechelic or ‘dumbbell-shaped’ POSS [151-153]. As the name suggests, the structure consists of two POSS ‘weights’ joined by an alkyl or similar ‘barbell’ chain. Both reported instances of dumbbell-POSS used them as an intermediate to prepare larger structures. Ceyhan et al [151] prepared dumbbell structures containing a ‘barbell’ with a phthalonitrile derivative in the centre. These structures were subsequently used as ligands to bind with metal ions, preparing metallophthalocyanine complexes. Su et al [152] synthesised dumbbell-POSS with azobenzene moieties in the ‘barbell’ centre, which were subsequently incorporated into bead and crosslinked network-type structures. The POSS structures provided the azobenzene groups with enhanced thermal stability, solubility and film-forming properties. Mather and colleagues [154-156] prepared a series of telechelic poly(ethylene glycol) structures with POSS attached to the end groups, observing changes in crystallisation behaviour, thermal stability and surface properties. However, these novel-
structured POSS are yet to be incorporated as filler into a polymer matrix. Furthermore, no research has been conducted to optimise architecture, such as ‘barbell’ length or chain type. This provides much potential for applications such as filler materials or as stable supports/substrates for dyes, metals and other functional groups.

The large range of functional groups and reactive molecules bonded with POSS highlights the importance and versatility of the hybrid filler as a compounding material. This encourages the potential for new, functionalised-POSS fillers with a range of architectures and properties capable of manipulating polymer matrix characteristics. In addition, the bulk of polymer-POSS nanocomposites are prepared using chemical grafting and various polymerisation techniques, due to the large degree of control they provide. This provides an opportunity to explore nanocomposite preparation using physical blending. Areas of particular interest and importance include optimising blending techniques, controlling filler-filler interactions to encourage adequate dispersion morphologies and controlling various polymer-filler interactions such as phase preference amongst POSS with various compatibilising groups. Physical blending gives the option of developing a quicker, more efficient and cost effective synthesis alternative.

2.4.2 Carbon nanotubes

Carbon nanotubes (CNTs) are arguably one of the most popular nanomaterials of the last 20 years. CNTs are cylindrical fullerene molecules comprised of consecutive carbon rings bonded entirely by sp² hybridisation. They typically exhibit diameters of 1-50 nm and lengths ranging from several microns to centimetres, with Wang et al [157] recently growing CNTs with lengths of over 18.5 cm. As displayed in Figure 2.9, CNTs can be categorised into two distinct groups based on structure; single-wall and multi-wall nanotubes. Single-wall nanotubes (SWNTs) are the simplest form of CNT, consisting of a one-atom thick layer of graphene ‘wrapped’ into a cylinder. In contrast, multi-wall nanotubes (MWNTs) are made up of two or more separate graphene cylinders. This can be in the form of a single graphene sheet wrapped around itself several times (scroll model), or a series of coaxial cylinders, each rolled out of separate sheets (Russian doll model), separated by the interlayer spacing within graphene (~3.4 Å) [158]. In addition to these
two main categories, other CNT structures prepared include nanofibres, torus (nanotori) and nanobud architectures [159].

![Image](image_url)

**Figure 2.9** (a) single-wall carbon nanotube, (b) multi-wall carbon nanotube [160]

MWNTs were first synthesised in 1991 by Iijima [161], with SWNTs following shortly [162]. However, CNTs were attracting attention prior to this, with Hyperion [163] registering the first patent regarding CNTs in 1987 and the first images of nanotubes were produced in 1975 [164]. The major source of interest in CNTs are their remarkable properties, in particular mechanical, thermal and electrical [165]. These unique properties stem from CNT's strong sp² covalent bonding (amongst the strongest found in nature and stronger than sp³ bonds found in diamond) and their ability to align due to van der Waals interactions. Several methods are available for the production of CNTs, including arc discharge [166], laser ablation [167] and various chemical vapour deposition processes [168]. The variety in synthesis techniques leads to variation of nanotube parameters, such as diameter, aspect ratio, crystallinity, entanglement and surface chemistry, which subsequently influence intrinsic properties [169]. When combining their unique characteristics and versatility of synthesis, it is of no consequence that CNTs have attracted interest in a broad range of fields, including electronics, biomedical, and optics [159, 170, 171].

2.4.2.1 Functionalised CNT-polymer nanocomposites

As with other nanoparticles, CNTs have attracted significant attention for use as nanofiller in polymer composites. This interest is fueled by CNTs extraordinary properties, nano-
sized dimensions, high aspect ratio and low percolation threshold [172]. Both MWNTs and SWNTs have been incorporated into a variety of polymer matrices, including PS [173], PU [174], PC [172], PLA [33], PMMA [103] and epoxy resin [107], with various reports of enhanced mechanical, thermal, electrical and membrane properties. Furthermore, functionalised CNT-polymer nanocomposites have been prepared, with a range of organic groups, dyes, metals and metal oxides used to prepare hybrid CNT fillers (refer to Table 2.2). The range of functionalities varies from encouraging dispersion (surfactants) to increasing nanotube electrical and optical properties. The unique intrinsic characteristics, popularity and versatility of CNTs make it an ideal candidate for a functionalised filler substrate.

Polymer-filler compatibility is one of several factors that determine the extent of property enhancement in polymer nanocomposites, with compatible fillers being able to achieve greater levels of dispersion and interaction with the matrix. Nismy et al [100] incorporated MWNTs into poly-(3-hexylthiophene)/[6,6]-phenyl-C<sub>61</sub>-butyric acid-methylfullerene photovoltaic devices, due to their excellent charge transport properties and ability to provide dissociation centres. The nanotubes were acid-functionalised prior to compounding to encourage dispersion and compatibility. Composites containing functionalised CNTs displayed higher fill factor and power conversion efficiency values than their untreated CNT counterparts for equal filler loadings. The enhancement in electrical properties in the functionalised composites was attributed to superior compatibility and degree of filler dispersion within the photovoltaic layer, allowing for fast exciton dissociation and offering good dissociation centres. Furthermore, Khan et al [175] synthesised water-soluble SWNTs functionalised with poly(ethylene glycol) or poly(aminobenzenesulfonic acid) and tetrahydrafuran-soluble SWNTs treated with octadecylamine. When incorporated into thermoplastic polyurethane, the films exhibited different mechanical properties, depending on the surface-functionalisation of the nanotubes. These differences were attributed to the SWNTs dispersing throughout either the hard or soft polymer segments and demonstrate how phase preference within a multi-segment polymer can be achieved.
In addition to aiding compatibility/dispersion, functionalisation can be utilised to enhance the characteristics of the substrate. Oh et al [106] incorporated silver- and nickel-plated CNTs (Fig. 2.10) into a silver-polymer composite, utilising the excellent conductivity properties of the nanotubes. Incorporation of the metal-plated nanotubes decreased material resistivity, with the silver-plated CNT composites displaying values 83% lower than the pure composite. The significant decrease in resistivity was attributed to excellent interaction and adhesion between the metal-coated CNTs. In addition, conductive bumps were screen-printed onto the composites containing metal-functionalised CNTs, displaying potential for use as multi-layer printed circuit boards.

![Figure 2.10 Functionalisation of CNT surface with silver [106]](image)

At present, the majority of functionalised-CNT fillers can be grouped into two categories; (1) nanotubes functionalised with surfactants or compounds to improve dispersion/polymer compatibility, (2) nanotubes functionalised with compounds and materials that enhance CNT properties (primarily electrical and conductive properties). Preparation of CNTs functionalised with a specific functionality (fluorescence, colour, magnetism, dichroism) and their incorporation into polymer matrices is rather limited, providing much potential for exploration in this field. By combining the mechanical and thermal properties of the CNT substrates and the specific functionality of the reactive group, polymer nanocomposites with a range of enhanced properties and use in numerous applications can be prepared.

### 2.5 Thermoplastic elastomers
Thermoplastic elastomers are a category of macromolecules (copolymers or polymer blends) which exhibit both thermoplastic and elastomer properties. First introduced in the 1960’s, these polymers are generally phase-separated systems, with one phase being hard
(glassy) and solid at ambient temperature while the other is a rubbery (continuous) elastomer, as shown in Figure 2.11. The glassy domains act as reversible, physical crosslinks, interacting with the continuous phase in the form of non-covalent interactions such as dipole, ionic and hydrogen bonds, providing the polymer with strength and form. When the glassy phase is dissolved in solvent or heated, the physical crosslinks effectively break, allowing the polymer to soften, melt and flow. Upon cooling the glassy phase solidifies and the physical crosslinks re-form. The intrinsic structure of thermoplastic elastomers provides several benefits, including recyclability, versatility in processing and applicability and low cost per volume (~US$1.50-2.50 per pound) [176]. These advantages, in conjunction with a growth in production and demand, has contributed towards the importance of thermoplastic elastomers as a polymer and material in a number of applications, including automotive parts, adhesives, consumer goods, footwear, wire and cable insulation [176, 177]. Furthermore, these polymers can undergo further processing, such as adjusting the rubber/glass domain ratio, or be compounded with various additives such as fillers or plasticisers, to produce novel, highly-customised materials.

Figure 2.11 Structure of an elastomer/block copolymer
2.5.1 Thermoplastic Polyurethanes

Thermoplastic polyurethanes (TPUs) are linear copolymers with alternating hard and soft segments. The soft block generally consists of an amorphous, flexible, relatively long polymer chain, derived from a hydroxy-terminated polyester, polyether or polyalkene [178]. The hard domains are usually highly-polar polyurethanes or polyureas, formed by reacting an excess of diisocyanate with a diol or diamine chain extender [176]. The generalised form of this reaction is shown in Equation 2.2. The resulting product is an ester of carbamic acid which forms the repeating unit within the polymer. The carbamic ester has the trivial name of ‘urethane’.

\[
\text{Diol} + \text{Diisocyanate} \rightarrow \text{Urethane group}
\]

(2.2)

Current processing techniques allow TPUs to be manufactured with a great deal of control over the properties of the final product. Of the various factors which influence polymer properties, the type of hard or soft segments used and the ratio between them are of particular importance. Ester-based TPUs exhibit superior tensile strength, load-bearing capacity and resistance to abrasion, oil, solvents and oxygen. Ether-based TPUs display enhanced low-temperature properties and resistance to hydrolysis [176]. Further alterations of properties can be made through the addition of fillers and additives. This versatility and reliability has lead to TPUs being used in various applications, including automotive components (Figure 2.12a), hosing and tubing, sports equipment (Figure 2.12b), shoe soles, coatings and wires and cabling [179].
Due to its versatility of manufacture and broad range of applications, TPUs continue to be amongst the most popular elastomers used as matrix components in polymer composites. Compounding with fillers provides a means of reducing resin cost and overcoming intrinsic TPU limitations, such as poor electrical properties and UV resistance [181]. Fillers including fumed silica [182, 183], CNTs [174], POSS [184, 185] and montmorillonite clay [186] have been incorporated into TPU matrices, with enhancements in mechanical, thermal, optical and electrical properties reported. In addition, functionalised polymer composites have been prepared using TPU matrices. Recently, polyurethane-based magneto-rheological elastomers have been synthesised, which exhibit tunable mechanical and rheological properties when the material is subjected to a magnetic field [187, 188]. Zhao et al [189] incorporated CNTs functionalised with para-phenylenediamine into TPU. The nanocomposites exhibited enhanced thermal diffusivity, mechanical and electrical properties, making them applicable for aerospace coating applications. These examples highlight the importance of TPUs and TPU-composites as materials.

2.5.2 Poly(styrene-\textit{b}-butadiene-\textit{b}-styrene)

Poly(\textit{styrene-\textit{b}-butadiene-\textit{b}-styrene}) (SBS) is a linear, triblock copolymer first introduced in the early 1960s [190]. Also known as styrene-butadiene block copolymer, its structure consists of a short polystyrene (PS) segment, followed by a longer polybutadiene (PB) segment, followed by another PS segment (Figure 2.13). Both ends of the butadiene chain are terminated with PS, enabling the styrene domains to act as physical crosslinks and
reinforce the soft, rubber domain [191]. Due to the thermodynamic immiscibility of the PB and PS domains, SBS is a phase-separated system which is present in both the solid and melt [192]. This attribute is particularly important since SBS and block copolymer physical properties are directly influenced by morphology [193, 194]. These intrinsic properties, combined with low production costs and ease of processing has led to SBS being used in a number of applications, including adhesives, coatings, packaging, consumer goods and sealants [181].

![Chemical structure of SBS](image)

**Figure 2.13** Chemical structure of SBS

The main pathway used in controlling the properties of SBS involves altering block concentration, composition and monomer units [195, 196]. Altering the molecular weight [197] and architecture [198] of the blocks has also been utilised. Thomann et al [199] classified commercially available SBS into two distinct groups based on block concentration; type I “thermoplastic elastomers” containing 60-80 %·wt polybutadiene and type II “transparent, ductile thermoplastics” containing ~20-30 %·wt of the soft domain. Type I exhibits properties comparable with vulcanized rubber [200] with high optical transparency, chemical stability and insulation properties. Comparison can also be drawn between type I SBS and plasticised PVC, with the former possessing enhanced yield strength, elastic recovery and elongation [199]. Type II contains greater styrene domains and is more suited to packaging film or products prepared using thermoforming or injection moulding. A consequence of altering the block concentration ratio (as well as molecular weight and domain compatibility) is the change in SBS morphology, as shown in Figure 2.14. In addition to the traditional sphere, cylinder and lamellae morphologies,
ordered bicontinuous (including double diamond [201] and double gyroid [202]), ‘mesh’ and ‘strut’ [203] morphologies have been observed in SBS block copolymers.

<table>
<thead>
<tr>
<th>Spheres</th>
<th>Hexagonal cylinders</th>
<th>Lamellae</th>
<th>Hexagonal cylinders</th>
<th>Spheres</th>
</tr>
</thead>
</table>

**Figure 2.14** Influence of block concentration on SBS morphology; the white regions represent styrene domains while the black regions correspond to butadiene [204]

SBS is seldom utilised in its pure state, often being compounded with PS to reduce cost and optimise mechanical properties [205, 206]. Additionally, a number of fillers have been compounded with SBS, including carbon nanotubes [207, 208], carbon black [209], montmorillonite clay [210], polymer fibres [211] silica [212] and alumina [213], with enhancements in various properties including mechanical, thermal, gas permeability, conductance and optical being reported. Despite their recent popularity as a filler, polyhedral oligomeric silsesquioxanes (POSS) have been scarcely incorporated into SBS [214-216]. In the few reported instances of SBS-POSS composites, significant changes in SBS material properties via the addition of POSS have been observed. An increase in SBS thermal stability was reported by Kashiwagi et al [217]. Fu et al observed increases in glass transition temperature and enhanced load-bearing capacity at elevated temperatures with the addition of POSS, while Drazkowski et al [214] determined how POSS can manipulate the rheological properties of SBS. Furthermore, Drazkowski et al [215] observed that POSS could be used to control the morphology and self-assembly of the SBS matrix. In all cases, the phase to which the POSS molecule was bonded (dispersed) and the corner ‘R’ group structure were the primary factors that governed ultimate material properties.

### 2.6 Core cross-linked star polymers

Core cross-linked star (CCS) polymers are unique three-dimensional macromolecules that consist of a ‘hard’ crosslinked core surrounded by numerous ‘soft’ linear arms, as shown in
Figure 2.15. These polymers are also referred to as star microgels or star nanogels [218]. Properties are influenced by the number of arms (functionality) and their length. Despite exhibiting a very high molecular weight, CCS polymers display solubility and viscosity parameters similar to linear and branched polymers of low molecular weight [218]. This combination of unique intrinsic properties and polymerisation techniques which allow for high structural control have led to significant interest in CCS polymers. Furthermore, these macromolecules show potential for use in various applications, including drug delivery, paint additives and membrane formation [219-221].

![Core cross-linked star polymer, composed of a poly(ethylene glycol dimethylacrylate) (PEGDMA) core and poly(methyl methacrylate) (PMMA) arms, courtesy of T. K. Goh, A. Blencowe and G. G. Qiao](image)

**Figure 2.15** Core cross-linked star polymer, composed of a poly(ethylene glycol dimethylacrylate) (PEGDMA) core and poly(methyl methacrylate) (PMMA) arms, courtesy of T. K. Goh, A. Blencowe and G. G. Qiao

CCS polymers are generally synthesised using living radical polymerisation techniques which allow for a high degree of structural control and narrow molecular weight distribution. These techniques include nitroxide-mediated radical polymerisation (NMP), atom transfer radical polymerisation (ATRP) and reverse addition-fragmentation chain transfer (RAFT) [222-224]. One particular feature which distinguishes CCS polymers from conventional star polymers is that the former are traditionally synthesised using the “arms first approach”. In this approach, a living macroinitiator (the arm) is reacted with a vinylic cross-linker to form a highly crosslinked ‘core’ from which the arms protrude [225]. In contrast, the “core first approach” involves the use of a multifunctional initiator (core) to initiate the polymerisation of vinylic monomers, forming the star polymer arms. One consequence of the “arms first approach” is that the resulting CCS polymer core constitutes 10-30 % of the polymers’ molecular weight ($M_w$), whereas star polymers prepared via the
“core first approach” possesses cores with negligible $M_W$ compared with the entire macromolecule. In addition, the highly-crosslinked CCS polymer core lacks the mobility associated with star polymer cores prepared via the “core first” method. The “arm first” and “core first” schemes are displayed in Figure 2.16.

Apart from novel synthesis techniques [226, 227], research areas of interest concerning CCS polymers include catalysis [228], encapsulation [229] and surface properties [230]. As with conventional star polymers, rheological properties [220, 231] are another key interest area of CCS polymer research. Goh et al [232] investigated the rheological properties of a series $\text{PMMA}_{\text{arm}}\text{PEGDMA}_{\text{core}}$ CCS polymers, focusing on the influence of star polymer ($M_w(\text{CCS})$) and arm ($M_w(\text{arm})$) molecular weight. Increasing $M_w(\text{CCS})$ and functionality caused an increase in viscosity and concentration dependence in CCS polymers with constant $M_w(\text{arm})$, that was attributed to the simultaneous increase in CCS polymer hydrodynamic volume. A similar enhancement in viscosity was observed for constant $M_w(\text{CCS})$ CCS polymers. $M_w(\text{CCS})$ and $M_w(\text{arm})$ also influenced dynamic behaviour, with a
transition from Newtonian to viscoelastic behaviour observed as both parameters were increased independently.

‘Molecular softness’, a phenomenon that readily occurs in star polymers involving the deviation of the arms from hard sphere behaviour, was observed for the CCS polymers. CCS polymers with constant $M_w(\text{arm})$ displayed similar molecular softness characteristics with increasing $M_w(\text{CCS})$ and functionality, due to the relatively similar segmental density amongst the materials. In contrast, constant $M_w(\text{CCS})$ CCS polymers displayed a strong relationship between functionality and molecular softness. Increasing the functionality leads to crowding and causes the arms to assume a highly-stretched conformation. This subsequently results in a decrease in molecular softness, causing the CCS polymer to behave as a hard sphere.

The literature available regarding linear-CCS polymer composites is limited, with almost no analyses regarding the solid-state structural relaxation, physical ageing, mechanical or morphological properties [233]. This is also the case for blends where the linear matrix and CCS polymer arms are the same macromolecule [234]. CCS polymers incorporated into a linear matrix are believed to behave in a similar manner to fillers or physical crosslinks, occupying empty volume and imparting restrictions on the segmental motions of the linear matrix chains. Meng et al [235] incorporated CCS polymers with PEO-b-PS arms into an epoxy thermoset, observing an increase in $T_g$ with CCS polymer concentration, that was attributed to an increase in crosslink density. CCS polymers generally exhibit glass transition temperatures ($T_g$) which correspond to the arms, with values similar to linear polymers of like composition [234, 236]. No transition is observed from the crosslinked core due to its confined structure and lack of mobility. The advantage these star polymers have over traditional fillers/crosslinks is the superior compatibility achieved when the linear matrix and CCS polymer arms are the same material. Furthermore, CCS polymers with functionalities including fluorescence [237] and selective dispersion [218] have been prepared, encouraging their use as a novel class of polymer additive. The ability to understand how this new class of hyperbranched polymer interacts with and affects a linear matrix can provide much insight into designing future polymer materials.
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2.7 Glass transition and structural relaxation

2.7.1 Introduction to glass transition

The state of a polymer is greatly dependent on temperature. At sufficiently low temperatures, all polymers are rigid and glassy. As a polymer is heated, it softens across a characteristic temperature range referred to as the glass-transition region, during which the polymer behaves in a leathery manner. Upon further heating, the polymer continues to soften, transforming into a supercooled liquid and becoming rubber-like in behaviour. The glass transition is a pseudo-second order phase transition, involving the onset of long-range, coordinated molecular motions [238]. The transition is characterised by a glass transition temperature ($T_g$), at which sufficient energy is gained for coordinated rotation of polymer chain segments. The $T_g$ is arguably a polymer’s most important intrinsic property, determining suitability and applicability. A full theoretical understanding of glass transition has not yet been developed, although several theories have been proposed to describe this phenomenon. The following paragraphs will give a brief description of three commonly accepted theories; free-volume theory, kinetic theory and thermodynamic theory, and describe the attempt to produce a (qualitatively) unified theory.

2.7.1.1 Free-volume theory

The free-volume theory, as implied by the name, suggests the glass transition is characterised by a state of iso-free volume. Eyring [239] first postulated that molecular motion in the bulk state is dependent on the presence of ‘holes’ or areas where there are vacancies/voids. When a molecule moves into a hole, the hole in turn changes places with the molecule. This concept can be extended to the motion of polymer chains, with the main difference being that several holes may be required to be in the same region due to the occurrence of cooperative motions [238]. The holes/voids are collectively referred to as free volume and are necessary for molecular motion to occur. This concept is illustrated in Figure 2.17a [240], which models the structure of an amorphous material. The material consists of volume occupied by molecules, $V_0$, and areas of free volume, $V_F$. $V_0$ is associated with the van der Waal’s radii of the molecules, or in the case of a polymer, the sum of the van der Waal’s volumes of each chain segment and the additional volume of vibrational
motions [241]. Other methods of calculating $V_0$ include taking the crystalline volume at 0 K and taking the difference between the total volume and fluctuation volume [242]. $V_F$ is the unoccupied volume into which the molecules will move as they undergo Brownian motion and it can be estimated by small angle X-ray scattering and positron annihilation lifetime spectroscopy. Figure 2.17b shows the temperature dependence of free volume. A change in the slope of the total volume, or coefficient of thermal expansion (CTE), is observed which often defines $T_g$.

![Free volume, $V_F$](image)

![Occupied volume, $V_0$](image)

**Figure 2.17** (a) Model showing free and occupied volume in an amorphous material, as reproduced from [240], (b) volume-temperature plot of an amorphous material showing temperature dependence of $V_F$

The basis of this theory stems from the internal mobility of a polymer (exhibited as flow/viscosity) requiring a critical amount of free volume. This empirical relationship was established by Doolittle [243] and is expressed by the equation:

$$\eta = A \exp \left(\frac{B}{f}\right)$$

(2.3)

where $\eta$ is the viscosity, $f$ is the fractional free volume (the ratio of free volume to total volume) and $A$ and $B$ are constants. The Doolittle viscosity equation provides a theoretical basis for the universal Williams-Landel-Ferry (WLF) equation [244]. When used to model the temperature dependence of liquid viscosity, the model assumes that above $T_g$ the
fractional free volume increases with temperature (Figure 2.16b) and that free volume is inversely proportional to viscosity. The WLF equation is expressed as:

\[
\log \alpha_T = \frac{C_1(T - T_R)}{C_2 + T - T_R}
\]

(2.4)

where \(\alpha_T\) is the temperature shift factor, \(T\) is temperature, \(T_R\) is a reference temperature and \(C_1\) and \(C_2\) are constants. When \(T_R = T_g\), \(C_1\) and \(C_2\) become almost universal constants for a large number of polymers, where \(C_1 = -17.44\) and \(C_2 = 51.6\) K. Therefore, Equation 2.4 becomes:

\[
\log \alpha_T = \frac{-17.44(T - T_g)}{51.6 + T - T_R}
\]

(2.5)

Although originally based on empirical observations, the WLF can be derived from the free volume theory, beginning with the Doolittle viscosity equation (Equation 2.3) [242]. The shift factor \(\alpha_T\) becomes:

\[
\alpha_T = \exp \left[ B \left( \frac{1}{f} - \frac{1}{f_r} \right) \right]
\]

(2.6)

where \(f_r\) is the fractional free volume at \(T_R\). If the reference temperature (\(T_R\)) is set to \(T_g\), it is assumed that \(f_r = f_g\), giving the equation:

\[
\alpha_T = \exp \left[ B \left( \frac{1}{f} - \frac{1}{f_g} \right) \right]
\]

(2.7)

The fractional free volume at temperature \(T\) can be obtained by:

\[
f = f_g + \alpha_T (T - T_g)
\]

(2.8)
where $\alpha_f$ is the coefficient of expansion of $f$. Inserting Equation 2.8 into Equation 2.7 gives:

$$\alpha_f = \left[ \frac{-B}{f_g} (T - T_g) \right] + T - T_g$$

Taking the logarithm of Equation 2.9 gives the following equation:

$$\log \alpha_f \approx \left[ \frac{-B}{2.303f_g} (T - T_g) \right] + \frac{f_g}{\alpha_f} \approx \alpha_f = \alpha_f$$

Equation 2.10 can be used in conjunction with the WLF equation to define the universal constants $C_1$ and $C_2$.

$$C_1 = -\frac{1}{2.303f_g} = -17.44 \Rightarrow f_g = 0.025$$

$$C_2 = \frac{f_g}{\alpha_f} = 51.6 K \Rightarrow \alpha_f = 4.8 \times 10^{-4} K^{-1}$$

As a result of the WLF equation having universal constants, the fractional free volume at $T_g$ and the thermal expansion coefficient of the free volume also exhibit universal values. Thus, Equation 2.10 can be re-written in its WLF form (Equation 2.5). Furthermore, both the WLF and Doolittle equations establish that the glass transition is an iso-free volume state. While free-volume theory establishes the relationship between the coefficients of expansion above and below $T_g$ and relates viscoelastic motion to time and temperature variables, one drawback of this theory is the limited insight into the actual molecular motions that occur [238]. Free-volume theory remains one of the most commonly accepted theories regarding glass transition behaviour.
2.7.1.2 Kinetic theory

The free-volume theory of glass transition (see Section 2.7.1.1), introduced the concept of free volume as a prerequisite for molecular motion. The WLF equation also introduces several kinetic factors. Equation (2.12) shows how viscosity is a time dependent quantity:

\[
\alpha_T = \frac{\eta_T}{\eta_R} = \frac{\tau_T}{\tau_R}
\]  

(2.12)

where \(\alpha_T\) is the temperature shift factor, \(\eta\) is the viscosity and \(\tau\) is the segmental relaxation time at temperatures \(T\) and \(T_R\), respectively. Thus, either \(\eta_T/\eta_R\) or \(\tau_T/\tau_R\) can be substituted in place of \(\alpha_T\) into the WLF equation. This relationship provides the basis of the kinetic theory of glass transition, which states that there is no true thermodynamic glass transition [242]. Instead, the theory describes the glass transition as a purely kinetic phenomenon and considers the molecular and macromolecular response within a varying time frame [238]. \(T_g\) is observed when the time-scale of the experiment and the \(\tau\) of the polymer are of the same order of magnitude [178]. Another prediction is that the specific volume and kinetic \(T_g\) are dependent on the heating/cooling rate \((q)\), as shown in Figure 2.18.

![Figure 2.18](image)

**Figure 2.18** The dependence of cooling rate on \(T_g\) as reproduced from [242]
For example, if the time frame of an experiment is decreased by a factor of 10, the \( T_g \) should increase by \( \sim 3 \) °C, as shown in Equation (2.13):

\[
\lim_{T \to T_g} \left( \frac{\log \alpha_T}{T - T_g} \right) = -0.338
\]

\[
T - T_g = -\frac{1.0}{-0.338} = +3.0
\]

while larger changes in the time frame will vary the \( T_g \) by 6-7 °C [238]. Tool, Davies and Jones [245, 246] proposed a one-parameter model to describe the volume recovery (also applicable to enthalpy):

\[
-\frac{d\delta_v}{dt} = q\Delta \alpha + \frac{\delta_v}{\tau_v}
\]

(2.14)

where \( \delta_v = (V - V_\infty)/V_\infty \), \( V \) is the actual volume, \( V_\infty \) is the equilibrium volume, \( q \) is the rate of temperature change, \( \Delta \alpha \) is the change of volume expansion coefficient at \( T_g \) and \( \tau_v \) is the isobaric volume relaxation time [247]. Doolittle’s viscosity equation was later incorporated into this equation, giving:

\[
-\frac{d\delta_v}{dt} = q\Delta \alpha + \frac{\delta_v}{\tau_v} \exp \left( \frac{B}{f_g} - \frac{B}{f} \right)
\]

(2.15)

Modifying Equation 2.13 to make the relaxation time dependent on free volume proved successful in describing the kinetic aspects, but failed to explain memory effects. Kovacs, Aklonis, Hutchinson and Ramos [248] attributed these memory effects to at least two independent relaxation mechanisms, involving two or more relaxation times. The authors proposed a multi-parameter model, where the relaxation process is divided into \( N \) sub-processes [242]. This model is referred to as the KAHR model:

\[
-\frac{d\delta_{vi}}{dt} = q\Delta \alpha + \frac{\delta_{vi}}{\tau_{vi}} \quad \delta_v = \sum_{i=1}^{N} \delta_{vi}
\]

\[1 \leq i \leq N\] (2.16)
Although heat capacities and shifts in $T_g$ with varying time frames can be determined, the theory is limited in that it fails to predict $T_g$ at an infinite time scale. Despite this limitation, the kinetic theory provides a unique insight into the time-dependent properties and behaviour of the glass transition phenomenon.

2.7.1.3 Thermodynamic theory

The thermodynamic theory of glass transition originated from the work of Gibbs and DiMarzio [249], who stated that although the observed glass transition is a kinetic phenomenon, underlying true transitions can possess equilibrium properties [238]. The theory attempted to explain the Kauzmann paradox, which states that when the entropy ($S$) and molar volume (both equilibrium properties) of a material are extrapolated through the glass transition, the corresponding values for the glass will be higher than those for the crystals [242]. The thermodynamic theory provides a solution by predicting a thermodynamic glass transition, $T_2$, reached when the conformational entropy ($S_C$) (that is, the number of different ways polymer chains/molecules can be spatially arranged) is zero as shown in Figure 2.19.

![Figure 2.19](image)

**Figure 2.19** The conformational entropy ($S_C$) of a polymer as a function of temperature

Polymer chains exist in many different possible spatial conformations in the melt state, with each of these conformations corresponding to a different energy state [241]. When a
polymer is cooled, the number of possible arrangements of the chains/molecules decrease with temperature. This is associated with a decrease in the number of holes, decrease in the permutation of holes and chain segments and the gradual occupation of the lower energy states by polymer chains [242]. Finally, at $T_2$, $S_C$ equals zero. The value of $T_2$ is $\sim 50 \, ^\circ C$ lower than the experimentally obtained value of $T_g$, which will be explained in Section 2.7.1.4.

The Gibbs-DiMarzio theory uses a lattice model similar to the one used by Flory for polymer solutions [250]. This lattice takes into consideration both high- and low-energy conformational states, the degree of polymerisation, number of holes and the intra- and inter-molecular energy. Using this model, a configurational partition function, $Q$, can be calculated, from which the entropy can be determined using Equation 2.17.

$$S = kT \left( \frac{\delta \ln Q}{\delta T} \right)_{\nu,n} + k \ln Q$$  \hspace{1cm} (2.17)

Limits of the thermodynamic theory include the infinite time scales are that required and the imprecise definition of $T_2$. However, the theory has been applied to explain the variation of $T_g$ with various factors, including molecular weight [251], plasticisation [252] and cross-linking [253].

2.7.1.4 Unified theory

An attempt to unify the rate (kinetic) and equilibrium (thermodynamic) effects of the glass transition was presented by Adam and Gibbs [254]. Rather than using free volume, the authors introduced the concept of a ‘cooperatively rearranging region’, defined as the smallest region that can undergo conformational change without a requisite simultaneous change outside the region. Examining the variation of region size with temperature revealed that at $T_2$ the region size was equal to sample size, due to only one conformation being available [238]. By rederiving the WLF equation and making $T = T_2$ (see Equation 2.9), Adam and Gibbs determined that:

$$\frac{T_2}{T} = 1.30 \pm 8.4 \%$$  \hspace{1cm} (2.18)
For example, an elastomer such as polyurethane displays a $T_g \equiv 238$ K. If Equation 2.18 is utilised, $T_2 \equiv 137$ K, which is $\sim 50$ K below the $T_g [254]$. Similarly, the WLF equation predicts that viscosity becomes infinite at $T - T_g = -51.6 \degree C$. While the method is somewhat confined to low-temperature materials, the idea of combining molecular, rate and equilibrium aspects of glass transition provides much insight.

### 2.7.2 Physical ageing and structural relaxation

It is well established that the kinetic nature of the glass transition results in glassy polymers exhibiting a non-equilibrium nature. When a polymer is cooled at a constant rate from the melt through the glass transition and held (annealed) at a constant temperature below its $T_g$, the specific volume will decrease in an attempt to attain equilibrium, as shown in Figure 2.20. This process is referred to as structural relaxation or structural recovery and it can be applied to other thermodynamic factors, including enthalpy and entropy. Segmental motion within the polymer is also hindered due to the reduction in volume. As a result, intrinsic properties such as creep, stress relaxation, permeability, viscosity and electrical properties are consequentially affected [238, 242]. Change in material properties due to structural relaxation is referred to as physical ageing. This behaviour highlights the importance of structural relaxation/physical ageing when considering material performance and potential applications.

![Figure 2.20](image) The structural relaxation process, as reproduced from [255]
The process of structural relaxation is closely related to the concept of free volume. The rate at which a polymer attains equilibrium is controlled by the segmental mobility (M) of the molecules and subsequently, the degree of packing or free volume. The polymer behaves as a fluid or rubber at temperatures above $T_g$, therefore the segmental mobility and free volume are large. $V_f$ and $M$ simultaneously decrease upon cooling, until the $T_g$ is reached. This change in free volume is brought about by a cooperative redistribution of the space between the molecules (holes/voids), while the rate of this rearrangement is determined by $M$ [256]. This process can be explained by a closed loop scheme, as shown in Equation 2.19;

$$V_f \Rightarrow M \Rightarrow \frac{dV_f}{dt}$$

(2.19)

where $dV_f/dt$ is the rate at which the free volume changes. The decrease in $V_f$ cannot continue indefinitely as the material is cooled, due to the drastic reduction in mobility at the $T_g$ and subsequent impact on the $V_f$ rate of change. However, below $T_g$, the mobility is small but not zero. $M$ and $V_f$ will continue to decrease since the free volume at this point is greater than at equilibrium, leading to structural relaxation/physical ageing. The scheme suggests that the volume-relaxation process is non-linear.

The importance of the glass transition phenomenon in material design and applications has lead to much academic interest. Research regarding structural relaxation can be categorised into two key areas, as summarised by Hahn [257]; (1) development of a quantitative theory to predict observed behaviour, and (2) experimental relaxation studies, mainly involving amorphous polymers. The main property altered by annealing below $T_g$ is mobility (see Equation 2.23), which is directly related to the relaxation time of a polymer [257]. As a result, numerous creep [258], stress-relaxation [259] and dynamic mechanical [260] experiments have been conducted to study physical ageing and its subsequent effect on mechanical properties. In addition, several other techniques including dielectric spectroscopy [261], X-ray diffraction [262], and calorimetry [263] have been used to investigate relaxation and ageing.
2.7.3.1 Observing structural relaxation using DSC

In addition to reducing the free volume, structural relaxation also reduces the entropy and internal energy of a polymer [256]. Therefore, a polymer will continuously lose heat, if only in miniscule amounts. When an annealed polymer is reheated through the \( T_g \), the heat lost during ageing will be reabsorbed. One of the most popular non-mechanical methods of observing structural relaxation is differential scanning calorimetry (DSC). When referring to characterising structural relaxation via the evolution of specific heat, enthalpy or volume, the terms “enthalpy relaxation” or “volume relaxation” are used [264]. A wide range of information can be obtained through DSC, including, crystallisation temperature, melting temperature, \( T_g \), enthalpy of transition and other properties. Structural evolution during the relaxation process can be characterised using the fictive temperature (\( T_f \)) [255]. \( T_f \) is defined as the temperature at which the glassy state of a polymer would be in thermal equilibrium and is obtained at the intersection of the extrapolated glassy line of the volume/enthalpy and equilibrium line (Figure 2.19) [265]. It can be considered the measure of the state of a polymer relative to the current temperature. At temperatures above \( T_g \), \( T_f = T \) since the polymer is in a liquid equilibrium state. When a polymer is held isothermally at an annealing temperature (\( T_a \)), the \( T_f \) decreases from an initial value and shifts towards \( T_a \).

A typical experiment displays the specific heat/heat capacity change of a material as it is heated over a temperature range, with the reabsorbed heat manifesting itself as an endothermic peak [256, 257]. The height of the peak increases with annealing time while the position of the peak on the temperature scale varies with both annealing time and temperature, as shown in Figure 2.21. This behaviour is associated with the enthalpy and free volume changes occurring within the material over time. Modulated-temperature differential scanning calorimetry (mT-DSC) has also been utilised to observe structural relaxation in various polymers and amorphous materials [266-268]. A conventional DSC endotherm consists of an enthalpic (non-reversing) peak superimposed on a reversing glass transition. By heating samples across a modulated-temperature program, these thermally reversing and non-reversing components can be separated, providing information on specific processes and phenomena.
Figure 2.21 Effect of annealing time (tₐ) on the relaxation endotherm of poly(vinyl chloride), annealed at 65 °C [256]

While it’s convenience as an experimental method is well established, using DSC for analysing the ageing process has several minor drawbacks. While the true origin of ageing is associated with volume and entropy changes, material properties are affected by changes in segmental mobility and τ [256]. Therefore, mechanical or dielectric methods of analysis may be better suited. Furthermore, it is well established that the only correct definition of Tₕ is obtained when a polymer is cooled from the liquid equilibrium state, since only these cooling definitions are independent of thermal history in the glassy state. However, the overwhelming majority of ageing experiments using DSC obtain Tₕ and thermal data through heating, due to the greater control available. Criticisms aside, DSC continues to remain a popular and useful method of structural relaxation analysis.

2.7.3.2 Observing structural relaxation using mT-TM

Modulated temperature–thermomechanometry (mT-TM) is a novel technique [269] that involves the application of an oscillating temperature to a linear/isothermal underlying heating rate [270]. The modulated temperature program induces a sinusoidal response in specimen dimension change that can be resolved into reversing (in-phase with ΔT) and non-reversing (out-of-phase with ΔT) components. While conventional thermomechanometry (TMA) has been used extensively to observe the effect of ageing on material expansion properties [271-274], the same cannot be said of mT-TM. The
technique allows for a volumetric approach to observing reversing and non-reversing behaviour due to structural relaxation, providing a method which compliments mT-DSC. Unlike mT-DSC, mT-TM enables in-phase and out-of-phase phenomena to be directly measured during isothermal annealing by recording the change in material dimension. In this respect, structural relaxation can be characterised from another approach, particularly in terms of free volume reduction during annealing and subsequent expansion following reheating through T_g. Furthermore, the novel technique can provide valuable insight into how functionalised nanoparticles influence the expansion and glass transition properties of amorphous polymers. The technique is discussed in greater detail in Section 3.4.3.

2.7.4 Modeling glass transition, relaxation and non-equilibrium behaviour

Glass transition and structural relaxation are generally believed to be influenced by two essential features; (1) the dependence of \( \tau \) on both temperature and the instantaneous structure of the material (non-linearity) and (2) the time dependence of the structural relaxation process not following an exponential function (non-exponentially). Appropriate phenomenological models used to further interpret and describe this non-equilibrium behaviour must account for these two features. This section will concentrate on the model developed by Moynihan et. al. [265] based on the prior work of Tool [246] and Narayanaswamy [275], known as the TNM model. Furthermore, variations of the TNM model, namely the alternative method of determining non-linearity proposed by Scherer [254, 276] and the introduction of annealing by Hodge and Berens [277] will also be discussed.

2.7.4.1 The Tool-Narayanaswamy-Moynihan model

Since its introduction over thirty years ago, the Tool-Narayanaswamy-Moynihan (TNM) model and its variations have remained amongst the most popular schemes for describing glass transition and relaxation behaviour, in particular for experimental data obtained using DSC [278-284]. The model evolved from Tool’s assumption [246], which states that \( \tau \) is dependent on both temperature and instantaneous structure of the material, the latter of which is characterised by \( T_f \). This assumption forms the basis of the non-linear
characteristic of structural relaxation. Tool proposed the rate of structural relaxation is given in Equation 2.20:

$$\frac{dT_i}{dt} = \frac{(T - T_i)}{\tau} \quad (2.20)$$

with relaxation time ($\tau$) at temperature ($T$) given by:

$$\tau = \tau_0 \exp^{-AT} \quad (2.21)$$

where $\tau_0$ and $A$ are constants. However, these two equations proved inadequate in describing volumetric expansion data, since the effect of change in structure on $\tau$ was not taken into account [255].

Tool’s concept of $T_f$ was elaborated on by Narayanaswamy [275] in an attempt to describe the non-exponentiality of glass transition. Narayanaswamy assumed that:

- the activation energy of the relaxation process is a constant,
- response function shape is independent of temperature,
- non-linearity occurs only due to the dependence of $\tau$ on both structure and temperature.

Using these assumptions, a linear response function could be introduced and Boltzmann superposition applied [255]. Furthermore, Narayanaswamy successfully proposed that an Arrhenius equation could be used to describe $\tau$, allowing for both structure and temperature dependence [275]. The scheme of Tool and Narayanaswamy was further extended by Moynihan [265] who incorporated a non-exponential decay process by using the stretched-exponential relaxation function of Kohlrausch, Williams and Watts (KWW) [285], giving a distribution of relaxation times. The KWW function is shown in Equation 2.22:

$$\phi(t) = \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right] \quad (2.22)$$
where \( \phi(t) \) is the relaxation function and \( \beta \) is the parameter of non-exponentially \((0 \leq \beta \leq 1)\). The relaxation time can be determined by using the TNM equation, shown in Equation 2.23:

\[
\tau = A_{TNM} \exp \left[ \frac{x\Delta h^{*}}{RT} + \frac{(1-x)\Delta h^{*}}{RT_f} \right]
\]

(2.23)

The use of Equation 2.23 in conjunction with Equation 2.22 is known as the TNM model. The temperature dependence of \( \tau \) is defined by the first term in Eq. 2.23, while the structural dependence is represented by the second term [286]. In Eq. 2.23, \( A_{TNM} \) is a pre-exponential constant which represents \( \tau \) at an infinitely high temperature, \( x \) is the non-linearity constant \((0 \leq x \leq 1)\) which describes the degree of structural dependence the relaxation process requires and \( \Delta h^{*}/R \) is the relative apparent activation energy [284]. The three parameters \((A, x, \Delta h^{*}/R)\) are assumed to be independent of \( T \) and \( T_f \). Interpreting the model parameters from a molecular point of view, Hodge [287] proposed that a smaller \( \beta \) and higher \( \Delta h^{*}/R \) value suggests a cooperative relaxation process. Furthermore, a decrease in the value of \( x \) indicated a greater structure dependence and increased cooperation [255].

At temperatures well above glass transition, where the material is at equilibrium and in the liquid state, \( T_f = T \). In the glassy state below \( T_g \), \( T_f \) is constant. Heating or cooling through the glass transition region causes the \( T_f \) to evolve from one limit to another, which can be calculated for any thermal history as follows:

\[
T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{ 1 - \exp \left[ - \left( \sum_{m=1}^{n} \frac{\Delta T_m}{q_m \tau_m} \right)^{\beta} \right] \right\}
\]

(2.24)

where \( T_0 \) is the initial temperature, \( \Delta T_j \) is the temperature change corresponding to the \( j \)th step and \( q_m \) is the heating/cooling rate. Calculations must commence from a temperature above \( T_g \) in order to validate Equation 2.24. In addition, small temperature steps \((\Delta T_j)\) must be utilised to avoid drastic changes in \( T_f \) and maintain linearity.
Hodge and Berens [277] introduced annealing into the TNM equation, allowing the evolution of $T_f$ during an isothermal hold after cooling from equilibrium to be determined. The annealing interval was subdivided into logarithmically spaced intervals, since enthalpy relaxation is directly proportional to the logarithm of annealing time [286]. The annealing step is introduced by replacing $\Delta T_m/q_m$ with an annealing time ($t_a$) to give Equation 2.25.

$$T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{ 1 - \exp \left[ - \left( \sum_{m=m_0}^{n} \frac{\Delta t_{a,m}}{q_m \tau_m} \right)^{\beta} \right] \right\}$$  \hspace{1cm} (2.25)

Scherer [276] proposed an alternate method of determining the non-linearity of structural relaxation by applying the theory of Adam-Gibbs. The concept was further improved by Hodge [288] through the use of a hyperbolic expression to give the Adam-Gibbs-Scherer (AGS) equation:

$$\tau = A_{AGS} \exp \left[ \frac{B}{T(1 - T_2/T_f)} \right]$$  \hspace{1cm} (2.26)

where $A_{AGS}$ is a pre-exponential constant, $B$ is a constant and $T_2$ is the temperature at which the configurational energy of the liquid disappears (often identical to the Kauzmann temperature, the temperature at which the difference in entropies between the liquid and glass phase becomes zero). Several comparisons between the TNM and AGS models have been undertaken [281, 289], with no significant improvement in quality observed.
CHAPTER 3: EXPERIMENTAL

3.1 Materials

3.1.1 Polymer matrices

The specifications of polymer matrix materials used are presented in Table 3.1. All polymers were treated overnight in a vacuum oven at 70 °C prior to compounding.

<table>
<thead>
<tr>
<th>Polymer Matrix</th>
<th>Trade name</th>
<th>Specifications</th>
<th>Density (g·cm$^3$)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>Austrex 103</td>
<td>Compression grade</td>
<td>1.05</td>
<td>Polystyrene Australia Pty. Ltd.</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>-</td>
<td>-</td>
<td>1.20</td>
<td>Aldrich Chemical Company</td>
</tr>
<tr>
<td>Poly(styrene-(b)-butadiene-(b)-styrene) (SBS)</td>
<td>Kraton-D-1102</td>
<td>29.5 %·wt bound styrene</td>
<td>0.938</td>
<td>Kraton Polymers LLC</td>
</tr>
<tr>
<td>Polyurethane (PU)</td>
<td>Pellethane 2103-85AE</td>
<td>Polyether thermoplastic polyurethane (TPU)</td>
<td>1.14</td>
<td>Dow Plastics</td>
</tr>
<tr>
<td>Polyurethane (PU)</td>
<td>Pellethane 2101-85A</td>
<td>Polyester TPU</td>
<td>1.13</td>
<td>Dow Plastics</td>
</tr>
</tbody>
</table>

3.1.2 Filler/reinforcement

Two types of POSS were obtained from Hybrid Plastics, Hattiesburg, USA; trisilanolheptisobutyl (SO1450) and trisilanolheptaphenyl (SO1458). Their specifications are shown in Table 3.2. Multi-wall carbon nanotubes (CNT) with an average diameter of 9.5 nm, average length of 1.5 μm and purity of 90 % were provided by Nanocyl Inc. Boltorn dendritic polymers were obtained from Perstorp Specialty Chemicals AB, Sweden. Boltorn H20 and H40 are hyperbranched aliphatic polyesters with molecular weights of 2100 and 5100 g·mol$^{-1}$ [290], respectively. Their structures are displayed in Figure 3.1. Boltorn H20 contains 16 hydroxyl groups while Boltorn H40 contains 64.
Figure 3.1 Boltorn dendritic polymers; (a) H20, (b) H40 [291]
3.1.3 Chemical functional groups

3.1.3.1 POSS end-groups on Boltorn dendrimers

Trisilanolheptisobutyl (SO1450) was used to functionalise Boltorn hyperbranched polyesters. Its details are outlined in Section 3.1.2 and structure is displayed in Table 3.2.

3.1.3.2 Dichlorotriazine dyes

CI Reactive Blue 4 (ICI Australia Ltd.) and CI Reactive Red 2 (Kraft Kolour, Pty. Ltd., Whittlesea, Australia) dichlorotriazine reactive dyes were used to functionalise the trisilanol POSS. Their structures and specifications are shown in Table 3.3.

3.1.3.3 Diacyl chloride ‘bridges’ in dumbbell POSS

Adipoyl and sebacoyl chloride used to ‘bridge’ amino-treated POSS molecules were obtained from Aldrich Chemical Company. 3-aminopropyltriethoxysilane and triethylamine were also obtained from Aldrich Chemical Company.
3.1.3.4 Magnetite

Iron (II) chloride tetrahydrate (FeCl₂·4H₂O) and iron (III) chloride hexahydrate (FeCl₃·6H₂O) were obtained from BDH Chemicals, sodium hydroxide (NaOH) was obtained from Chem-Supply Pty. Ltd. and nitric acid (HNO₃, 65 %) was obtained from Merck Chemicals.

Table 3.3 Dichlorotriazine and fluorescent dye characteristics

<table>
<thead>
<tr>
<th>Colour Index name</th>
<th>Trade name</th>
<th>Structure</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI Reactive Blue 4</td>
<td>Procion Blue MX-R</td>
<td><img src="image" alt="Structure of CI Reactive Blue 4" /></td>
<td>ICI Australia Ltd.</td>
</tr>
<tr>
<td>CI Reactive Red 2</td>
<td>Procion Red MX-5B</td>
<td><img src="image" alt="Structure of CI Reactive Red 2" /></td>
<td>Kraft Kolour Pty. Ltd., Whittlesea, Australia</td>
</tr>
</tbody>
</table>

3.2 Filler synthesis and functionalisation

3.2.1 Core cross-linked star polymers

Core cross-linked star (CCS) polymers consisting of a poly(ethylene glycol dimethacrylate) core and linear polystyrene or poly(methyl methacrylate) arms were synthesised by T. K. Goh and A. Blencowe using previously established atom transfer radical polymerisation (ATRP) methods [222]. The general scheme is displayed in Figure 3.2.
3.2.2 Functionised POSS

3.2.2.1 Preparation of amino-POSS

Amino-isobutyl POSS: TrisilanolheptisobutylPOSS (5.00 g, 6.32 mmol) and 3-aminopropyltriethoxysilane (1.44 g, 6.5 mmol) were dispersed in 40 mL tetrahydrofuran and stirred at ambient temperature overnight. The solution was poured into 100 mL methanol and stirred for 10 min, before being suction filtered, washed with methanol and deionised water and dried in a vacuum oven at 75 °C for 12 h.

Amino-phenyl POSS: TrisilanolheptaphenylPOSS (4.59 g, 4.93 mmol) was dispersed into 40 mL toluene and stirred in an ice bath for 20 min. 3-aminopropyltriethoxysilane (1.11 g, 5.03 mmol) was added to the solution which was stirred overnight and equilibrated to ambient temperature. The solution was poured into 100 mL of acetonitrile and stirred for 10 min, before being suction filtered, washed with methanol and deionised water and dried in a vacuum oven (75 °C, 12 h).

3.2.2.2 Functionalisation of POSS with dichlorotriazine reactive dyes

The preparation of dye-functionalised POSS is displayed in Figure 3.3. To 50 mL of dichloromethane were added the amino-treated POSS (5 g), dichlorotriazine dye (5 %·wt) and diisopropylethylamine (5 mL). The solution was stirred at 35 °C for 1 h. The POSS-dye
hybrid was filtered, washed with methanol and stored in a desiccator at 0 % relative humidity.

**Figure 3.3** Functionalisation of POSS with dichlorotriazine reactive dyes

3.2.2.3 Preparation of dumbbell-POSS

The complete process for preparing dumbbell-POSS is displayed in Figure 3.4. Amino-treated POSS (2.07 mmol) and triethylamine (2.31 mmol) were dispersed in 50 mL THF and stirred under nitrogen for 20 min. Sebacoyl or adipoyl chloride (1 mmol) was added dropwise and the solution was stirred overnight. After evaporating the solvent, the dumbbell-shaped POSS were washed with methanol and dried in a vacuum oven at 25 °C for 12 h.
3.2.3 Magnetite-functionalised carbon nanotubes

Magnetite-functionalised CNTs were synthesised by I. Kong using the following method; CNTs were dispersed in a round-bottomed flask containing HNO₃ solution using an ultrasonic water bath for 1 h. The solution was refluxed at 80 °C with vigorous mixing for 24 h. The acid-modified CNTs were collected by centrifugation and dried at 80 °C for 24 h. In a separate flask, FeCl₂.4H₂O and FeCl₃.6H₂O (molar ratio 1:2) was dissolved in 200 mL deoxygenated water with constant stirring for 10 min. The acid-modified CNTs were added...
to the Fe²⁺/Fe³⁺ solution and dispersed using ultrasonic disruption for 10 min under nitrogen, followed by stirring room temperature for 2 h. While stirring, NaOH was added dropwise into the solution to precipitate magnetite-functionalised CNTs. The black precipitate was magnetically isolated and the solution decanted. The functionalised CNTs were washed repeatedly with distilled water and dried in a vacuum oven at 35 °C for 24 h.

### 3.2.4 POSS-functionalised dendritic polymers

Boltorn H20 or H40 (1 mmol) was dispersed in 150 mL of THF and stirred at room temperature for 2 h. Amino-treated isobutylPOSS (1 mmol) was added and the solution was stirred for a further 24 h at room temperature. The solution was cast into glass Petri dishes and the solvent was allowed to evaporate in air overnight. The POSS-functionalised dendritic polymer was washed with acetone and methanol and dried in a vacuum oven at 25 °C for 12 h. The POSS-Boltorn materials were stored in sealed plastic bags kept in a desiccator at 0 % relative humidity. FTIR absorbance spectra were used to determine the number of POSS molecules bonded to a single Boltorn dendrimer. The method of calculation is detailed in Appendix A. Eight POSS molecules were bonded to one Boltorn H20 dendrimer, while thirty-one POSS molecules were bonded to one Boltorn H40 dendrimer.

### 3.3 Preparation of nanocomposite films

#### 3.3.1 Melt-mixing

A Haake Rheomix 600 Batch Intensive Mixer with Rheocord 90 Control System was used to mix magnetite-functionalised carbon nanotube-polyurethane composites, as displayed in Figure 3.5a. The TPU matrix was Pellethane 2103-85AE. Materials were mixed for 5 min using roller-blade type impellers (Figure 3.5b) at 50 rpm. The mixing temperature was 190 °C to ensure complete polymer melting.
3.3.2 Solvent dispersion

Solvent dispersion was utilised to disperse functionalised nanoparticles throughout several polymer matrices. A detailed summary of material composition, dispersion solvent, mixing
Chapter 3: Experimental

time, precipitation solvent and vacuum oven treatment specifications are presented in Table 3.4. The solvent dispersion method used was similar for all composite materials. Polymer was dissolved in a minimal amount of solvent at room temperature. For linear-CCS polymer composites, the hyperbranched fillers were added to the solution and magnetically stirred until they dispersed. For all other polymer nanocomposites, functionalised filler was added to the solution and subjected to ultrasonic disruption (10 min, 25 °C, 20 kHz) to ensure even distribution of the filler throughout the matrix. The solution was poured into an excess of solvent to precipitate the nanocomposite material and to restrict filler migration. The nanocomposite precipitate was isolated using suction filtration and dried in a vacuum oven.

Table 3.4 Solvent dispersion specifications of polymer nanocomposites

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler</th>
<th>Functional group</th>
<th>Solvent</th>
<th>Precipitant</th>
<th>Vacuum oven (temperature, minimum time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>IsobutylPOSS and phenylPOSS</td>
<td>Adipoyl and sebacoyl chloride</td>
<td>CH₂Cl₂</td>
<td>MeOH</td>
<td>Ambient, 12 h</td>
</tr>
<tr>
<td>SBS</td>
<td>IsobutylPOSS and phenylPOSS</td>
<td>Dichlorotriazine dyes</td>
<td>CH₂Cl₂</td>
<td>MeOH</td>
<td>Ambient, 12 h</td>
</tr>
<tr>
<td>PU (Pellethane 2101-85A)</td>
<td>Boltron H20 and H40</td>
<td>IsobutylPOSS</td>
<td>THF</td>
<td>MeOH</td>
<td>25 °C, 12 h</td>
</tr>
<tr>
<td>PU (Pellethane 2103-85AE)</td>
<td>CNTs</td>
<td>Magnetite</td>
<td>THF</td>
<td>MeOH</td>
<td>75 °C, 12 h</td>
</tr>
<tr>
<td>PS</td>
<td>CCS polymer</td>
<td>PS arms</td>
<td>CH₂Cl₂</td>
<td>MeOH</td>
<td>Ambient, 10 h</td>
</tr>
<tr>
<td>PMMA</td>
<td>CCS polymer</td>
<td>PMMA arms</td>
<td>CH₂Cl₂</td>
<td>MeOH</td>
<td>Ambient, 10 h</td>
</tr>
</tbody>
</table>

3.3.3 Film preparation by heated press

Films for subsequent use were prepared using a heated press (IDM Instruments, model number: L0003-1). Films were heated to a specified temperature, summarised in Table 3.5, 6 tonne of mass applied, held for 2 min and cooled to ambient within 5 min. Pressed films were stored in sealed plastic bags in a desiccator cabinet (Secador 3.0) at 0 % relative humidity.
Table 3.5 Heated press temperature specifications of polymer nanocomposites

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler</th>
<th>Functional group</th>
<th>Pressing Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>IsobutylPOSS and phenylPOSS</td>
<td>Adipoyl and sebacoyl chloride</td>
<td>150</td>
</tr>
<tr>
<td>SBS</td>
<td>IsobutylPOSS and phenylPOSS</td>
<td>Dichlorotriazine dyes</td>
<td>150</td>
</tr>
<tr>
<td>PU</td>
<td>Boltorn H20 and H40</td>
<td>IsobutylPOSS</td>
<td>175</td>
</tr>
<tr>
<td>PU</td>
<td>CNTs</td>
<td>Magnetite</td>
<td>175</td>
</tr>
<tr>
<td>PS</td>
<td>CCS polymers</td>
<td>PS arms</td>
<td>190</td>
</tr>
<tr>
<td>PMMA</td>
<td>CCS polymers</td>
<td>PMMA arms</td>
<td>190</td>
</tr>
</tbody>
</table>

3.4 Characterisation of materials

3.4.1 Differential scanning calorimetry

3.4.1.1 Introduction

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the amount of energy absorbed or released by a material in relation to an inert reference is measured as a function of temperature, while both sample and reference are subjected to identical temperature programs. Two varieties of DSC systems are in common use; power compensation DSC (Figure 3.6a) and heat-flux DSC (Figure 3.6b). A power compensation DSC utilises separate heaters for the sample and reference, each with their own temperature program. The instrument consists of two temperature control circuits. An average temperature control circuit monitors the progress of the temperature control program, ensuring the set temperature scanning program matches the average temperature of the sample and reference. A differential temperature control circuit monitors the relative temperature of the sample and reference, adjusting the power supply of both heaters to ensure the temperatures are identical. The output of this circuit is used to plot the DSC endotherm or exotherm. In a heat flux DSC, heat is transferred to the sample and reference pans through a disk made of either constantan (copper-nickel alloy) or silver. The heat difference between the sample and reference is measured by a thermocouple located beneath the pans. The temperature difference signal is converted to heat flow by a calibration equation.
Since its development by Watson and O’Neill [292] in the 1960s, DSC has become one of the most useful thermal analysis techniques, due to the significance of the thermal data which can be obtained. This includes, but is not limited to, crystallisation temperature ($T_c$), melting temperature ($T_m$), glass transition temperature ($T_g$), enthalpy ($\Delta H$) and crystallinity ($\chi$). For this project, the use of DSC allows physical ageing and structural relaxation to be observed, by isothermally annealing materials at a temperature below the onset of $T_g$. Spectra obtained by reheating annealed materials reveal changes in material properties due to reductions in free volume and molecular mobility.

3.4.1.2 Experimental conditions

A Perkin-Elmer Pyris 1 DSC (Figure 3.7) was used to measure the thermal transitions of the linear-CCS polymer composites including glass transition ($T_g$), heat capacity and enthalpies of transition ($\Delta H$). Measurements were conducted with an ice-water slurry heat-sink, while high purity indium ($T_m = 156.6 \, ^\circ\text{C}, \Delta H_m = 28.45 \, \text{J} \cdot \text{g}^{-1}$) and zinc ($T_m = 429 \, ^\circ\text{C}$) standards were used for calibration. A 20 mL·min$^{-1}$ nitrogen purge through the cell chamber provided an inert atmosphere. Small masses (~5 mg) of film were accurately weighed using a Mettler Toledo MX5 microbalance with internal standard mass calibration. The films were encapsulated in standard 10 μL hermetically sealed aluminium pans, with a similar empty pan used as a reference. Samples were heated to 210 °C to eliminate prior thermal history and held for 5 min. Films were subsequently cooled to 30 °C at 20 °C·min$^{-1}$ before being heated at various heating rates (2, 5 and 10 °C·min$^{-1}$).
3.4.1.3 Annealing studies

The influence of annealing at a predetermined temperature on $T_g$ was investigated. Films were heated to 210 °C to eliminate prior thermal history and held for 5 min prior to cooling to the annealing temperature ($T_a$), which was just before the onset of $T_g$. Samples were held at $T_a$ for various annealing times ($t_a$) before being cooled to 30 °C at 20 °C·min$^{-1}$. The films were subsequently heated to 210 °C at various heating rates (2, 5 and 10 °C·min$^{-1}$).

3.4.2 Modulated temperature – differential scanning calorimetry

3.4.2.1 Introduction

Introduced by Reading in 1993 [293], modulated temperature – differential scanning calorimetry (mT-DSC) involves the application of a low frequency sinusoidal or periodic non-sinusoidal temperature program over the linear temperature program (Figure 3.8). Modulation is achieved by superimposing a periodic wave form of small amplitude on the linear heating/cooling program [294]. Unlike conventional DSC, mT-DSC allows the separation of components which are in-phase and out-of-phase with temperature modulation, as well as reversing and non-reversing thermal events. This provides additional information regarding time-dependent thermal events, kinetics and enthalpy evolution.
Figure 3.8 Modulated temperature programs; (a) sinusoidal oscillation, (b) dynamic DSC in isothermal/scan mode, (c) dynamic DSC in heat/cool mode. $\Delta T$ is the difference in temperature, $T_a$ is temperature amplitude and $p$ is period of modulation. Adapted from [294, 295]

The mT-DSC heat capacities obtained by deconvoluting the heat flow signal are displayed in Figure 3.9. The total heat capacity ($C_p$) is equivalent to a conventional DSC curve and is obtained by dividing the average heat capacity/heat flow by the average heating rate. The mT-DSC signal can be separated into in-phase and out of phase components. The storage heat capacity ($C_p'$), also known as the reversing heat capacity, is the in-phase component corresponding to reversible thermal events at time and temperature, such as the glass-rubber transition. The out-of-phase component is the loss or kinetic heat capacity ($C_p''$) which shows structure-changing kinetic responses that are irreversible. The vector sum of the reversing and kinetic heat capacities is referred to as the complex heat capacity ($C_p^*$). The non-reversing heat capacity ($C_{p\text{ non}}$) is obtained from the difference of the total and reversing heat capacities and reveals additional irreversible and kinetic events, such as enthalpy recovery across the $T_g$. Behaviour not observed in the reversing heat capacity may also be revealed. This is particularly useful for observing physical ageing and structural relaxation.
3.4.2.2 Experimental conditions

A linear heat-cool program with temperature amplitude of 1.5 °C, period of 60 s and frequency of 16.7 mHz was used for mT-DSC analysis, with materials heated from 50 to 150 °C at 2°C·min⁻¹. Prior to analysis, samples were heated to 150 °C at 40 °C·min⁻¹ and held for 5 min to remove prior thermal history, before being cooled to 30 °C at 10 °C·min⁻¹. Annealing was performed by using an identical thermal program to that used for conventional DSC. In addition to the total heat capacity, the in-phase/reversing (storage), out-of-phase/kinetic (loss) and non-reversing (difference of total and reversing) heat capacities were separated and analysed to reveal the glass transition, dissipative and enthalpy relaxation components, respectively.

3.4.3 Modulated temperature – thermomechanometry

3.4.3.1 Introduction

Modulated temperature – thermomechanometry (mT-TM) is a novel technique [269] that involves the application of an oscillating temperature to a linear/isothermal underlying
heating rate [270]. The modulated temperature program induces a sinusoidal response in specimen dimension change that can be resolved into reversing (in-phase with ΔT) and non-reversing (out-of-phase with ΔT) components. Fourier transformation is applied in real time to continuously determine the average value and amplitude value of the modulated temperature and modulated dimension change signals [296].

The overall governing equation of mT-TM is expressed as

$$\frac{dL}{dT} = \alpha \cdot \frac{dT}{dt} + f(t, T) \tag{3.1}$$

$$L_{\text{total}} = L_{\text{reversing}} + L_{\text{non-reversing}} \tag{3.2}$$

where L is length, T is temperature, t is time, \( \alpha \) is the thermal expansion coefficient, and \( f(t, T) \) is a function of time or temperature that describes changes in dimension due to deformation under applied load or relaxation of stresses within the material [269]. The left-hand part of Equation 3.1, referred to as the total dimension change, is composed on the right-side of two components; a reversing dimension change proportional to the time rate of change of temperature and a non-reversing dimension change obtained from the absolute values of temperature [296]. This relationship can be rewritten using Equation 3.2, while the various dimension changes in relation to one another are displayed in Figure 3.10.
This technique allows phenomena such as thermal expansion, glass-rubber transition, thermal and structural relaxation, polymer shrinkage and morphological changes to be observed. This is useful for characterisation of materials utilised in fields such as packaging, drug delivery and electrical applications. However, unlike conventional thermomechanical analysis (TMA), mT-TM enables the thermal expansion event of materials to be separated into the reversing curve, excluding non-reversible phenomena such as shrinkage, creep and flow. In addition, mT-TM allows relaxation behaviour to be directly measured during isothermal annealing. This enables the physical ageing properties of many materials to be probed.

3.4.3.2 Experimental conditions

A TA Instruments Q400EM Thermomechanical Analyser (Figure 3.11a) with quartz expansion probe (Figure 3.11b) was to measure the thermal transitions of the linear-CCS polymer composites. Dimension changes which are in-phase (reversible) and out-of-phase (non-reversible) with the modulated temperature program were separated and analysed. Samples with a height of ~2 mm were heated from 80 to 150 °C at a rate of 0.5 °C·min⁻¹. A sinusoidal modulation with 2 °C amplitude and 180 s period was superimposed on the
temperature ramp. Prior to testing, all samples were heated to and maintained at 150 °C for 5 min in order to eliminate any prior thermal history. The samples were cooled at 10 °C·min⁻¹ to 80 °C for testing. In order to study the effects of ageing, samples were cooled from 150 °C to a temperature just below the glass transition temperature (T₉) and held there for 1, 10 or 100 h before cooling to 80 °C and testing. Annealing temperatures (Tₐ) of 95 °C and 110 °C were used for the PS-CCS and PMMA-CCS films, respectively. The linear coefficient of thermal expansion (α) was calculated above the T₉ using Equation 3.3;

$$\alpha = \frac{dL}{dT} \cdot \frac{1}{L_0}$$  \hspace{1cm} (3.3)$$

where dL is the change in dimension, dT is the change in temperature and L₀ is the initial length of the sample.

![Figure 3.11](a) TA Instruments Q400 TMA, (b) quartz expansion probe

### 3.4.4 Colourimetry

A Konica Minolta CR-400 Chroma Meter was used to analyse the colourimetric properties of the dye-functionalised nanocomposites. CIELAB (L*, a*, b*) colour space coordinates were obtained, with results presented being the average of 10 measurements. A white ceramic tile (Y = 93.9, x = 0.3134, y = 0.3197) was used as a calibration reference.
3.4.5 Magnetometry

Magnetometric analysis was performed using a Lakeshore Model 7404 Vibrating Sample Magnetometer at 25 °C. The measurements were carried out in a maximum field of 12 kOe, which was applied parallel to the sample. Test specimens were made into disc shapes of ~5 mm in diameter, with results presented being the average of three repeats. Magnetic parameters including saturation magnetisation (M_s), remanence (M_r) and coercivity (H_c) were determined.

3.4.6 Thermomechanical analysis

An Instron Universal Test Instrument Model 4465, TA Instruments Q800 Dynamic Mechanical Analyser and Perkin Elmer Diamond DMA were used to characterise the thermomechanical properties of the polymer materials, including stress-strain, creep-recovery and modulated force – thermomechanometry (mf-TM). Specific analysis parameters for all polymer nanocomposites are provided in the respective Results chapters.

3.4.6.1 Creep and recovery models

A creep-recovery experiment involves the instantaneous application of a constant stress (σ) to a material under isothermal conditions, while observing the change in strain (ε) during this time. Following the creep period, the load is instantaneously removed and the material attempts to ‘recover’ towards its initial dimensions. A typical creep-recovery curve of a polymer is displayed in Figure 3.12, within which several distinct regions are noticeable. Firstly, an instantaneous increase in strain occurs with the application of a constant load, due to the elastic response of the polymer. This is followed by the viscoelastic response, involving time-dependent molecular rearrangement. Viscous flow of the polymer is observed towards the end of the load application period. Removal of the applied load results in a rapid drop in strain response, which is equal to the initial elastic response. The recovery period involves time-dependent molecular relaxations as the polymer attempts to regain original dimensions [297, 298]. Since the polymers experienced viscous flow, full recovery is unattainable resulting in permanent deformation.
Various models have been developed in an attempt to describe creep. Ideal materials that exhibit only elastic behaviour are represented using spring elements. This implies that energy stored by the material can be completely regained, resulting in instantaneous material deformation and complete recovery upon the application and removal of load, respectively [295]. In contrast, completely viscous materials (Newtonian fluids) exhibit time-dependent, non-instantaneous deformation and do not completely recover. These materials are represented by a dashpot element.

Two of the most popular early creep models are those of Maxwell and Kelvin-Voigt, however both have their limitations. The Maxwell model (Figure 3.13a) consists of a dashpot and spring element in series, although the sharp corners produced at region changes and continued deformation as long as stress is applied make it unsuitable for describing creep. In contrast, the Kelvin-Voigt model (Figure 3.13b) is composed of a dashpot and spring element in parallel, representing a reversible time-dependent response. However, it fails to show instantaneous response or continued flow under equilibrium stress. The four-element model (Figure 3.13c) combines the previous two models and allows a basic yet practical method of describing creep. Alternatively, the four-element model can be written as
The correlation between the four-element model and experimental creep-recovery curve components is displayed in Figure 3.14. More complex models exist, composed of many more elements to describe the complex nature of polymer molecular structure and behaviour.

\[
\varepsilon(f) = \left(\frac{\sigma_0}{E_1}\right) + \left(\frac{\sigma_0}{\eta_1}\right) + \left(\frac{\sigma_0}{E_2}\right) \cdot \left(1 - e^{-t/\tau}\right)
\]

(3.4)

where

\[
\tau = \frac{\eta_2}{E_2}
\]

(3.5)

Figure 3.13 Creep models; (a) Maxwell model, (b) Kelvin-Voigt model, (c) four-element model [299]
Of the numerous models available to explain recovery, the stretched exponential function of Kohlrausch, Williams and Watts (KWW) \cite{285, 300} is one of the most suitable, fitting experimental recovery data well. The KWW equation is expressed in Equation 3.6

\[ \phi = A \exp\left(-\frac{t}{\tau}\right)^\beta \] (3.6)

where A is the pre-exponential coefficient, t is time, \( \tau \) is the retardation time and \( \beta \) is the non-linearity coefficient (\( 0 < \beta < 1 \)). In this project, the four-element model and KWW equation were used to interpret the respective creep and recovery behaviour of polymer nanocomposites and blends.

### 3.4.6.2 Time-temperature superposition

Time-temperature superposition (TTS) is utilised to determine the temperature dependence of the rheological behaviour of a polymer liquid or to expand the time or frequency at a temperature at which the material is being characterised \cite{301}. It operates on the principle that low temperature corresponds to a high frequency response and vice-versa \cite{302}. The TTS method in this project involves analysing materials over a range of frequencies (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 Hz) at constant temperature increments (10 °C). From the resulting isothermal curves (x-axis = frequency, y-axis = storage modulus, loss modulus or \( \tan(\delta) \)) a reference curve was selected. All remaining
curves were shifted horizontally and vertically to superimpose on the reference curve, creating an expanded master curve as shown in Figure 3.15.

**Figure 3.15** Storage modulus ($E'$) frequency profiles of PMMA; (a) before shifting, (b) master curve generated after shifting ($T_r = 120 \, ^\circ C$)

The magnitude of horizontal and vertical shifting is expressed as a shift factor (horizontal shift factor = $\alpha_T$, vertical shift factor = $\alpha_V$). Vertical shift factors are utilised to account for changes in density at different temperatures and were calculated using Equation 3.7
where $\rho_g$ is the density at $T_g$ and $\rho$ is the density at temperature, $T$. Horizontal shift factors were determined using the Williams-Landel-Ferry (WLF) [244] model, as shown in Equation 3.8

$$\log(\alpha_T) = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$

(3.8)

where $C_1$ and $C_2$ are constants. $C_1$ is inversely proportional to the fractional free volume at $T_g$ ($f_g$), while $C_2$ is inversely proportional to the free volume expansion coefficient ($\alpha_f$) [303], as described in Equation 3.9 and 3.10.

$$C_1 = \frac{B}{\ln(10)f_g}$$

(3.9)

$$C_2 = \frac{f_g}{\alpha_f}$$

(3.10)

where $B$ is an arbitrary constant.

### 3.4.7 Fourier transform infrared spectroscopy

A Perkin-Elmer Spectrum 2000 FTIR spectrometer working in diffuse reflectance spectroscopy (DRIFTS) mode was used to characterise the molecular vibration of the functional groups in the POSS and reactive dyes. Anhydrous potassium bromide (KBr) was used as dispersing material and all spectra were scanned within the range 400-4000 cm$^{-1}$, with a total of 20 scans and a resolution of 8 cm$^{-1}$.

### 3.4.8 Thermogravimetry

A Perkin-Elmer TGA-7 thermogravimetric analyser with TAC-7/DX thermal analysis controller was used to analyse the thermal stability of the composites. Samples of $\sim$10 mg were heated to 850 °C at 20 °C·min$^{-1}$ in an inert environment provided by a 20 mL·min$^{-1}$
nitrogen purge. The mass loss and its derivative were recorded as a function of temperature.

The Coats and Redfern equation [304] (Equation 3.11) was used to evaluate the thermal stability of the polymer composites;

\[
\ln \left[ -\ln \left( \frac{1 - \alpha}{T^2} \right) \right] = \ln \left[ \left( \frac{AR}{\phi} \right) \cdot \left( 1 - \left( \frac{2RT}{E_a} \right) \right) \right] - \left( \frac{E_a}{RT} \right)
\]  

(3.11)

where \( \alpha \) is the fraction decomposed at temperature \( (T) \), \( \phi \) is the heating rate, \( R \) is the universal gas constant and \( A \) is the Arrhenius frequency factor. The equation assumes (a) only one reaction mechanism operates at a time, (b) the calculated activation energy for degradation (\( E_a \)) is for this mechanism and (c) product disappearance can be expressed using Equation 3.12 [305].

\[
\frac{d\alpha}{dt} = k(1 - \alpha)^n
\]

(3.12)

The fraction decomposed (\( \alpha \)) corresponds to the ratio of actual mass loss to total mass loss as shown in Equation 3.13;

\[
\alpha = \frac{M_0 - M}{M_0 - M_f}
\]

(3.13)

where \( M \) is the actual mass, \( M_0 \) is the initial mass and \( M_f \) is the final mass of the material. If the reaction order (\( n \)) is assumed to be 1, plotting \( \ln[-\ln(1 - \alpha)/T^2] \) vs. \( 1/T \) gives a straight line with the slope equal to \(-E_a/R\).

3.4.9 Ultraviolet-visible spectroscopy

A Varian 50 Bio UV visible spectrophotometer was used to analyse the absorbance and transmittance of the nanocomposites. Samples were scanned from 800 to 200 nm using a duel beam at a scan rate of 108 nm-min\(^{-1}\).
3.4.10 Small angle X-ray scattering

A Bruker AXS Nanostar was used to study the morphology of the polymer composites. A Cu X-ray source (\(\lambda = 0.1542\) nm) was generated at kV = 40 and mV = 35. The distance from the sample to detector was 106 cm. The radius of gyration (R_g) of polymer materials was determined by plotting ln(I) vs. q^2. This gives a linear graph from which the slope can be substituted into Equation 3.14 to obtain R_g.

\[-\text{slope} = \frac{R_g^2}{3}\]  

(3.14)

3.4.11 Scanning electron microscopy

Scanning electron microscopy (SEM) images of the nanocomposites were taken using a FEI Quanta 200 environmental scanning electron microscope (ESEM) operating at 20 kV under low vacuum. Composites with average dimensions \(~4.00 \times 4.00 \times 0.70\) mm^3 were mounted to the specimen holder using conducting carbon-impregnated tape.

3.4.12 Transmission electron microscopy

The morphology of the magnetite-functionalised carbon nanotubes was characterised using a JEOL 10-10 high-resolution transmission electron microscope (TEM) operating at 100 kV of accelerated voltage. Samples were dissolved in absolute ethanol and ultrasonically vibrated for 10 min before being dropped onto a 200 mesh carbon-coated copper grid. The ethanol was allowed to dry in air.
CHAPTER 4: GLASS TRANSITION, RELAXATION AND EXPANSION OF LINEAR-CORE CROSS-LINKED STAR POLYMER BLENDS*

4.1 Introduction

A polymeric material’s glass transition properties are arguably one it’s most important characteristics, ultimately determining the active service applications and influencing other material attributes, such as mechanical and rheological properties. A similarly related phenomenon is that of structural relaxation, where the specific volume within a polymer decreases as the material attempts to attain equilibrium during isothermal annealing below its $T_g$. This behaviour can significantly alter polymer characteristics, the effects of which are known as physical ageing. The understanding and control of such phenomenon are vital in synthesising and processing polymers with specific applications and properties.

The most common way of altering a polymer’s glass transition properties is through blending with other polymers or addition of fillers or additives. However, properties may be difficult to manipulate due to issues arising with co-polymer and/or matrix-filler compatibility and filler aggregation and agglomeration. These hindrances may be overcome through blending with core cross-linked star (CCS) polymers. CCS polymers have attracted significant academic and industrial attention within the last 10-20 years, due to their unique properties and synthesis techniques that allow for a great deal of architectural structural control. Although the glass transition, structural relaxation and thermal expansion have been extensively studied, the literature available regarding similar properties of like linear-CCS polymer blends [234] is virtually non-existent. It is proposed that polymer properties influenced by the degree of chain segmental rotation and free volume, including glass transition temperature ($T_g$), enthalpy ($\Delta H$) and linear coefficient of

thermal expansion (CTE, \(\alpha\)) can be manipulated by the inclusion of CCS polymers into a linear matrix. The hypothesis is that CCS polymers behave in a similar manner to physical crosslinks.

This chapter focuses on blends of linear, amorphous PS or PMMA and CCS polymers. The CCS polymers are composed of a poly(ethylene glycol dimethacrylate) core and linear PS or PMMA arms to ensure complete compatibility with their respective polymer matrices. The influence of CCS polymers on the glass transition, structural relaxation and expansion properties are determined enthalpically and volumetrically using conventional and modulated temperature – DSC and mT-TM, respectively. By utilising the two complimentary modulated temperature analysis techniques, data can be separated into reversing and non-reversing components that provide specific information about glass transition, relaxation and expansion processes. Structural relaxation is evaluated by annealing materials below the \(T_g\) for logarithmically spaced time intervals (1, 10, 100 h). Furthermore, volumetric relaxation during isothermal annealing was directly measured using mT-TM in a novel application of the technique.

4.2 Materials and methods

4.2.1 Materials, experimental details and blend nomenclature

Material information, blend preparation procedures and characterisation methods are detailed in Chapter 3. Table 4.1 displays the composition and nomenclature of the linear-CCS polymer blends. CCS polymers were added at concentrations of 10 and 30 %·wt to determine the influence of low and high loadings, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear polymer concentration (%·wt)</th>
<th>CCS polymer concentration (%·wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>PS-02</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>PS-03</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>
4.3 Results and discussion

4.3.1 Conventional DSC

4.3.1.1 Contribution of CCS polymer concentration

PS-CCS polymer blend endotherms heated at 2 °C·min⁻¹ are presented in Figure 4.1a, with the data scaled and shifted 0.2 J·°C⁻¹ g⁻¹ apart for clarity. The $T_g$ data is summarised in Table 4.2. It is well established that the only correct definition of $T_g$ is obtained when a polymer is cooled from the liquid equilibrium state, since only these cooling definitions are independent of thermal history in the glassy state. However, the overwhelming majority of ageing experiments using DSC obtain $T_g$ and thermal data through heating, due to the greater control in calibration and temperature change available. Pure linear PS (PS-01) displayed a broad, single relaxation endotherm, with a $T_g$ of 95 °C. The incorporation of CCS polymer into the linear PS matrix caused the glass transition temperature to increase, with PS-02 and PS-03 displaying $T_g$ values of 98 and 99 °C, respectively. Similarly, the $T_g$ of PMMA increased with the addition of the hyperbranched particles as shown in Figure 4.1b, ranging from 114 °C (PMMA-01) to 118 (PMMA-02) and 121 °C (PMMA-03).

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ (°C), $q_h = 2$ °C·min⁻¹</th>
<th>$T_g$ (°C), $q_h = 5$ °C·min⁻¹</th>
<th>$T_g$ (°C), $q_h = 10$ °C·min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_a =$ 0 h</td>
<td>$t_a =$ 1 h</td>
<td>$t_a =$ 10 h</td>
</tr>
<tr>
<td>PS-01</td>
<td>95</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>PS-02</td>
<td>98</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>PS-03</td>
<td>99</td>
<td>99</td>
<td>100</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>114</td>
<td>112</td>
<td>114</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>118</td>
<td>117</td>
<td>118</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>121</td>
<td>120</td>
<td>121</td>
</tr>
</tbody>
</table>
Chapter 4: Glass Transition, Relaxation and Expansion of Linear-CCS Polymer Blends

Figure 4.1 Endotherms of linear-CCS polymer blends heated at 2 °C·min⁻¹; (a) PS-CCS blends, (b) PMMA-CCS blends

The relaxation enthalpy (ΔH) of the pure polymers and blends are displayed in Table 4.3. Enthalpy values were determined by taking the difference of the peak areas under the aged and unaged endotherms, respectively, as described by Equation 4.1

$$\Delta H = \int_{T_1}^{T_2} \Delta C_p \, dT$$  \hspace{1cm} (4.1)
where $T_2$ is taken sufficiently above $T_g$ to ensure that the sample is at equilibrium and $T_1$ is taken sufficiently below $T_g$ where the difference in specific heat for annealed and unannealed samples, at different annealing times, is negligible [306]. The reference unannealed material has a $\Delta H$ value of 0. Following heating at 2 °C·min$^{-1}$, PS-01 and PMMA-01 annealed for 1 h yielded $\Delta H$ values of 0.76 and 1.16 J·g$^{-1}$, respectively. As summarised in Table 4.3, both PS and PMMA films experienced a decrease in enthalpy with CCS polymer concentration.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta H$ (J·g$^{-1}$), $q_h = 2$ °C·min$^{-1}$</th>
<th>$\Delta H$ (J·g$^{-1}$), $q_h = 5$ °C·min$^{-1}$</th>
<th>$\Delta H$ (J·g$^{-1}$), $q_h = 10$ °C·min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_a = 1$ h</td>
<td>$t_a = 10$ h</td>
<td>$t_a = 100$ h</td>
</tr>
<tr>
<td>PS-01</td>
<td>0.76</td>
<td>1.38</td>
<td>2.70</td>
</tr>
<tr>
<td>PS-02</td>
<td>0.62</td>
<td>1.16</td>
<td>2.46</td>
</tr>
<tr>
<td>PS-03</td>
<td>0.54</td>
<td>1.02</td>
<td>2.11</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>1.16</td>
<td>1.90</td>
<td>2.88</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>0.84</td>
<td>1.77</td>
<td>2.71</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>0.88</td>
<td>0.92</td>
<td>2.03</td>
</tr>
</tbody>
</table>

The observed increase in $T_g$ and decrease in $\Delta H$ suggests that the CCS polymers behave as physical crosslinks [307-309], as displayed in Figure 4.2. The arms on the CCS polymer have one end tethered to the crosslinked core, leaving the branches free to entangle within the linear matrix. However, since one end of the CCS polymer arm is bonded to the crosslinked core, chain motion is hindered, leading to the CCS polymer arms restricting segmental chain motions of the linear matrix. Furthermore, CCS polymer entanglements can reduce the length of linear chain segments, restricting the degree of rotation the segment can experience. As shown in Figure 4.1, endotherms became broader and diminished in intensity with the incorporation of CCS polymers, suggesting a reduction in the degrees of freedom as the blend experiences glass-rubber transition across a broader temperature range. The glass transition contributions observed within the linear-CCS polymer blends are attributed to only the linear matrix and CCS polymer arms. The PEGDMA core displayed no $T_g$ of its own due to its rigidity and hindered mobility. The glass transition behaviour of star and dendritic polymers are generally believed to be dependent
only on the molecular weight of an arm or dendron, not the molecular weight of the entire molecule [310]. A single endotherm was observed for all blends, along with the increase in \( T_g \) and \( \Delta H \). This confirms good miscibility of CCS polymer arms/branches within the linear matrices, with no evident occurrence of phase separation. This was expected because of the excellent solubility properties of star polymers [311] and due to the CCS polymer arms and linear matrix being the same polymer.

The endotherms of PS-01 and PS-02 heated at 2, 5 and 10 °C·min\(^{-1}\) are displayed in Figure 4.3. Increasing the heating rate \( (q_h) \) yielded endotherms that shifted towards higher temperatures, subsequently resulting in increased \( T_g \) values. PS-01 exhibited \( T_g \) values ranging from 95 °C \( (q_h = 2 \text{ °C·min}^{-1}) \) to 97 °C \( (q_h = 10 \text{ °C·min}^{-1}) \), with PS-02 yielding a \( T_g \) range of 98 to 100 °C for the same respective heating rates. This behaviour is indicative of the kinetic nature of the glass transition and relaxation processes and is in correlation with results obtained by Papageorgiou et al [312]. The kinetic theory of glass transition considers the molecular and macromolecular response within a varying time frame, predicting that \( T_g \) is dependent on the heating and cooling rate [238]. \( T_g \) can be defined as the temperature at which the relaxation time of a material is identical to the experimental
time scale [259]. Slower $q_h$ values give the polymer chain segments more time to undergo segmental motion. Increasing $q_h$ reduces this time-frame, effectively limiting motions until higher temperatures, with the polymer remaining denser. The experimentally observed increase in $T_g$ with $q_h$ is in agreement with the theory prediction. $\Delta H$ was observed to increase with heating rate. This at first appears to be contrary to the well-known enthalpy being independent of $q_h$ [313]. However, increasing heating rate did decrease heat capacity, as shown in Figure 4.3. Since enthalpy and heat capacity are inversely proportional at constant pressure [314], the reduced heat capacities resulted in increased $\Delta H$ values with $q_h$.

![Figure 4.3](image)

**Figure 4.3** Endotherms of (i) PS-01 and (ii) PS-02, heated at various rates

### 4.3.1.2 Effect of isothermal annealing

In order to observe the effect of physical ageing on the glass transition and relaxation properties, the materials were annealed by maintaining them at a constant temperature (annealing temperature, $T_a$) for logarithmically spaced time intervals (annealing time, $t_a$). The $T_a$ was before the onset of glass transition. Non-annealed and annealed endotherms of PS-01 are presented in Figure 4.4a. Annealing for 1 h at 90 °C yielded a taller endotherm with increased peak area compared with non-annealing. Peak area continued to increase with $t_a$, with samples annealed for 100 h producing the tallest peaks. During isothermal sub-$T_g$ annealing, the internal energy (free volume/enthalpy) decreases as the material...
approaches thermal equilibrium. When an annealed polymer is reheated through and above $T_g$, increased segmental mobility allows for rapid equilibration with associated enthalpy absorption, manifesting itself in the endotherm peak. This behaviour is presented in Figure 4.4b. Since longer annealing times will result in a greater amount of time to approach equilibrium (and subsequent energy absorption past the $T_g$), samples annealed for the longest $t_a$ (in this case, 100 h) yielded the largest peak area/ΔH values (refer Table 4.3). Similar trends were observed by Doulache et al [315] who determined physical ageing reduced segmental mobility with $t_a$, leading to an increase in ΔH.

On annealing for 1 h, the peak temperature of PS-01 shifted to 99 °C. Increasing $t_a$ caused the endotherm peak to shift back towards the non-annealed peak temperature. PS-02 and PS-03 displayed similar behaviour, exhibiting more pronounced peak shifts than pure PS. Accompanying this shift in endotherm peak location was a corresponding shift in $T_g$, as shown in Figure 4.5. Upon annealing for 1 h, the $T_g$ of PS-01 heated at 2 °C·min$^{-1}$ shifted to 94 °C, slightly lower than its non-annealed counterpart. Increasing $t_a$ subsequently caused the $T_g$ to increase, following the same trend as the peak temperatures. The $T_g$ of PS-01 reached a maximum of 97 °C at $t_a$ = 100 h. The slightly exponential behaviour was also displayed by PMMA films. Blends displayed higher $T_g$ and lower ΔH values than pure matrices annealed for identical time periods, confirming that the CCS polymers continued to restrict molecular motions during the ageing process.
Figure 4.4 (a) Influence of annealing on endotherm of PS-01 heated at 2 °C·min⁻¹, (b) schematic of rapid equilibration following sub-\(T_g\) isothermal annealing.
As summarised in Table 4.2, most films heated at 2 °C·min⁻¹ displayed lower \( T_g \) and peak temperatures following annealing for 1 h. As the heating rate increased, materials annealed for 1 h exhibited an increase or no change in endotherm location. Although the behaviour may seem insignificant, this initial decrease in endotherm location followed by a gradual increase was observed by Struik [256], who related the process of physical ageing to the
concept of free volume \( (V_F) \). The transport mobility of particles in a closely packed system primarily depends on the degree of packing (free volume). Above \( T_g \), the free volume and mobility are large. Upon cooling, both free volume and mobility decrease simultaneously. Furthermore, when a polymer is cooled to below \( T_g \) and held for a period of time, the mobility is small although not zero. Due to this reduced mobility, the \( V_F \) is greater at this stage than at equilibrium. This increased volume is responsible for the endotherm peak shift to lower temperatures and alteration of polymer properties. As \( t_a \) is increased, the \( V_F \) and mobility will continue to decrease gradually, shifting the peaks back towards the non-annealed peak location and eventually surpassing it. Overall, \( T_g \) and \( \Delta H \) increased with \( t_a \), as predicted by Figures 4.4b and 4.5.

In order to further examine structural evolution during annealing, the fictive temperature \( (T_f) \) of the linear-CCS polymer blends was determined. The \( T_f \) is defined as the temperature at which the glassy state of a polymer would be in thermal equilibrium and is obtained at the intersection of the extrapolated glassy line of the volume/enthalpy and equilibrium line [265]. The limiting value of the fictive temperature \( (T'_f) \) can be obtained by extrapolating from a temperature deep in the glassy state [279]. The \( T'_f \) values of all materials are summarised in Table 4.4. The limiting fictive temperature was determined using the method proposed by Moynihan et al [316] displayed in Equation 4.2

\[
\int_{T'}^{T_f} (C_{pl} - C_{pg})dT_f = \int_{T}^{T*} (C_{p} - C_{pg})dT
\]

where \( C_{pl} \) and \( C_{pg} \) are the heat capacity of the liquid and glassy regions, respectively, and \( T* \) and \( T' \) are temperatures above and below the glass transition region, respectively. Non-annealed PS-01 displayed a \( T'_f \) of 94 °C, lower than its \( T_g \). This behaviour was observed for all materials, with the \( T'_f \) being lower than the glass transition temperature as is expected of the fictive temperature in the glassy region. Increasing the annealing time caused the \( T'_f \) to decrease, reaching a minimum of 88 °C at \( t_a = 100 \) h. This is consistent with various reported instances of the \( T'_f \) decreasing with increasing annealing time [289, 317, 318]. Similar behaviour was observed for PMMA, with \( T'_f \) diminishing with increasing \( t_a \). The blends continued to display higher \( T'_f \) values than pure linear polymers, due to the crosslink-like behaviour of CCS polymers.
Table 4.4 $T'_f$ data of linear-CCS polymer blends obtained from conventional DSC

<table>
<thead>
<tr>
<th>Material</th>
<th>$T'_f$ ($^\circ$C), $q_h$ = 2 °C·min$^{-1}$</th>
<th>$T'_f$ ($^\circ$C), $q_h$ = 5 °C·min$^{-1}$</th>
<th>$T'_f$ ($^\circ$C), $q_h$ = 10 °C·min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_a$ = 0 h</td>
<td>$t_a$ = 1 h</td>
<td>$t_a$ = 10 h</td>
</tr>
<tr>
<td>PS-01</td>
<td>94</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>PS-02</td>
<td>97</td>
<td>95</td>
<td>93</td>
</tr>
<tr>
<td>PS-03</td>
<td>98</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>113</td>
<td>111</td>
<td>109</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>116</td>
<td>111</td>
<td>110</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>121</td>
<td>113</td>
<td>112</td>
</tr>
</tbody>
</table>

4.3.2 Modulated temperature – differential scanning calorimetry

4.3.2.1 Contribution of CCS polymer concentration

The total heat capacity of PMMA-CCS blends are displayed in Figure 4.6a. This data is equivalent to a conventional DSC endotherm and consists of the storage component (reversing) and a superimposed non-reversing component. As with their conventional DSC counterparts, a single, broad glass transition region was observed for all total heat capacities. The addition of CCS polymer shifted these endotherms towards higher temperatures. The storage (reversing) component isolates the $T_g$ of an amorphous polymer and is clearly observed as a step-change in heat capacity, as shown in Figure 4.6b. Storage $T_g$ values are summarised in Table 4.5 PMMA-01 exhibited a $T_g$ value of 118 °C, which increased with the addition of CCS polymers to 119 (PMMA-02) and 122 °C (PMMA-03). Similarly, the $T_g$ of pure PS was observed to increase from 99 °C, to 101 and 103 °C for PS-02 and PS-03, respectively. The $T_g$ values obtained from the storage heat capacity inflections were slightly higher than their total and conventional DSC equivalents. This is due to the reversing heat capacity $T_g$ inflection being determined from the response to instantaneous heating rate rather than the underlying heating rate [266]. mT-DSC allows for better resolution of $T_g$ and a greater instantaneous heating rate than conventional DSC. This clear shift in endotherm (and $T_g$) to higher temperatures is indicative of the effect CCS polymers have on segmental motions of matrix chains.
Chapter 4: Glass Transition, Relaxation and Expansion of Linear-CCS Polymer Blends

(a) Total Heat Capacity (J°C⁻¹g⁻¹) vs Temperature (°C)

(b) Storage Heat Capacity (J°C⁻¹g⁻¹) vs Temperature (°C)
Figure 4.6 mT-DSC endotherms of PMMA-CCS polymer blends; (a) total, (b) storage, (c) loss, (d) non-reversing
Table 4.5 $T_g$ data of linear-CCS polymer blends obtained from mT-DSC (storage heat capacity)

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_a$ = 0 h</th>
<th>$t_a$ = 1 h</th>
<th>$t_a$ = 10 h</th>
<th>$t_a$ = 100 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>99</td>
<td>99</td>
<td>100</td>
<td>102</td>
</tr>
<tr>
<td>PS-02</td>
<td>101</td>
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<td>PS-03</td>
<td>103</td>
<td>104</td>
<td>105</td>
<td>107</td>
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<tr>
<td>PMMA-01</td>
<td>118</td>
<td>120</td>
<td>121</td>
<td>124</td>
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<tr>
<td>PMMA-02</td>
<td>119</td>
<td>121</td>
<td>123</td>
<td>127</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>122</td>
<td>124</td>
<td>128</td>
<td>129</td>
</tr>
</tbody>
</table>

The loss heat capacities of the PMMA-CCS blends (Figure 4.6c) display a broad endotherm, with a single dissipation event noticeable (the glass-rubber transition). Increasing CCS polymer content caused the endotherms to move towards higher temperatures, as with their respective total and storage counterparts. The loss heat capacity provides information regarding changes in structure and entropy. The loss endotherm areas decreased with CCS polymer concentration because of a reduction in enthalpy. These results are in good correlation to the enthalpy data obtained using conventional DSC. The non-reversing (difference of total and storage heat capacities) endotherms of PMMA-CCS polymer blends are displayed in Figure 4.6d, while the non-reversing enthalpy values of the blends are presented in Table 4.6. As with the total and storage heat capacities, the non-reversing endotherms of PMMA-02 and PMMA-03 shifted towards higher temperatures, accompanying the increase in $T_g$. PMMA-01 annealed for 1 h displayed a $\Delta H$ value of 1.94 J·g$^{-1}$, which decreased with increasing CCS polymer concentration, reaching values of 1.46 and 1.65 J·g$^{-1}$ for PMMA-02 and PMMA-03, respectively, at $t_a$ = 1 h. The reduced enthalpy in blends is attributed to the CCS polymers confining matrix chains and complimenting the observed increase in $T_g$ and endotherm location.
Chapter 4: Glass Transition, Relaxation and Expansion of Linear-CCS Polymer Blends

Table 4.6 Enthalpy data of linear-CCS polymer blends obtained from mT-DSC (non-reversing heat capacity)

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_a = 1\ h$</th>
<th>$t_a = 10\ h$</th>
<th>$t_a = 100\ h$</th>
</tr>
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<tbody>
<tr>
<td>PS-01</td>
<td>2.35</td>
<td>2.63</td>
<td>3.43</td>
</tr>
<tr>
<td>PS-02</td>
<td>2.09</td>
<td>2.57</td>
<td>2.61</td>
</tr>
<tr>
<td>PS-03</td>
<td>1.26</td>
<td>1.93</td>
<td>2.29</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>1.94</td>
<td>2.38</td>
<td>3.01</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>1.46</td>
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<tr>
<td>PMMA-03</td>
<td>1.65</td>
<td>1.84</td>
<td>2.42</td>
</tr>
</tbody>
</table>

4.3.2.2 Effect of isothermal annealing

The total heat capacities of PS-01 and PS-02 annealed for logarithmically spaced time intervals are displayed in Figure 4.7a. As with conventional DSC, the characteristic increase in endotherm peak temperature and area with $t_a$ is observed. The increase in peak position and intensity correspond to the superimposed storage and non-reversing components, respectively. Separating the storage heat capacity (Figure 4.7b) reveals the evolution of $T_g$ during the ageing process. An increase in $T_g$ with annealing time is clearly visible, as expected for the decrease in polymer chain mobility that occurs during structural relaxation. Unlike the total heat capacity, no peak is observed in the storage heat capacity. The storage heat capacity provides information on the glass transition only, with the kinetic process removed from the endotherm. The loss heat capacities (Figure 4.7c) show an increase in peak area with $t_a$, indicative of the greater amount of heat dissipation (energy loss) as the physical ageing time-period is increased. As with the total and storage heat capacities, the loss endotherms shift to higher temperatures with glass transition temperature and annealing time, with $t_a = 100\ h$ yielding the largest shift.

It is well established that enthalpy lost during the isothermal annealing period is regained as an excess endotherm during subsequent reheating through the $T_g$. In order to analyse this event, the non-reversing heat capacities of PS-01 and PS-02 were separated and are displayed in Figure 4.7d. As with all other DSC endotherms, the non-reversing peaks shift towards higher temperatures. Of particular importance is the evolution of enthalpy
recovery, which can be isolated and examined using the non-reversing peak area. PS-01 annealed for 1 h displayed a ΔH of 2.35 J·g⁻¹. Enthalpy continued to increase with annealing time, reaching a maximum value of 3.43 J·g⁻¹ at tₐ = 100 h. Increasing the annealing time enables an amorphous material to approach thermal equilibrium. Since equilibrium at Tₐ is a lower energy state than that at Tₕ and the enthalpy must be recovered, a greater amount of energy is required to heat materials through the glass transition. When reheated, the energy dissipated during annealing is manifested in the peak of the non-reversing endotherm, with materials annealed for longer times yielding the largest area (more energy is required). PS-02 displayed a similar increase in ΔH with tₐ, displaying values ranging from 2.09 (tₐ = 1 h) to 2.61 J·g⁻¹ (tₐ = 100 h). PS-02 and PS-03 continued to display lower enthalpy values than pure PS for materials annealed at equal annealing times. This suggests that CCS polymer has placed restrictions on polymer chain motions and played an active role in suppressing enthalpy recovery.
4.3.3 Modulated temperature – thermomechanometry

Up to this point, the enthalpic glass transition and relaxation properties of linear-CCS polymer blends have been characterised using DSC. In order to analyse the volumetric properties, modulated temperature – thermomechanometry (mT-TM) was utilised. As with mT-DSC, in-phase and out-of-phase data can be separated using mT-TM. This allows reversing and non-reversing behaviour to be obtained without interference from other in-phase/out-of-phase data. In addition, mT-TM allows dimension change during relaxation to be observed in real time, a novel application which is yet to be attempted and reported.

mT-TM and DSC are complimentary techniques, especially when the method of determining the measurable parameter (y-axis) is considered. The coefficient of thermal expansion (obtained from mT-TM) and heat capacity (obtained from DSC) are calculated using Equations 4.3 and 4.4, respectively

\[
\alpha = \frac{dD}{dT} \tag{4.3}
\]
\[ C_p = \frac{dH}{dT} \] (4.4)

where, \( \alpha \) is the coefficient of thermal expansion (CTE), \( D \) is dimension change, \( C_p \) is heat capacity and \( H \) is enthalpy. As displayed by the previous equations, the primary difference between the two techniques is the value being measured, enthalpy (DSC) or dimension/volume change (mT-TM). To directly highlight the similarity between the techniques, measured data obtained using both DSC and mT-TM are compared in Figure 4.8. The red curves show the heat capacity and reversing dimension change; data regularly obtained from DSC and mT-TM, respectively. Taking the 1\textsuperscript{st} derivative of the reversing dimension change provides the coefficient of thermal expansion. When plotted against temperature, the resulting curve resembles that of a heat capacity endotherm. Similarly, integrating the heat capacity endotherm yields an enthalpy curve which mirrors the reversing dimension change graph. This similarity in calculation and spectra demonstrates the ability to bridge enthalpic and volumetric data by utilising DSC and mT-TM in combination.
Figure 4.8 Schematic displaying complimentary nature of DSC and mT-TM
4.3.3.1 Contribution of CCS polymer concentration

The reversing and non-reversing dimensional curves of the PS-CCS polymer blends are shown in Figure 4.9a and b, respectively, while the $T_g$ of the materials are summarised in Table 4.7. The reversing (in-phase) curve displays only the thermal expansion component of the material, removing non-reversing phenomena such as creep and flow. Pure PS exhibited an increase in dimension change (expansion) with temperature, with a single inflection and $T_g$ of 101 °C. Incorporation of CCS polymers into the matrix caused the $T_g$ to increase, with PS-02 and PS-03 both exhibiting $T_g$ values of 103 °C, respectively. As displayed in Figure 4.10a and b, PMMA films displayed higher $T_g$ values following the addition of CCS polymers, ranging from 120 °C (PMMA-01) to 124 °C (PMMA-02) and 125 °C (PMMA-03). The $T_g$ values obtained from mT-TM are several degrees higher than those observed using DSC, due to differences in measurement mechanisms and technique sensitivity. However, $T_g$ trends observed using both techniques were identical and can be considered to be in good correlation with one another.

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_a = 0$ h</th>
<th>$t_a = 1$ h</th>
<th>$t_a = 10$ h</th>
<th>$t_a = 100$ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>101</td>
<td>102</td>
<td>104</td>
<td>105</td>
</tr>
<tr>
<td>PS-02</td>
<td>103</td>
<td>104</td>
<td>105</td>
<td>106</td>
</tr>
<tr>
<td>PS-03</td>
<td>103</td>
<td>105</td>
<td>106</td>
<td>108</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>120</td>
<td>123</td>
<td>125</td>
<td>126</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>124</td>
<td>125</td>
<td>125</td>
<td>128</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>125</td>
<td>126</td>
<td>126</td>
<td>128</td>
</tr>
</tbody>
</table>
Figure 4.9 mT-TM curves of PS-CCS polymer blends; (a) reversing, (b) non-reversing
The linear coefficient of thermal expansion (CTE, $\alpha$) of the materials were calculated from the reversing curves using Equation 4.3 (refer Section 4.3.3) and are summarised in Table 4.8. The CTE was determined both below and above the $T_g$, although the former is generally considered to be more useful since polymers lose most of their mechanical properties above the $T_g$ [319]. PS-01 exhibited a below-$T_g$ $\alpha$ value of 135. Incorporating CCS polymer into the PS matrix reduced $\alpha$, with PS-02 and PS-03 displaying values of 94 and 85, respectively. This occurrence was also noticeable visually by the decrease in curve gradient.
in the blends. PMMA films showed similar trends, with $\alpha$ values below the $T_g$ reducing from 151 (PMMA-01) to 134 (PMMA-02) and 106 (PMMA-03). Above the $T_g$, thermal expansion occurred at a faster rate, due to the polymer experiencing greater flow in the liquid state. As with their sub-$T_g$ counterparts, $\alpha$ values above the $T_g$ decreased with CCS polymer content. The non-reversing curves show that shrinkage (reduction in dimension) occurs in all materials at temperatures above the $T_g$. The degree of shrinkage is proportional to the degree of thermal expansion, since the former is dependent on the latter. As CCS polymer content was increased, the gradient of the curves past the $T_g$ decreased. This indicates that shrinkage and flow occur at a slower rate and over a greater temperature range, suggesting that CCS polymers provide an active role in dimensional stability brought about by network promotion.

**Table 4.8** Linear coefficient of thermal expansion data of linear-CCS polymer blends

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha (10^{-6} \text{C}^{-1})$ - Below $T_g$</th>
<th>$\alpha (10^{-6} \text{C}^{-1})$ - Above $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_a = 0$ h</td>
<td>$t_a = 1$ h</td>
</tr>
<tr>
<td>PS-01</td>
<td>135</td>
<td>101</td>
</tr>
<tr>
<td>PS-02</td>
<td>94</td>
<td>84</td>
</tr>
<tr>
<td>PS-03</td>
<td>85</td>
<td>81</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>151</td>
<td>149</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>134</td>
<td>125</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>106</td>
<td>80</td>
</tr>
</tbody>
</table>

As for the heat capacity change, thermal expansion in polymers is governed primarily by conformational changes within the material, with vibrational modes providing smaller contributions [320]. The addition of CCS polymer restricts the conformational changes of the matrix polymer chains, resulting in a decrease in $\alpha$ below the $T_g$. The reduction in thermal expansion above the $T_g$ in the blends is attributed to the restrictions the CCS polymer arms impart on the flow of the matrix, reducing its expansion ability. This restriction in segmental motion is in correlation with results observed using conventional and mT-DSC and is characteristic of the ability of star polymers to manipulate flow properties. The magnitude of thermal expansion within blends is dependent on both the linear and CCS polymer components and the interactions between the two [319].
significant reduction in $\alpha$ and the observation of a single inflection point in both the reversing and non-reversing curves confirms that no phase separation has occurred.

4.3.3.2 Effect of isothermal annealing

The DSC annealing studies provided information regarding the influence CCS polymers have on enthalpy relaxation. Utilising mT-TM allows relaxation to be examined from a linear dimension, providing a second approach from which physical ageing can be interpreted. Figure 4.11a shows the reversing curves of the PMMA-01 (linear PMMA) and PMMA-03 (30 %·wt CCS polymer content) annealed for 1, 10 and 100 h at 110 °C. Annealing for 1 h produced curves with similar characteristics to their non-annealed counterparts. Increasing the annealing time ($t_a$) to 10 h caused the gradient of the curves past the $T_g$ to increase, while materials annealed for 100 h produced the steepest curves.

As summarised in Table 4.8, below-$T_g$ $\alpha$ values decreased with annealing time. Conversely, the above-$T_g$ $\alpha$ was observed to increase with annealing time. This is phenomenon is due to the material recovering free volume lost during annealing, requiring expansion to occur more rapidly to return to equilibrium at high temperature. At $t_a = 100$ h, materials required the greatest recovery of $V_F$, displaying the fastest rate of expansion past $T_g$. This behaviour can be compared with the increase in DSC peak enthalpy that occurs following reheating through the glass transition region (refer Figure 4.4a). Similarly, the decrease/increase in thermal expansion with $t_a$ resulted in a proportional decrease/increase in polymer shrinkage, as shown in Figure 4.11b. PMMA-01 exhibited a $T_g$ of 120 °C. Upon annealing for 1 h, the $T_g$ increased to 123 °C, eventually reaching 126 °C at $t_a = 100$ h. The blends (PMMA-02 and PMMA-03) showed similar trends to their un-annealed counterparts, exhibiting higher $T_g$ and lower $\alpha$ and shrinkage rates than pure PMMA. Similar trends were observed in PS-CCS blends. These results are in good correlation with those observed using conventional and mT-DSC.
4.3.3.3 Volume relaxation during isothermal annealing

As mentioned previously, \( V_F \) decreases during annealing as a polymer attempts to attain thermal equilibrium. Robertson \[321\] attributed volume relaxation to polymer chain backbone bond transitions, arising from the different packing arrangements available to trans and gauche bonds. The subsequent reduction in physical space during annealing leads to a subsequent decrease in material dimension as occupied volume increases and the polymer becomes denser. Figure 4.12 shows material dimension length as a function of
time during isothermal annealing below $T_g$. Initially, following $\sim 1$ h of relatively little change, material dimension begins to decrease rapidly. As $t_a$ is increased, the rate of dimension change progressively slows as the polymer approaches thermal equilibrium. The total dimension change during annealing decreased as CCS polymer concentration increased, due to the partial restrictions imparted to restrain/resist flow and expansion ability. Although experimental techniques including DSC and dilatometry have been utilised to observe volume relaxation [255, 263], this is the first reported use of mT-TM.

Figure 4.12 Relaxation curves of PMMA-CCS polymer blends ($q_c = 5 \, ^\circ\text{C}\cdot\text{min}^{-1}$, $t_a = 10$ h, $T_a = 110$ °C)

The KWW stretched-exponential function was utilised in order to interpret the relaxation data. This function has successfully been applied to various relaxation processes in a wide range of materials. The equation parameters are summarised in Table 4.9. Incorporating CCS polymers into the linear matrix caused the average relaxation time ($\tau$) to increase, ranging from 28 min (PS-01) and 22 min (PMMA-01) to 355 min (PS-03) and 327 min (PMMA-03). Although real polymers display a range of relaxation times due to their molecular weight distribution, a single $\tau$ provides a convenient and effective estimate on how changes in material structure can influence behaviour [299]. The increased $\tau$ values of the blends indicate that CCS polymers retard the rate of structural relaxation. This can be attributed to CCS polymers occupying vacant volume and restricting the cooperative motions of polymer matrix chains, thereby increasing the time needed to attain thermal
equilibrium and reducing the amount of molecular rearrangement that can occur. These observations displayed similarities to the influence crosslinks have on relaxation and ageing [308, 322].

Table 4.9 KWW parameters of linear-CCS polymer blends, obtained from mT-TM annealing analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>$q_c = 10 , ^\circ \text{C} \cdot \text{min}^{-1}$</th>
<th>$q_c = 5 , ^\circ \text{C} \cdot \text{min}^{-1}$</th>
<th>$q_c = 2 , ^\circ \text{C} \cdot \text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$\tau$ (min)</td>
<td>$\beta$</td>
</tr>
<tr>
<td>PS-01</td>
<td>0.0004</td>
<td>28</td>
<td>0.15</td>
</tr>
<tr>
<td>PS-02</td>
<td>117.10</td>
<td>103</td>
<td>0.009</td>
</tr>
<tr>
<td>PS-03</td>
<td>190.39</td>
<td>355</td>
<td>0.002</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>316.03</td>
<td>22</td>
<td>0.004</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>450.99</td>
<td>140</td>
<td>0.002</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>273.21</td>
<td>327</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The dimensionless parameter ‘$\beta$’ is a direct measure of non-exponentiality or the skewness of the distribution of relaxation times [277]. Although the values were numerically small, blends displayed smaller $\beta$ values than their respective unfilled linear matrices, indicating that CCS polymers increase the range relaxation times are distributed across (non-exponentiality). These values correlate well with the experimental data, with blends yielding narrower relaxation curves. Furthermore, $\beta$ can provide an indication of the degree of co-operativity or the number of chain segments involved in the relaxation process. Since the CCS polymer arms inter-connect the linear matrix chains, the total number of chains able to potentially undergo segmental motions increases, as indicated by the reduced $\beta$ value. However, due to effective physical-crosslink restraints within the blends, the total amount of chain movement will be limited.

The relaxation curves of PS-02 during isothermal annealing at 95 °C, cooled from above $T_g$ at various cooling rates ($q_c$) are shown in Figure 4.13. As $q_c$ is increased the average relaxation time decreases, with films cooled at 10 °C·min$^{-1}$ exhibiting the lowest $\tau$ values. Increasing the cooling rate decreases the time allowed for a polymer to experience segmental motion, ‘freezing’ chain segments and not enabling rearrangement or structural relaxation within the applied timescale. When $T_a$ is reached there is a greater amount of ‘entrapped’ free volume available, increasing the rate of structural relaxation and physical
aging. This greater amount of volume resulted in the larger dimension loss observed with increasing $q_c$. The materials were observed to become more non-exponential with increased $q_c$, as indicated by the reduction in $\beta$. The increased free volume allows for a greater number of polymer chains to experience segmental motion during annealing. In addition, the material is further from equilibrium when the relaxation process begins. These observations are consistent with the inverse relationship between enthalpy/volume and non-exponentiality proposed by Bendler and Ngai [323]. The experimental and calculated results support the general concept that structural relaxation is both non-linear and non-exponential.

![Graph of relaxation curves of PS-02 annealed at 95 °C, cooled at various rates](image)

**Figure 4.13** Relaxation curves of PS-02 annealed at 95 °C, cooled at various rates

### 4.4 Conclusion

The $T_g$ of the linear PS and PMMA matrices increased with CCS polymer concentration, while $\Delta H$ relaxation decreased. This was attributed to the CCS polymers restricting segmental motions of polymer matrix chains. The behaviour observed suggests that when dispersed throughout a like-linear matrix, star polymers behave in a similar manner to crosslinks. Isothermal annealing increased $T_g$ and $\Delta H$, with materials annealed for 100 h yielding the greatest values. This was due to the reduction in free volume and mobility which occurred during annealing. Increasing $t_a$ increased heat lost during annealing, requiring materials to equilibrate at a faster rate when heated above $T_g$. $T_f$ decreased with
increasing $t_a$. Blends continued to display higher $T_g$, $T_f$ and lower $\Delta H$ values than their pure, linear counterparts annealed at identical times, indicating that CCS polymers continue to restrict segmental motion during structural relaxation.

CTE and shrinkage decreased with the incorporation of CCS polymers, due to the restrictions placed on matrix flow and conformational motions that govern expansion behaviour. The value of $\alpha$ below the $T_g$ decreased with increasing annealing time due to the reduced free volume inhibiting the expansion ability of polymer chains. Conversely, above-$T_g$ $\alpha$ values increased with $t_a$, which was attributed to the greater expansion rate required to regain $V_F$ lost during annealing. Volume relaxation during annealing was determined to be non-linear and non-exponential in behaviour. Increasing the cooling rate increased the rate of relaxation on annealing, due to the greater amount of $V_F$ ‘entrapped’ within the material which allowed for faster equilibration. The average relaxation time and nonlinearity were observed to increase with CCS polymer content, suggesting that these hyperbranched polymers hinder molecular motions and hence retard the relaxation process.

The results highlight the suitability of mT-TM as a method of analysing structural relaxation. The parallel approach of mT-DSC and mT-TM illustrates the complementary nature of heat capacity and thermal expansion as sensors of molecular structure and equilibration. The data presented encourages the potential for CCS polymers as effective fillers for controlling glass transition and expansion properties.
CHAPTER 5: THERMOMECHANICAL, MORPHOLOGICAL, THERMAL AND OPTICAL PROPERTIES OF LINEAR-CORE CROSS-LINKED STAR POLYMER BLENDS*

5.1 Introduction
In this chapter, the thermomechanical, thermal, morphological and optical properties of linear-CCS polymer blends are characterised. This work builds on the glass transition, structural relaxation and thermal expansion properties covered in Chapter 4, where CCS polymers were observed to behave as physical crosslinks. It is proposed that this crosslink-like behaviour may influence other material properties in a similar manner, such as increasing material strength and providing greater resistance to creep deformation. Although the mechanical properties of linear-conventional star polymer blends [198, 324, 325] and star-like block copolymers [326-329] have been analysed, the same cannot be said of linear-CCS polymer blends. In addition, most analyses of linear-star blends have been performed in the molten state or in solution, with an emphasis on rheometry. Analysing the solid-state thermomechanical properties is important in determining relaxation dynamics and viscoelastic properties achieved by incorporating branched polymers into a linear matrix. The advantage of like-linear CCS polymer blends over conventional polymer blends and composites is that the diminished mechanical, thermal and optical properties caused by poor co-polymer and/or matrix-filler compatibility and filler aggregation/agglomeration are non-existent.

5.2 Materials and methods

5.2.1 Materials, experimental details and blend nomenclature

Material information, blend preparation procedures and characterisation methods are detailed in Chapter 3. The composition and nomenclature of the blends is identical to that listed in Table 4.1.

5.2.2 Thermomechanical analysis

A TA Instruments Q800 Dynamic Mechanical Analyser (Figure 5.1) operating in tensile mode was used to characterise the thermomechanical and viscoelastic properties of the linear-CCS polymer blends. Test specimens had average dimensions of \(~12.00 \times 4.50 \times 0.70 \text{ mm}^3\).

Figure 5.1 TA Instruments Q800 Dynamic Mechanical Analyser

5.2.2.1 Stress-strain

Stress-strain (dynamic force – thermomechanometry, df-TM) analysis was performed by subjecting samples to an increasing force of 1 N·min\(^{-1}\) at 30 °C. All results presented are the average of five measurements.

5.2.2.2 Creep-recovery

Creep-recovery (static force – thermomechanometry, sf-TM) analysis was performed by subjecting films to an applied stress (20 MPa for PMMA-CCS and 10 MPa for PS-CCS blends) for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The
applied stress chosen was within the linear viscoelastic region of all polymer films. Tests were conducted at 30 °C and all results presented are the average of triplicate measurements.

5.2.2.3 Modulated force – thermomechanometry

Single frequency temperature scans were conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus (E'), loss modulus (E'"), loss tangent (\(\tan \delta\)) and associated \(T_g\) of the films were measured as a function of temperature from 50 to 150 °C at a heating rate of 2 °C·min\(^{-1}\). Multi-frequency scans for subsequent time-temperature superposition analysis were performed by subjecting samples to frequencies of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 Hz across a temperature range of 30 to 150 °C. Data was collected at 10 °C intervals with a soak time of 5 min.

5.3 Results and discussion

5.3.1 Thermal stability of linear-CCS polymer blends

The mass loss curves of the PS-CCS blends are shown in Figure 5.2a while the derivative mass loss curves are displayed in Figure 5.2b. Pure linear PS (PS-01) experienced thermal degradation in a single mass-loss step, beginning at ~300 °C, with the temperature at which the maximum rate of degradation occurs (\(T_d\)) being 423 °C. The degradation pathway of polystyrene proceeds by chain scission, followed by depolymerisation and the formation of products including styrene monomer, dimmer and trimer [330]. Incorporation of CCS polymer into the linear PS matrix had no significant influence on thermal stability, with PS-02 and PS-03 yielding \(T_d\) values of 426 and 425 °C, respectively and displaying similar curves to PS-01. Furthermore, all PS materials displayed similar derivative mass values of ~57 %·min\(^{-1}\), indicating that the rate of mass loss remained similar. The degradation pathway of PS is independent of factors such as tacticity and molecular architecture [331], therefore the incorporation of CCS polymers had little influence on the PS degradation mechanism.
Figure 5.2 Thermogravimetric curves of PS-CCS polymer blends; (a) mass loss, (b) derivative mass loss

The mass loss and derivative mass loss curves of the PMMA-CCS blends are displayed in Figure 5.3a and 5.3b, respectively. Pure linear PMMA (PMMA-01) experienced a three-step thermal degradation mechanism distributed across two mass loss events. Firstly, (i) end-initiated depropagation of unsaturated end groups occurs from 240-332 °C. This is followed by the second mass loss event which involves (ii) chain-end initiation of the vinylidene ends and (iii) random scission processes [332], until 458 °C when degradation is complete. This degradation pathway is typical for radically polymerised PMMA [333].
PMMA-01 exhibited $T_d$ values for these two mass-loss steps at 303 and 398 °C, respectively. The incorporation of 10 %·wt CCS polymers into the matrix had little influence on thermal behaviour, with PMMA-02 yielding values and curves similar to PMMA-01. Increasing the CCS polymer concentration to 30 %·wt CCS increased the thermal stability of the first degradation step, with PMMA-03 yielding a $T_d$ of 320 °C, 17 °C higher than pure PMMA. The first degradation step of PMMA-03 was also observed to occur across a broader temperature range.

Figure 5.3 Thermogravimetric curves of PMMA-CCS polymer blends; (a) mass loss, (b) derivative mass
Chapter 5: Thermomechanical, Morphological and Optical Properties of Linear-CCS Polymer Blends

The increase in thermal stability is attributed to the difference in structure of the linear PMMA and PMMA arms on the CCS polymer [232]. PMMA-01 chains contain unsaturated end groups, while CCS polymer PMMA arms do not. Unsaturated end groups are considered a ‘weak link’ which initiates the degradation process. It is well established that PMMA without unsaturated end groups and head-to-head linkages, such as PMMA synthesised using ARTP, exhibit superior thermal stability [332, 334]. As CCS polymer concentration is increased, the total amount of unsaturated end groups and head-to-head linkages decreases. This retards the first degradation step (unsaturated end group decomposition) and increases the thermal stability of the blend.

The Coats and Redfern equation (Equation 3.11) was used to determine the activation energy of degradation ($E_a$) of the linear-CCS polymer blends. Plots of the linear-CCS blends are displayed in Figure 5.4 while the $E_a$ values are summarised in Table 5.1. PS-01 displayed an $E_a$ of 287 kJ·mol$^{-1}$. The incorporation of CCS polymers had negligible effects on activation energy, with PS-02 and PS-03 yielding values of 311 and 292 kJ·mol$^{-1}$, respectively. PMMA-01 exhibited $E_a$ values of 113 and 241 kJ·mol$^{-1}$ for its first and second degradation steps, respectively. Increasing the CCS concentration had negligible effects on the activation energy of the first degradation step, while a decrease in $E_a$ with CCS polymer concentration was observed for the second step.

**Table 5.1** Linear-CCS polymer blend activation energies of degradation

<table>
<thead>
<tr>
<th>Material</th>
<th>1$^{\text{st}}$ step $E_a$ (kJ·mol$^{-1}$)</th>
<th>2$^{\text{nd}}$ step $E_a$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>287</td>
<td>-</td>
</tr>
<tr>
<td>PS-02</td>
<td>311</td>
<td>-</td>
</tr>
<tr>
<td>PS-03</td>
<td>292</td>
<td>-</td>
</tr>
<tr>
<td>PS-04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>113</td>
<td>241</td>
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<tr>
<td>PMMA-02</td>
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<td>164</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

116
The similarity in $E_a$ values for PS-CCS polymer blends suggests adequate interaction between the linear and CCS-polymer arms chains. Furthermore, the minor variation in $E_a$ is in correlation with experimentally observed minor shifts in thermal stability, confirming that the PS arms on the CCS polymer have little impact on the thermal degradation behaviour of linear PS. PMMA-CCS polymer blends exhibited similar $E_a$ values for their first degradation step, although increasing the CCS polymer concentration caused a decrease in
$E_a$ for the second step, indicating that at higher loadings the CCS polymers experience thermal degradation more readily. One possible explanation is that free radicals formed during the degradation of CCS polymer arms may interact with PMMA-01 chain segments or their intermediates [335], lowering the energy barrier required for thermal degradation. As mentioned previously, the second mass-loss step consists of two mechanisms; chain-end initiation of the vinylidene ends and random scission. Chang et al [336, 337] calculated the $E_a$ for thermal degradation of PMMA across the second mass-loss event, concluding that $E_a$ values have little physical meaning due to competition between the two mechanisms. The Coats and Redfern model assumes the occurrence of one degradation mechanism at a time, therefore $E_a$ values for the second step should not be considered absolute.

### 5.3.2 Morphology of the linear-CCS blends

The one-dimensional SAXS profiles of the linear-CCS polymer blends are displayed in Figure 5.5, while material data obtained from SAXS is summarised in Table 5.2. The relative intensity was plotted against the magnitude of the scattering vector ($q$). Similar trends are observed for both PS-CCS and PMMA-CCS blends with the incorporation of CCS polymers. PS-01 exhibited three distinct maxima ($q_{\text{max}}$) at $q$ = 0.008, 0.016 and 0.021 nm$^{-1}$. Similarly, PMMA-01 displayed three $q_{\text{max}}$ at $q$ = 0.009, 0.015 and 0.018 nm$^{-1}$. Increasing CCS polymer concentration caused a reduction in peak intensity, with secondary peaks (0.016 and 0.021 nm$^{-1}$ for PS-CCS and 0.015 and 0.018 nm$^{-1}$ for PMMA-CCS) becoming broader and tapered. Trimmel et al [338] also observed a decrease in scattering intensity of crosslinked-PMMA as cross-linking density increased. They attributed the reduced scattering intensity to restricted packing ability within PMMA. In addition, cross-linking is known to ‘lock-in’ the morphology of a polymer [339]. The diminished scattering peaks confirm that CCS polymers behave in a similar manner to physical crosslinks, with hyperbranched arms entangling within segments of linear polymer, leaving the morphology intact.
Chapter 5: Thermomechanical, Morphological and Optical Properties of Linear-CCS Polymer Blends

Figure 5.5 One-dimensional SAXS profiles of linear-CCS polymer blends; (a) PS-CCS, (b) PMMA-CCS

PS-01 and PMMA-01 exhibited d-spacing values of 785 and 736 nm, respectively \( (d = 2\pi/q_{\text{max}}) \). The addition of CCS polymers caused the primary peak maximum to shift to higher q values. This lead to blends containing 30 %·wt CCS polymer displaying the lowest d-spacing values of 735 and 678 nm for PS-03 and PMMA-03, respectively. Increased q values were observed in interpenetrating polyurethane networks by Russell et al [339], who attributed the shift to enhanced miscibility and reduced phase size. This can be
Chapter 5: Thermomechanical, Morphological and Optical Properties of Linear-CCS Polymer Blends

applied to the linear-CCS blends. Firstly, the identical chemical structure of linear chains and CCS polymer arms leads to adequate miscibility and compatibility between the two polymers. The enhanced miscibility enables the CCS polymer arms to entangle throughout the linear matrix, reducing the total amount of unoccupied volume. The result is reduced phase size and a ‘frozen’ morphology. Similar findings were reported by Junker et al [340], who correlated higher q values to a less mobile, more restricted interpolated polymer structure. The one-dimensional supports the hypothesis that CCS-polymers behave as physical crosslinks and restrict motions of linear chains, correlating to the DSC and mT-TM experimental data (refer Chapter 4).

**Table 5.2** SAXS data of linear-CCS polymer blends

<table>
<thead>
<tr>
<th>Material</th>
<th>d-spacing (nm)</th>
<th>R&lt;sub&gt;g&lt;/sub&gt; (nm)</th>
<th>Porod slope</th>
<th>D&lt;sub&gt;f&lt;/sub&gt;</th>
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</thead>
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<td>2.80</td>
<td>2.80</td>
</tr>
<tr>
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<td>7.8</td>
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<td>9.4</td>
<td>2.90</td>
<td>2.90</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>678</td>
<td>8.4</td>
<td>2.95</td>
<td>2.95</td>
</tr>
</tbody>
</table>

To determine the size of the scattering “particle” following the incorporation of CCS polymer, the radii of gyration (R<sub>g</sub>) of the blends were determined by constructing Guinier plots, as shown in Figure 5.6. Plotting ln(I) vs. q<sup>2</sup> gave a linear graph from which R<sub>g</sub> can be determined using Equation 3.14. The R<sub>g</sub> values of the linear-CCS blends are summarised in Table 5.2. PS-01 displayed an R<sub>g</sub> value of 10.6 nm. The addition of CCS polymers caused R<sub>g</sub> to decrease to 9.0 (PS-02) and 7.8 nm (PS-03). Similar trends were observed in PMMA-CCS blends, with R<sub>g</sub> reducing from 10.1 nm (PMMA-01) to 9.4 (PMMA-02) and 8.4 nm PMMA-03. The observations are in agreement with results obtained by Le [341], who observed a reduction in R<sub>g</sub> values with increasing hyperbranched polymer content in simulated linear-hyperbranched polymer blends. The results imply that as CCS polymer concentration increase, the hyperbranched macromolecules become more compact within the linear matrix. This can be attributed to two reasons; (1) the reduced amount of unoccupied
volume due to the addition of CCS polymers, (2) mobility restrictions imparted on CCS polymer arms due to one end being tethered to the highly cross-linked core.

Porod plots were constructed, using the slope to determine the fractal dimension ($D_f$) of linear-CCS polymer blends as shown in Equation 5.1 and 5.2

\[ \text{For } 1 < \text{slope} < 3 \quad \text{slope} = D_f \quad (5.1) \]

\[ \text{For } \text{slope} < 1 \quad \text{slope} = 1 \quad (5.2) \]
For $3 < \text{slope} < 4 \quad \text{slope} = 6 - D_f$ (5.2)

The plots are displayed in Figure 5.7 while $D_f$ values are summarised in Table 5.2. PS-01 displayed a Porod slope of 3.60 and $D_f$ of 2.40, characteristic of rough interfaces and a surface fractal. The incorporation of CCS polymers caused $D_f$ to increase, reaching values of 2.80 (PS-02) and 2.98 (PS-03). Similar trends were recorded for PMMA-CCS polymer blends with $D_f$ increasing from 2.78 (PMMA-01) to 2.90 (PMMA-02) and 2.95 (PMMA-03). The Porod slopes and $D_f$ of the blends containing CCS polymers lie between 2 and 3, which is typical of branched polymers and indicates that the materials are mass fractals. Incorporating a hyperbranched polymer into a linear is expected to increase $D_f$ [342], indicating that the polymer chains are more compact [343]. As the CCS polymer concentration and $D_f$ increase, the number of global contacts between an interpenetrating CCS polymer arm and linear chain is enhanced [344]. However, the increased hyperbranched polymer content leads to a reduction in the amount of unoccupied volume within the blend, causing polymer chains to become more contorted and compact. These observations correlate with the reduced $R_g$ calculated from the Guinier plots and indicate that CCS polymer arms entangle throughout linear chains. Furthermore, PS-CCS polymer blends displayed lower $R_g$ values than their PMMA-CCS polymer counterparts, indicating the former possesses a more compact structure. This is due to structural differences between PS and PMMA chains.
5.3.3 Thermomechanical properties

5.3.3.1 Stress-strain

The stress-strain curves of the unfilled linear matrices and linear-CCS blends are presented in Figure 5.8, while the tensile properties are summarised in Table 5.3. All materials exhibited stress-strain curves with similar features, typical of glassy polymers. Application of load caused an initial linear increase in strain, due to the occurrence of elastic
deformation. This extension continued until reaching a maximum at the elongation at break, at which sample failure occurred. Pure PS displayed a tensile modulus (E) of 1.8 GPa. The modulus increased with CCS polymer concentration, with PS-02 and PS-03 displaying E values of 2.3 and 2.6 GPa, respectively. Similar trends were observed in PMMA-CCS blends, with the E values of PMMA-01 increasing from 1.7 GPa to 2.0 GPa (PMMA-02) and 2.8 GPa (PMMA-03). The enhancement in modulus indicates that CCS polymers within a like-linear matrix behave in a similar manner to physical crosslinks. The arms on the CCS polymer have one end tethered to the cross-linked core, leaving the branches free to entangle within the linear matrix, restricting segmental chain motions. These restrictions are further facilitated by excellent matrix-filler miscibility, since the matrix and CCS polymer arms are the same material. The experimental results correlate with the kinetic theory of rubber elasticity proposed, which states that the modulus is proportional to crosslink density [345].

Table 5.3 Tensile properties of linear-CCS polymer blends

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Modulus (GPa)</th>
<th>Break Stress (MPa)</th>
<th>Elongation at break (%)</th>
<th>Strain hardening modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>1.8</td>
<td>89.6</td>
<td>4.5</td>
<td>-</td>
</tr>
<tr>
<td>PS-02</td>
<td>2.3</td>
<td>90.0</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>PS-03</td>
<td>2.6</td>
<td>104.6</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>1.7</td>
<td>161.6</td>
<td>6.5</td>
<td>83.3</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>2.0</td>
<td>190.9</td>
<td>5.9</td>
<td>100.4</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>2.8</td>
<td>200.9</td>
<td>5.2</td>
<td>135.7</td>
</tr>
</tbody>
</table>
Figure 5.8 Stress-strain curves of linear-CCS polymer blends; (a) PS-CCS, (b) PMMA-CCS

The break stress of the materials increased with filler content, with blends containing 30 %·wt CCS polymer displaying maximum values of 200.9 MPa (PMMA-03) and 104.6 MPa (PS-03), respectively. This correlates well with the increase in E values and is further indicative of the reinforcing nature of the CCS-polymers. Accompanying the increase in modulus and strength with CCS polymer concentration was a corresponding decrease in elongation at break. This reduction in material elasticity was due to the
increased restrictions on material elongation with increasing CCS polymer (crosslink) concentration. Smaller segments of matrix chain are available for stretching which reduces the probability of chain slippage, resulting in increased brittleness [346]. Strain hardening was observed for all PMMA materials, due to the orientation of covalent chains during plastic deformation [347]. The degree of strain hardening increased with CCS polymer concentration ranging from 83.3 GPa (PMMA-01) to 100.4 (PMMA-02) and 135.7 GPa (PMMA-03), suggesting the blends display an increased resistance to deformation at large stress loadings. This behaviour is due to the restrictions CCS polymers exert on chain elongation and movement and is similar to results obtained from various authors characterising cross-linked polymers [348-350].

5.3.3.2 Creep-recovery

The creep and recovery curves of the linear-CCS polymer blends are presented in Figure 5.9. Several regions are visible in the creep and recovery curves of the pure, linear polymers with the application and removal of load. Firstly, an instantaneous increase in strain occurs, due to the elastic response of the polymer. This is followed by the viscoelastic response, involving time-dependent molecular rearrangement. Viscous flow of the polymer becomes apparent towards the end of the load application period. In amorphous materials, these molecular motions consist of chain sliding mechanisms. Removal of load results in a rapid drop in strain response, which is equal to the initial elastic response. The recovery period involves time-dependent molecular relaxations as the polymer attempts to regain original dimensions [297, 298]. Since the polymers experienced viscous flow, full recovery is unattainable resulting in permanent deformation.

As shown in Figure 5.9, creep deformation decreased with increasing CCS polymer content. At CCS polymer concentrations of 30 %·wt, blends exhibited flatter creep curves with a lower gradient, indicating a decrease of deformation of the viscous component. The incorporation of hyperbranched macromolecules allows the untethered portion of the arms to entangle within the linear matrix, restricting molecular motions of chain segments. This reduced deformation is similar to the influence crosslinks impart on creep behaviour. In addition to chain motion, secondary bonds also influence resistance to
deformation [351]. Within PS and PMMA these secondary bonds comprise of van der Waal [352] and hydrogen bonds [353], respectively. The identical chemical structure of the matrix and CCS polymer arm components ensures excellent compatibility and miscibility and allows the benefits of the aforementioned secondary bonds to be exploited.

The parameters of the four-element model were calculated for the pure linear polymers and blends, the results are summarised in Table 5.4. PS-01 and PMMA-01 displayed Maxwell modulus ($E_1$) values of 1.93 and 0.89 MPa, respectively. The addition of CCS
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polymers increased $E_1$ values, with PS-03 and PMMA-03 displaying respective $E_1$ values of 2.61 and 1.60 MPa. This is attributed to the arms on the CCS polymers limiting the flow of the linear matrix, preventing chains from sliding past one another. Similarly, an increase in Maxwell viscosity ($\eta_1$) with filler content was observed, confirming the CCS polymers contribute to resisting deformation. Unrecovered strain was observed in all materials, which is characteristic of viscoelastic materials and is attributed to molecular slippage during load application [354]. Permanent deformation increased with CCS polymer concentration, due to the hyperbranched fillers restricting the relaxation of matrix chains, increasing irreversible chain slippage and hindering the reformation of random coils. The increase in Voigt viscosity ($\eta_2$) represents an increase in the matrix polymer chain's resistance to uncoiling [299]. PS-CCS blends displayed larger parameters than their PMMA-CCS counterparts, indicating greater resistance to flow. This can be related to the SAXS data (refer Section 5.3.2) that confirmed PS-CCS polymer blends as having more constrained and tightly-packed chains. The close proximity of polymer chains and minimal vacant volume imparts restrictions on flow.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_1$ (MPa)</th>
<th>$\eta_1$ (MPa·s$^{-1}$)</th>
<th>$E_2$ (MPa)</th>
<th>$\eta_2$ (MPa·s$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>Permanent deformation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>1.93</td>
<td>116.95</td>
<td>15.75</td>
<td>101.84</td>
<td>6.45</td>
<td>2</td>
</tr>
<tr>
<td>PS-02</td>
<td>2.33</td>
<td>119.58</td>
<td>28.89</td>
<td>105.12</td>
<td>3.64</td>
<td>3</td>
</tr>
<tr>
<td>PS-03</td>
<td>2.61</td>
<td>125.07</td>
<td>36.79</td>
<td>106.07</td>
<td>2.88</td>
<td>4</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>0.89</td>
<td>87.27</td>
<td>6.04</td>
<td>23.13</td>
<td>3.84</td>
<td>2</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>1.07</td>
<td>95.61</td>
<td>7.40</td>
<td>28.45</td>
<td>3.73</td>
<td>3</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>1.60</td>
<td>99.50</td>
<td>9.37</td>
<td>31.93</td>
<td>3.41</td>
<td>5</td>
</tr>
</tbody>
</table>

In order to calculate the Voigt viscosity ($\eta_2$), the retardation time ($\tau$) is required (refer Equation 3.5). This is the time required for the Voigt element to recover to 63.21 % (or 1-$1/e$) of its total deformation. Although real polymers display a range of retardation times due to their molecular weight distribution, a single $\tau$ provides a quick and simple estimate of how changes in structure can influence behaviour [299]. Increasing the CCS polymer content decreased the $\tau$, indicating that the blends became more solid-like in behaviour.
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with the addition of hyperbranched polymers. Furthermore, flatter recovery curves were observed in highly filled blends (PS-03 and PMMA-03), which was indicative of a faster recovery of the viscoelastic and elastic components.

The KWW stretched exponential function was applied to the blends to examine the recovery behaviour. The results are presented in Table 5.5. The pre-exponential constant and shape fitting parameter \( \beta \) changed with CCS polymer content. \( \beta \) is influenced by various factors, including structure, the presence of fillers, crosslinks and crystallinity [355]. These observations strongly suggest that the incorporation of CCS polymers restricts the flow of linear matrix chains. The relaxation time provides an indication of the degree of mobility molecules within the polymer possess. Increasing CCS polymer content caused the relaxation time to decrease. The decrease suggests the blends are more solid-like in behaviour and correlates with experimental creep-recovery data.

Table 5.5 KWW parameters of linear-CCS polymer blends

<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>( \beta )</th>
<th>( \tau ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>0.10</td>
<td>0.19</td>
<td>36.41</td>
</tr>
<tr>
<td>PS-02</td>
<td>0.09</td>
<td>0.19</td>
<td>30.47</td>
</tr>
<tr>
<td>PS-03</td>
<td>0.07</td>
<td>0.16</td>
<td>24.42</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>0.58</td>
<td>0.17</td>
<td>24.70</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>0.47</td>
<td>0.13</td>
<td>17.46</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>0.23</td>
<td>0.19</td>
<td>11.42</td>
</tr>
</tbody>
</table>

5.3.3.3 Modulated force – thermomechanometry

Figure 5.10 shows the storage moduli (\( E' \)) of the linear-CCS polymer blends. Below the glass transition temperature (\( T_g \)), the addition of CCS polymers into a PS matrix increased the modulus from 1.8 GPa (PS-01) to 2.0 (PS-02) and 2.1 (PS-03) at 70 °C. This observation is indicative of the ability of CCS polymers impart stiffness into the material and is in correlation with stress-strain data (refer Section 5.3.4.1). The \( E' \) values of the PMMA-CCS blends remained relatively constant below the \( T_g \) displaying values of about 7.5 GPa at 70 °C. As the polymers approached the glass-rubber transition, the moduli began to decrease. Heating through and above \( T_g \) provides sufficient activation energy for bond
rotation and segmental rearrangements in the polymer. In all cases, the progressive reduction in $E'$ indicates a loss in material rigidity. At this temperature, the influence of CCS polymers becomes less effective as larger scale co-ordinated motions (slippage, etc.) of the matrix become more dominant.

Figure 5.10 Linear-CCS polymer storage moduli curves; (a) PS-CCS, (b) PMMA-CCS

Two particular observations are apparent with the introduction of CCS polymers into the linear matrix. The first is the retainment of modulus towards higher temperature with increasing CCS polymer content; the hyperbranched polymers providing reinforcement. The second and more subtle effect is the maintenance of $E'$ over broader temperature after
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$T_g$, being more pronounced at higher CCS polymer concentrations. This behaviour is indicative of the effect of physical crosslinking, where the linear matrix is supported through chain entanglements, hindering and imparting physical restraints.

The loss moduli ($E''$) of the blends are presented in Figure 5.11. The $T_g$ is determined by the peak of the $E''$ curve, since that is where maximum heat dissipation occurs. Pure PS exhibited a $T_g$ of 113 °C. The incorporation of CCS polymers caused the $T_g$ to increase to 115 °C (PS-02) and 117 °C (PS-03). PMMA-CCS polymer blends displayed a similar trend, increasing from 118 °C (PMMA-01) to 121 °C (PMMA-02) and 124 °C (PMMA-03). The increase in $T_g$ is attributed to the arms of the CCS polymers restricting the motions of matrix polymer chains and is in agreement with DSC and mT-TM data (refer Chapter 4). Blends exhibited a glass-rubber transition over a larger temperature range than the pure linear matrices, as indicated by the broader $E''$ peaks. Verghese et al. [356] attributed the increase in peak breadth to an increase in the segmental relaxation time of the polymer matrix. Likewise, here the relaxation time was significantly increased due to constraints arising from linear-CCS polymer arm interactions. Furthermore, the single $T_g$ observed in all blends is indicative of the excellent miscibility of CCS polymers within their linear matrices. No $T_g$ is observed for the highly-crosslinked PEGDMA core due to its lack of mobility and confined structure.
The loss tangent (tan (δ)) of the blends are shown in Figure 5.12. $T_g$ can be determined from the maximum of the tan (δ) curve, though the maximum of the $E''$ curve is shown to be consistent with other determinations of $T_g$. $T_g$ values obtained from $E'$ and tan (δ) maxima are compared in Table 5.6. The tan (δ) $T_g$ values were ~9-10 °C higher for PS blends and ~16-17 °C higher for PMMA blends than the loss modulus curves. Glass transition temperatures derived from the loss tangent maximum displayed identical trends to those
obtained from loss modulus curves, that is they increased with CCS polymer content. The amplitude of the tan (δ) peak provides an indication of the number of kinetic units mobile enough to contribute to the glass transition [357]. The decrease in peak intensity with the addition of CCS polymers indicates that the hyperbranched fillers restrict motions of polymer chains and increase segmental motion times, increasing stiffness and reducing the dampening ability of the material. As with the $E''$ curves, peak broadening of the tan (δ) curves was observed with increasing filler concentration. Since the peak breadth is an indication of structural ‘heterogeneity’, the wider peaks suggest an increase in segmental relaxation time brought on by linear-CCS polymer interactions.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E''$ peak $T_g$ (°C)</th>
<th>Tan (δ) peak $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>113</td>
<td>123</td>
</tr>
<tr>
<td>PS-02</td>
<td>115</td>
<td>124</td>
</tr>
<tr>
<td>PS-03</td>
<td>117</td>
<td>126</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>118</td>
<td>134</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>121</td>
<td>137</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>124</td>
<td>141</td>
</tr>
</tbody>
</table>
The relaxation dynamics of linear-star polymer blends has received some attention [358-360], providing insight into the complex nature of relaxation processes by introducing these hyperbranched polymers. At low star polymer loadings, relaxation dynamics of linear-star polymer blends are dominated by constraint release processes [359, 361], although $M_W$ of the linear chains has a weak influence on terminal properties. At high star
polymer concentrations, the situation becomes more complicated, with terminal properties being dictated by a combination of $M_W$ and star polymer concentration effects [361].

The reptation model of de Gennes [362] provides a useful method of describing the dynamics of linear entangled polymer chains as they are heated through $T_g$ into the melt. The model states that effective restraints due to entanglements with neighbouring chains restrict the motion of individual polymer chains. This is represented in Figure 5.13a, where randomly placed dots represent fixed obstacles to chain motion. During relaxation, a polymer chain must move through these obstacles in a tube-like region which follows its own contour, as shown in Figure 5.13b. The scenario is slightly different for star polymers, due to the tethering of the arms to the core. Several authors have proposed a mechanism where the star polymer arms retract down their respective tubes [363-365]. Lee et al [324] proposed a model to describe relaxation within linear-star polymer blends based on the work of Milner et al [366]. Following the relaxation of linear chains via reptation, star polymer arms relax as though they are confined within the same tube as before linear polymer chain relaxation. Star arms move by Rouse-like motions through the larger “super-tube” created by relaxation of linear chains. The end result is either complete relaxation if the diameter of the explored area is similar to the unrelaxed star polymer arm, or loss of a single entanglement constraint if the explored diameter is similar to “super-tube” diameter. A basic schematic of this behaviour is presented in Figure 5.14. Although the model refers to linear-star polymer blends that are molten or in solution, similar principles can be applied to linear-CCS polymer blends.

![Figure 5.13 Reptation model of a polymer chain; (a) with obstacles (dots), (b) with tube region (adapted from [367])](image-url)
5.3.3.4 Time-temperature superposition

In order to further probe the dynamic mechanical properties of the linear-CCS polymer blends, master curves were constructed from the $E'$, $E''$ and $\tan(\delta)$ (Figure 5.15, 5.16 and 5.17, respectively) values obtained at various frequencies. The storage modulus master curves of the linear-CCS polymer blends are displayed in Figure 5.15. Several distinct regions are observed across the log(frequency) domain. At higher frequencies (glassy state), a broad flat region is observed which corresponds to the terminal zone. As the frequency decreases and the material approaches the glass-rubber transition, a sharp drop in log($E'$) occurs. At lower frequencies the polymer enters the rubbery state and approaches the plateau zone. Incorporation of CCS polymer increased log($E'$), which was indicative of the restrictions placed on linear matrix chains by the CCS polymer arms and increase in stiffness observed in static mechanical and single frequency dynamic analysis. The gradient of the linear-CCS polymer blends remained unchanged in the terminal zone, CCS polymers having limited influence in the glassy state (at higher frequencies). Lee et
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al [324] obtained similar results from dynamic storage and loss moduli of linear-star polymer blends of 1,4-polybutadiene using rheometry. They observed minimal influence of star polymers at higher frequencies and higher, flatter plateaus as frequency decreased. The plateau region in Figure 5.15 is not clearly evident due to the frequency not being low enough to induce viscous phenomena.

**Figure 5.15** Storage modulus master curves of linear-CCS blends; (a) PS-CCS, (b) PMMA-CCS
Master curves (log(E') vs. log(f)) shifted to lower frequencies with increasing filler content, corresponding to the increase in \( T_g \) observed in single frequency measurements. Likewise trends were observed in the tan (δ) master curves, with curve inflections moving to lower frequencies with filler content. E'' master curves did not shift with the addition of CCS polymer, which was expected since E'' location is independent of filler concentration [368]. The E'' and tan (δ) master curves are presented in Figure 5.16 and 5.17, respectively.
Master curve peak broadening was observed with increasing CCS polymer content, suggesting an increase in distribution of segmental relaxation times due to linear-hyperbranched polymer interactions, while tan(δ) master curves decreased with CCS polymer concentration due to increased material stiffness and reduced dampening ability.

The WLF equation (Equation 3.7) was utilised to describe the temperature dependence of viscoelastic relaxation times within the glass-rubber transition. The WLF constants $C_1$ and $C_2$...
$C_2$ are summarised in Table 5.7. PS-01 exhibited $C_1$ and $C_2$ values of 4.3 and 26.5 K, respectively. The addition of CCS polymer caused the WLF constants to increase, reaching maximum values at PS-03 ($C_1 = 7.5$, $C_2 = 37.4$). Similar trends were observed in PMMA-CCS polymer blends, with the increase in $C_1$ and $C_2$ with CCS polymer being greater in magnitude. $C_1$ is inversely proportional to the fractional free volume at $T_g$ ($f_g$), while $C_2$ is inversely proportional to the free volume expansion coefficient ($\alpha_f$) [303], as described in Equation 5.3 and 5.4.

$$C_1 = \frac{B}{\log f_g}$$

(5.3)

$$C_2 = \frac{f_g}{\alpha_f}$$

(5.4)

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_1$</th>
<th>$C_2$ (K)</th>
<th>$f_g$</th>
<th>$\alpha_f$</th>
<th>$E_a(T_g)$ (kJ·mol$^{-1}$)</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-01</td>
<td>4.3</td>
<td>26.5</td>
<td>0.10</td>
<td>0.0038</td>
<td>716</td>
<td>97</td>
</tr>
<tr>
<td>PS-02</td>
<td>6.1</td>
<td>32.3</td>
<td>0.07</td>
<td>0.0022</td>
<td>746</td>
<td>100</td>
</tr>
<tr>
<td>PS-03</td>
<td>7.5</td>
<td>37.4</td>
<td>0.06</td>
<td>0.0016</td>
<td>807</td>
<td>108</td>
</tr>
<tr>
<td>PMMA-01</td>
<td>1.3</td>
<td>65.7</td>
<td>0.06</td>
<td>0.0009</td>
<td>865</td>
<td>115</td>
</tr>
<tr>
<td>PMMA-02</td>
<td>13.3</td>
<td>84.6</td>
<td>0.03</td>
<td>0.0004</td>
<td>910</td>
<td>120</td>
</tr>
<tr>
<td>PMMA-03</td>
<td>20.5</td>
<td>108.9</td>
<td>0.02</td>
<td>0.0002</td>
<td>935</td>
<td>123</td>
</tr>
</tbody>
</table>

The observed increase in WLF constant values with hyperbranched polymer concentration suggests that CCS polymers behave as physical crosslinks, reducing free volume within the blend and restricting the expansion ability of linear polymer matrix. Using Equations 5.3 and 5.4, the fractional free volume and free volume expansion coefficients of the linear-CCS polymer blends were calculated, respectively. The results are summarised in Table 5.7. Both $f_g$ and $\alpha_f$ decrease with increasing CCS polymer content, confirming the proposed hypothesis that CCS polymers reduced free volume and behave as physical crosslinks within a linear matrix. The results correlate well with enthalpic/volumetric observations in Chapter 4 and experimental data within this chapter.
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Fragility is a concept introduced by Angell [369], based on the observation that “strong” liquids exhibit Arrhenius behaviour with large activation energies ($E_a$) over the entire temperature range, while “fragile” liquids exhibit super-Arrhenius behaviour at low temperatures and low $E_a$ values at higher temperature ranges [370]. The terms “strong” and “fragile” refer to the tendency of these liquids to form strong, directed or weak, undirected intermolecular bonds, respectively. By observing the magnitude of the decrease of $\log(\tau)$ or $\log(a_T)$ with decreasing $T_g/T$ [371], fragility can be quantified using the steepness index, $m$:

$$m = \left. \frac{d\log(\tau)}{d(T_g/T)} \right|_{T=T_g} = \left. \frac{d\log(a_T)}{d(T_g/T)} \right|_{T=T_g}$$

(5.5)

Alternatively, values of $m$ may be directly obtained using the apparent activation energy, using Equation 5.6 [372].

$$m = \frac{E_a(T_g)}{\log RT_g}$$

(5.6)

where

$$E_a(T) = R \log \frac{d\log(a_T)}{d(1/T)}$$

(5.7)

A value of $m = 16$ corresponds to the “strong” limit, while $m > 200$ refers to the “fragile” limit [373]. The values of apparent activation temperature at $T_g$ ($E_a(T_g)$) and $m$ calculated using Equation 5.7 and 5.6, respectively, are summarised in Table 5.7. The fragility referred to here is the dynamic or kinetic fragility related to relaxation behaviour, as opposed to thermodynamic fragility. $E_a$ is temperature dependent, reaching maximum values at temperatures corresponding to the $T_g$ due the transition between Arrhenius and exponential behaviour [372]. PS-01 displayed an $E_a(T_g)$ value of 716 kJ·mol$^{-1}$, increasing to 746 and 807 kJ·mol$^{-1}$ for PS-02 and PS-03, respectively. Similarly, the $E_a(T_g)$ of PS-CCS polymer blends increased with the addition of the hyperbranched polymers, ranging from 865 kJ·mol$^{-1}$ (PMMA-01) to 935 kJ·mol$^{-1}$ (PMMA-03).
Chapter 5: Thermomechanical, Morphological and Optical Properties of Linear-CCS Polymer Blends

PMMA-01 and PS-01 displayed m values of 115 and 97, respectively, indicating that pure PMMA and PS are kinetically fragile systems. Fragility increased with CCS polymer concentration, with PMMA-03 and PS-03 exhibiting m values of 123 and 108, respectively. This observation confirms that the CCS polymers impose restraints on the segmental mobility of linear matrix chains [372, 374], with several authors observing an increase in fragility with the degree of crosslinking [375]. Dudowicz et al [376, 377] recently proposed that fragility in polymeric systems is dependent on packing ability, with rigid chains and bulky side groups hindering this process. The restrictions that chain connectivity imposes on movement of individual repeat units (such as those imposed by CCS polymers on linear chains) leads to inefficient packing, leaving pockets of free volume and increasing fragility [378]. In addition, Zhang et al [379] proposed that the incorporation of crosslinks alters the average free volume size, cutting larger voids into smaller ones. This reduces the total free volume within the system but also hinders packing ability due to the remaining voids, leading to the blends displaying an increase in fragility.

5.4 Conclusion

The thermal and thermomechanical properties of linear-CCS polymer blends were characterised. CCS polymers had little influence on the thermal stability of PS, while PMMA exhibited enhanced thermal stability due to the structure of CCS polymer arms. Blends displayed decreased radii of gyration and increased fractal dimension, indicating the polymer chains become more constrained and contorted. Tensile modulus and strength increased with hyperbranched polymer loading while elongation at break decreased. PMMA blends displayed an increase in strain hardening with CCS polymer concentration. Creep deformation decreased and permanent strain increased with CCS polymer content, due to the restricted molecular motions caused by CCS polymer arms. The four-element and KWW models were successfully applied to interpret creep and recovery behaviour, respectively. Storage modulus, loss modulus and T_g increased with the addition of CCS polymers. Master curves shifted to lower frequencies as CCS polymer content increased, with segmental relaxation occurring across a broader time scale. CCS polymers increased dynamic fragility and apparent activation energy while decreasing fractional free volume and the free volume expansion coefficient. The results indicate that CCS polymer behaved...
in a similar manner to physical crosslinks; CCS polymer arms entangled throughout linear chains, restricting segmental motions and relaxation dynamics of linear matrix chains.
CHAPTER 6: POSS-SUBSTITUTED HYPERBRANCHED POLYESTER BLENDS WITH THERMOPLASTIC POLYURETHANE*

6.1 Introduction
An important class of dendritic polymers, hyperbranched polymers have attracted significant attention due to their unique three-dimensional architecture, simple synthesis and useful properties such as high reactivity, high solubility and low viscosity. Aliphatic hyperbranched polyesters based on dimethylolpropionic acid have been extensively studied since their introduction in 1993 [380] and commercialisation by Pertorp under the trade name Boltorn [381]. The chemical structure of the Boltorn family of dendrimers contains hydroxyl end groups, allowing for the introduction of functional groups. This versatility has lead to these hyperbranched polymers finding use in various fields, including coating, drug delivery and processing aid applications [381]. Boltorn dendrimers have been blended with other polymers [382], most often used as crosslinking agents in PU [383-385] and tougheners in epoxy resins [386-389]. Although various inorganic groups have been introduced onto the Boltorn structure, including silicate [390] and montmorillonite clay [391], no research has been performed regarding the incorporation of inorganic functionalised Boltorn into polymers and the influence these hybrid organic-inorganic materials have on thermal stability and thermomechanical properties.

Chapters 4 and 5 highlighted how hyperbranched polymers are capable of manipulating the intrinsic properties of amorphous, linear polymers with the same chemical structure. In this chapter, the influence of hyperbranching on the material properties of elastomers is discussed as blends of Boltorn hyperbranched dendrimer and linear thermoplastic polyurethane (TPU) were prepared and characterised. Both TPU and Boltorn polymers

possess a polyester chemical structure, allowing for a high degree of compatibility. Boltorn hyperbranched polymers were functionalised with polyhedral oligomeric silsesquioxanes (POSS) prior to blending with TPU, by reacting amino-treated POSS with hydroxyl end groups on the Boltorn dendrimers. Subsequently, the influence of functionalisation on material properties is also examined. As shown in Figure 6.1, dendritic polymers have great potential for use as functional materials. It is proposed that the introduction of rigid POSS will enhance the thermal stability and thermomechanical properties of TPU-Boltorn blends.

**Figure 6.1** Properties and applications of functionalised dendritic polymers [392]

### 6.2 Materials and methods

#### 6.2.1 Materials, experimental details and blend nomenclature

Material information, functionalisation and blend preparation procedures and characterisation methods are detailed in Chapter 3. The method of determining the number of POSS molecules bonded to a single Boltorn dendrimer using FTIR is detailed in Appendix A. The nomenclature of the PU-Boltorn-POSS nanocomposites is PU-x-y; where x corresponds to the Boltorn hyperbranched dendrimer (H20 or H40) and y corresponds to the concentration of POSS-functionalised Boltorn within the linear thermoplastic polyurethane (1, 5, 10 %·wt).
6.2.2 Thermomechanical analysis

All materials were analysed in tensile mode. An Instron Universal Testing Instrument, Model 4465 with 5 kN load (Figure 6.2) was used to perform df-TM using dumbbell-shaped test bars according to ASTM D638 – 97, specimen type IV. A TA Instruments Q800 Dynamic Mechanical Analyser was used to perform sf-TM analysis, with test specimens displaying average dimensions of ~12.80 x 5.50 x 0.80 mm$^3$. mf-TM analysis was performed using a Perkin Elmer Diamond DMA (Figure 6.3) with test specimens displaying average dimensions of ~10.00 x 5.50 x 0.80 mm$^3$.

![Instron Universal Testing Instrument, Model 4465](image)

**Figure 6.2** Instron Universal Testing Instrument, Model 4465

![Perkin Elmer Diamond DMA, tensile mode fixture](image)

**Figure 6.3** (a) Perkin Elmer Diamond DMA, (b) tensile mode fixture
6.2.2.1 Stress-strain
A strain rate of 50 mm·min$^{-1}$ was applied to each sample at ambient temperature. Results presented are the average of five measurements.

6.2.2.2 Creep-recovery
Creep-recovery (static force – thermomechanometry, sf-TM) analysis was performed by subjecting films to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all polymer films. Tests were conducted at 30 °C and all results presented are the average of triplicate measurements.

6.2.2.3 Modulated force – thermomechanometry
Single frequency temperature scans were conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus ($E'$), loss modulus ($E''$), loss tangent ($\tan \delta$) and associated $T_g$ of the films were measured as a function of temperature from -80 to +110 °C at a heating rate of 2 °C·min$^{-1}$.

6.3 Results and discussion
6.3.1 Chemical structure of POSS-functionalised Boltorn
FTIR spectroscopy was utilised to characterise the structure of the chemical components and to confirm functionalisation. The infrared spectra of amino-treated POSS and POSS-functionalised Boltorn are presented in Figure 6.4. The amino-treated POSS displays several bands characteristic of its structure; 1100 cm$^{-1}$ (Si-O-Si stretching), 1462 cm$^{-1}$, 1400 cm$^{-1}$, 1366 cm$^{-1}$ and 1328 cm$^{-1}$ (CH$_2$ and CH$_3$ bending vibrations and deformation), 2950 cm$^{-1}$ and 2868 cm$^{-1}$ (CH$_3$, CH$_2$ and CH vibrational stretching of isobutyl 'R' groups'). In addition, the lack of a broad peak at ~3300 cm$^{-1}$ indicates the lack of hydroxyl (OH) groups and confirms successful amino-treatment of the POSS.
The spectrum of POSS-functionalised Boltorn H20 and Boltorn H40 displayed similar spectra, characteristic of their polyester structure; 3430 cm\(^{-1}\) (OH stretching vibrations), 1733 cm\(^{-1}\) (C=O stretching vibrations). Several bands indicated the presence of the amino-treated POSS. The characteristic Si-O-Si band is clearly visible at 1100 cm\(^{-1}\), as well as the various bands corresponding to the alkyl groups on the isobutyl ‘R’ compatibilising molecules. The bands at 2950 cm\(^{-1}\), 2868 cm\(^{-1}\), and 1472 cm\(^{-1}\) correspond to vibrational stretching of the POSS isobutyl ‘R’ groups. The large band at 3388 cm\(^{-1}\) corresponds to the OH end groups on the Boltorn dendrimer. This suggests that interaction between the hyperbranched dendrimer and POSS has occurred at some, though not all, hydroxyl groups. The benefit in retaining several OH groups is that they provide an affinity between the Boltorn dendrimer and polar groups within linear TPU.

### 6.3.2 Morphology of PU-POSS-Boltorn blends

#### 6.3.2.1 Scanning electron microscopy

The scanning electron microscope images of selected PU-POSS-Boltorn blends are displayed in Figure 6.5. Blends containing 1 %·wt POSS-functionalised Boltorn displayed an even distribution of hyperbranched dendrimer, with non-evident aggregation. As the
concentration increased to 5 % wt, POSS aggregates began to form. Figure 6.5a and 6.5b display several instances of clustering due to interactions between the POSS molecules, with agglomerates displaying average diameters of \(\sim 30\, \mu m\). This was facilitated due to the difference in polarity between the non-polar POSS and polar hydroxyl groups on Boltorn and linear TPU. At Boltorn concentrations of 10 % wt (Figure 6.5c and 6.5d), the frequency of agglomerates increased, due to the increased volume of POSS functional groups. However, the average agglomerate diameter remained at \(\sim 30\, \mu m\). No distinction in agglomerate dimension or frequency was observed for Boltorn H20 and Boltorn H40 blends. The unreacted hydroxyl groups on the Boltorn hyperbranched polyesters are available to interact with the linear TPU matrix. The specific interactions between the Boltorn and TPU provide a bridge/link between the linear polyurethane and the POSS end groups.
6.3.2.2 Small angle X-ray scattering

Figure 6.6 presents the one-dimensional SAXS profiles of the PU-POSS-Boltorn blends, while the data obtained from SAXS analysis is summarised in Table 6.1. The relative intensity was plotted against the scaling vector (q) magnitude. Pure TPU displayed a scattering profile with two maxima; a primary peak at $q = 0.01428 \text{ nm}^{-1}$ and shoulder at $q = 0.1949 \text{ nm}^{-1}$. The maxima correspond to the respective soft and hard segments that are characteristic of thermoplastic polyurethane structure. The incorporation of POSS-
functionalised Boltorn diminished peak intensity, causing primary peaks to become broader and tapered. At dendrimer loadings of 10 %·wt the distinction between the soft and hard segment maxima is reduced, with PU-H20 10 and PU-H40 10 displaying scattering profiles with one broad maximum. Fu et al [393] related the reduction in scattering intensity in polyurethane to a break-down or reduction of hard segments. In the case of the PU-POSS-Boltorn blends, the weaker peak intensities can be attributed to an increase in polyester (soft segment) content with the addition of the Boltorn aliphatic polyester, causing reduced scattering between the hard and soft segments [394]. This also accounts for the diminished hard segment shoulder at higher blend concentrations. In addition, several authors [338, 395] have reported reduced scattering intensity with increasing crosslink-density. Crosslinks are known to restrict packing ability, ‘freezing’ the morphology and preventing microphase separation [339]. The diminished scattering peaks of the blends indicate that Boltorn may entangle and interpenetrate linear TPU chains, displaying behaviour similar to a physical crosslink.

Figure 6.6 One-dimensional SAXS profiles of PU-POSS-Boltorn blends. Spectra have been shifted for clarity

TPU exhibited a d-spacing value of 503 nm, determined from the maximum of the primary peak by \( d = \frac{2\pi}{q_{\text{max}}} \). The incorporation of POSS-Boltorn hybrid dendrimer shifted the primary peak maximum to higher q values. Consequently, 10 %·wt blends displayed the lowest d-spacing values of 483 (PU-H20 10) and 477 nm (PU-H40 10). Increased q or
reduced d-spacing values in polyurethanes have been associated with enhanced miscibility and reduced phase size [339, 396]. The similar chemical structure of TPU and Boltorn promotes compatibility between the macromolecules. This enables the polyester arms of Boltorn to entangle throughout the soft segments within linear TPU, reducing unoccupied volume and making the polymer structure more compact and less mobile [340]. Figure 6.7 displays a proposed model of how POSS-functionalised Boltorn interacts with linear TPU. Boltorn H40 blends displayed lower d-spacing values than their H20 counterparts. This was due to the structure and large dimensions of Boltorn H40 that enable greater interaction and restrictions on TPU chains. Furthermore, POSS has been observed to reduce phase separation within polyurethane [185, 393, 397, 398].

![Figure 6.7 Distribution of POSS-functionalised Boltorn throughout the soft (polyester) segment within TPU](image)

The radii of gyration ($R_g$) of the linear TPU hard segment within the blends were determined by constructing Guinier plots, as shown in Figure 6.8, while the values are
summarised in Table 6.1. Plotting ln(I) vs. q² gave a linear graph from which $R_g$ can be determined using Equation 3.14. The addition of functionalised Boltron caused $R_g$ to decrease, ranging from 13.0 nm (TPU) to 8.5 (PU-H20 10) and 8.2 nm (PU-H40 10). One probable explanation for this behaviour can be related to the observed reduction in d-spacing values with increasing functionalised-Boltron concentration. Romiszowski and Sikorski [399] studied the effects of confinement on linear and branched polymers, observing a reduction in $R_g$ as the polymer became more confined and compact. The behaviour was attributed to the polymer chains changing their structure from three-dimensional to a flat, two-dimensional conformation. Incorporation of POSS-functionalised Boltron into linear PU reduced phase separation and created a more compact structure. This was indicative of the reduction in d-spacing values, suggesting the hard domains are closer together than in pure TPU. The effects of confinement and reduced unoccupied volume can lead to the domains becoming ‘flatter’ in dimension, causing $R_g$ to decrease. Boltron H40 blends exhibited the lowest $R_g$ values due to the greater influence on chain motion and larger occupied volume these dendrimers are responsible for. Several authors [400-402] have documented the relationship between molecular weight and $R_g$ of branched polymers, observing reduced $R_g$ values as $M_W$ of the hyperbranched polymer increases. This relationship is in agreement with comparisons of Boltron H20 and H40 blends, however it should be noted that polyurethane hard domains are the primary contributors to scattering.

<table>
<thead>
<tr>
<th>Material</th>
<th>d-spacing (nm)</th>
<th>$R_g$ (nm)</th>
<th>$D_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>503</td>
<td>13.0</td>
<td>2.14</td>
</tr>
<tr>
<td>PU-H20 1</td>
<td>496</td>
<td>12.0</td>
<td>2.36</td>
</tr>
<tr>
<td>PU-H20 5</td>
<td>491</td>
<td>9.8</td>
<td>2.44</td>
</tr>
<tr>
<td>PU-H20 10</td>
<td>483</td>
<td>8.5</td>
<td>2.68</td>
</tr>
<tr>
<td>PU-H40 1</td>
<td>490</td>
<td>11.5</td>
<td>2.41</td>
</tr>
<tr>
<td>PU-H40 5</td>
<td>487</td>
<td>9.6</td>
<td>2.58</td>
</tr>
<tr>
<td>PU-H40 10</td>
<td>477</td>
<td>8.2</td>
<td>2.84</td>
</tr>
</tbody>
</table>
Porod plots were constructed by plotting log(I) vs. log(q) to give a linear graph. Using the slope and Equation 5.1, the fractal dimension (D_f) of blends was determined. The Porod plots are shown in Figure 6.9 while the D_f values are presented in Table 6.1. Pure TPU displayed a D_f value of 2.14. The addition of POSS-functionalised Boltron into the matrix increased $D_f$ values, with PU-H20 10 and PU-H40 10 displaying maximum values of 2.68 and 2.84, respectively. $D_f$ values between 2 and 3 are characteristic of mass fractal
structures, such as polymer networks. All blends exhibited $D_t$ values between 2 and 3, that is typical for branched polymers and confirms that the blends maintain a mass fractal geometry. The increased fractal dimensionality is indicative of a more compact chain structure [343] and is anticipated for linear-hyperbranched polymer blends [342]. As Boltorn concentration is increased, the total number of contact points between the dendrimer and linear chain is enhanced [344]. Increasing dendrimer size or dimension has a similar effect; hence the Boltorn H40 blends displayed larger $D_t$ values than those containing Boltorn H20. The observations are in agreement with the reduced $R_g$ and confirm interaction and entanglement of Boltorn and TPU chains. Furthermore, the SAXS data indicates that morphology of the blends is primarily dictated by the Boltorn dendrimer, with minor contributions from POSS.
6.3.4 Thermal stability of PU-POSS-Boltorn blends

The mass loss curves of TPU and PU-POSS-Boltorn blends are presented in Figure 6.10a. Pure TPU experienced thermal degradation in two steps, corresponding to decomposition of the hard (1\textsuperscript{st} step) and soft (2\textsuperscript{nd} step) segments. The first step involves depolycondensation \[403\], resulting in the formation of isocyanate, alcohols, primary or secondary amines, olefins and carbon dioxide \[404\]. In the second step, isocyanates are
dimerised to carbodiimides, which react with alcohol groups to form stable substituted ureas [405]. The addition of POSS-functionalised Boltron increased the thermal stability of the blends, with curves shifting towards higher temperatures and reaching maximum values at filler loadings of 10 %·wt. Blends containing 5 and 10 %·wt Boltron H40 exhibited greater thermal stability properties than their Boltron H20 counterparts for equal concentrations. Similar results were reported by Vuković et al [406], who observed that thermal stability of hyperbranched polyesters increased with generation. The enhanced thermal properties were attributed to an increase in molar mass [407] and greater number of -OH end groups. The more numerous hydroxyl end groups allows for a greater degree of specific interactions between; (a) the linear and hyperbranched polymers and (b) between the dendrimers. This retards molecular vibrations and rotation that occurs at the onset of thermal degradation. In addition, the greater number of POSS bonded to Boltron H40 (as calculated in Appendix A) provide a greater contribution to thermal stability than those bonded to Boltron H20.

As shown in the derivative mass loss curves (Figure 6.10b), pure TPU exhibited two $T_d$ values of 335 and 399 °C, for the first and second degradation steps, respectively. The addition of functionalised Boltron H20 increased $T_d$ values, ranging from 341 and 401 °C (PU-H20 1) to 372 and 442 °C (PU-H20 10). Similar trends were observed for blends containing Boltron H40, with $T_d$ values increasing from 340 and 400 °C (PU-H40 1) to 374 and 459 °C (PU-H40 10). Blends displayed lower mass loss rates, with the rate decreasing as Boltron concentration increased. This is indicative of the increase in thermal stability and confirms that the functionalised dendrimers decrease the rate of thermal degradation within polyurethane.
The thermal stability of PU is dependent on several factors, including hard segment volume, chain extender volume/type and the diisocyanate type [408]. The addition of fillers or blending with other polymers can additionally influence thermal properties. Dendritic polyesters have been shown to exhibit superior thermal stability to linear counterparts [406], due to their unique architectural structure. The incorporation of Boltron into a polyurethane matrix results in intra/intermolecular bridges between the
linear and dendritic polymers via hydroxyl groups. These interactions restrict molecular vibrations and rotations that occur when thermally excited [404], increasing thermal stability. The enhanced thermal behaviour correlates with results obtained by Maji and Bhowmick [397], who prepared polyurethanes with Boltorn crosslinks. The polymers exhibited increased thermal stability, attributed to increased molecular weight and polyurethane-Boltorn interactions. During thermal degradation, polymer chains must break-up/de-bond into smaller segments to allow for elimination of parts of the structure. Increasing the cross-link density or molecular weight results in materials fragmenting into larger segments than otherwise. These larger polymer segments require more energy to break into portions small-enough to be eliminated, exhibiting increase thermal stability in the process.

In addition to Boltorn, the inorganic structure of POSS leads to the molecule exhibiting a high intrinsic thermal stability. A number of mechanisms have been proposed to explain how POSS improves thermal stability in polymer composites. One possible explanation is that POSS restrict polymer chain motions, due to polymer-filler interactions or by the large inertia exhibited by segments of polymer containing POSS [147, 409]. Alternatively, polymer segments near POSS molecules may degrade more slowly due to the POSS providing heat shielding and the “most torturous path” for elimination of degradation products. The results indicate that Boltorn and POSS provide a synergistic effect in increasing the thermal stability of TPU, a valuable attribute.

### 6.3.4 Thermomechanical properties of PU-POSS-Boltorn blends

#### 6.3.4.1 Stress-strain

The stress-strain curves of PU-POSS-Boltorn blends are presented in Figure 6.11, while the stress-strain data is summarised in Table 6.2. Pure TPU displayed a tensile modulus (E) of 15.32 GPa and break stress of 16.13 MPa. The incorporation of POSS-functionalised had a positive effect on E, with values increasing from 15.98 (PU-H20 1) to 20.24 GPa (PU-H20 10) in materials blended with Boltorn H20. Similar results were observed for Boltorn H40 blends, with E values ranging from 15.53 (PU H40 1) to 24.62 GPa (PU-H40 10). Accompanying the enhanced tensile modulus was an increase in break strength.
with functionalised Boltorn concentration, reaching maximum values of 21.40 (PU-H20 10) and 20.57 MPa (PU-H40 10).

![Stress-strain curves of PU-POSS-Boltorn blends](image)

**Figure 6.11** Stress-strain curves of PU-POSS-Boltorn blends

In linear-dendritic polymer blends, enhancement of mechanical properties will occur if (a) entanglements are present, (b) if the dendrimer possess a rigid structure due to the presence of aromatics or (c) if it is crystalline [410, 411]. Both of the first two factors can be applied to the PU-POSS-Boltorn blends. Firstly, unreacted hydroxyl end groups on the Boltorn hyperbranched polyester provide compatibility with the linear TPU, leading to hydrogen bonding between the linear and dendritic polymer chains. These interactions encourage the hyperbranched dendrimers to entangle throughout the linear TPU chains, creating a restriction in segmental motion. Secondly, the presence of POSS provides inherent rigidity to the Boltorn structure, providing additional restrictions on chain motion. A consequence of the increased rigidity and segmental restrictions was the decrease in elongation at break, with 10 %·wt blends displaying the least-elastic behaviour. Furthermore, the intrinsic strength of POSS allows it to absorb applied stress. This is facilitated by Boltorn acting as a ‘compatibiliser’ or ‘bridge’ between the TPU and POSS, allowing stress to be transferred from the former to the latter.
Table 6.2 Stress-strain data of PU-POSS-Boltorn blends

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Modulus (GPa)</th>
<th>Break Stress (MPa)</th>
<th>Elongation at break (mm-mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>15.32</td>
<td>16.13</td>
<td>4.9</td>
</tr>
<tr>
<td>PU-H20 1</td>
<td>15.98</td>
<td>16.87</td>
<td>4.7</td>
</tr>
<tr>
<td>PU-H20 5</td>
<td>17.83</td>
<td>19.38</td>
<td>4.3</td>
</tr>
<tr>
<td>PU-H20 10</td>
<td>20.24</td>
<td>21.40</td>
<td>4.1</td>
</tr>
<tr>
<td>PU-H40 1</td>
<td>15.53</td>
<td>15.71</td>
<td>4.4</td>
</tr>
<tr>
<td>PU-H40 5</td>
<td>19.16</td>
<td>19.05</td>
<td>4.2</td>
</tr>
<tr>
<td>PU-H40 10</td>
<td>24.62</td>
<td>20.57</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Differences in static mechanical properties were observed for Boltorn H20 and Boltorn H40 blends, particularly in tensile modulus and elongation at break. Films containing Boltorn H40 displayed larger tensile moduli and were more brittle than their Boltorn H20 counterparts, especially at concentrations of 5 and 10 % wt. This observation correlates with results presented by Maji and Bhowmick [397]. They observed that increasing the dendrimer generation increased E values and reduced elasticity in polyurethane-Boltorn blends. The enhanced moduli values were attributed to the increased functionality (number of –OH end groups) in higher generation Boltorn polyesters. Boltorn H40 theoretically has 64 primary hydroxyl groups, compared with 16 on Boltorn H20 [412], allowing for greater linear-dendritic polymer interaction and further restrictions on chain mobility. The reduction in elasticity was attributed to shorter segments of linear TPU chain between Boltorn dendrimers, which become smaller with increased Boltorn concentration and dendrimer generation. As chain segment length decreases, so does the maximum length which the uncoiled chains can be extended to under applied stress. This increases the brittleness of the material and promotes the earlier onset of failure.

6.3.4.2 Creep-recovery

The creep-recovery curves of the PU-POSS-Boltorn blends are displayed in Figure 6.12. Increasing the POSS-functionalised Boltorn concentration decreased creep deformation.
This indicates that linear polyurethane chain motions are suppressed during applied load. The results correlate to those obtained from stress-strain analysis and can be attributed to the influence of Boltorn and POSS. Firstly, the Boltorn hyperbranched polyesters are able to interact with the linear TPU chains, restricting segmental motions. Secondly, the rigid POSS impart stiffness and reduced ductility into the polymer matrix. As observed in the stress-strain data, blends containing Boltorn H40 displayed greater resistance to creep deformation than their Boltorn 20 counterparts, particularly at concentrations of 5 and 10 %·wt. This was due to the greater number of OH end groups on Boltorn H40, which provide the dendrimer more sites to interact with the linear TPU matrix. Furthermore, the segments of linear PU chain between dendrimers are shorter for Boltorn H40 blends than those containing Boltorn H20, causing a reduction in elastic behaviour.

![Figure 6.12 Creep-recovery curves of PU-POSS-Boltorn blends](image)

Table 6.3 summaries the four-element model parameters calculated to interpret the creep behaviour of the blends. Pure TPU displayed the greatest strain response to applied load. Blends displayed a reduced creep response, providing restrictions to both elastic and viscous components of the model. The Maxwell modulus ($E_1$) increased with Boltorn content, confirming the POSS-dendrimer hybrids effect flow properties of linear TPU. Similarly, the Maxwell ($\eta_1$) viscosity increased with blend concentration, confirming
resistance to deformation. Blends containing Boltorn H40 exhibited larger Maxwell component (E₁ and η₁) values than their Boltorn H20 counterparts, reflecting experimental observations. Unrecovered strain was observed for all materials, due to chain slippage and detachment of hard segments from the soft segments that occur during deformation. Increasing the dendrimer concentration resulted in greater permanent deformation, due to chain relaxation being hindered by Boltorn and POSS. This leads to irreversible chain slippage and unraveling and changes to the polyurethane structure. Consequently, the Voigt viscosity (η₂) increased with blend concentration, indicating a decrease in the likelihood of TPU chain uncoiling.

Table 6.3 Creep-recovery data of PU-POSS-Boltorn blends

<table>
<thead>
<tr>
<th>Material</th>
<th>E₁ (MPa)</th>
<th>η₁ (MPa·s⁻¹)</th>
<th>E₂ (MPa)</th>
<th>η₂ (MPa·s⁻¹)</th>
<th>τ (min)</th>
<th>Permanent deformation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>0.42</td>
<td>18.04</td>
<td>0.10</td>
<td>1.58</td>
<td>15.80</td>
<td>10</td>
</tr>
<tr>
<td>PU-H20 1</td>
<td>0.45</td>
<td>22.12</td>
<td>0.11</td>
<td>1.63</td>
<td>14.82</td>
<td>11</td>
</tr>
<tr>
<td>PU-H20 5</td>
<td>0.56</td>
<td>28.59</td>
<td>0.18</td>
<td>2.12</td>
<td>11.77</td>
<td>11</td>
</tr>
<tr>
<td>PU-H20 10</td>
<td>0.63</td>
<td>30.82</td>
<td>0.26</td>
<td>2.23</td>
<td>8.58</td>
<td>12</td>
</tr>
<tr>
<td>PU-H40 1</td>
<td>0.49</td>
<td>20.58</td>
<td>0.13</td>
<td>1.67</td>
<td>12.85</td>
<td>10</td>
</tr>
<tr>
<td>PU-H40 5</td>
<td>0.64</td>
<td>32.89</td>
<td>0.17</td>
<td>2.17</td>
<td>12.77</td>
<td>12</td>
</tr>
<tr>
<td>PU-H40 10</td>
<td>0.74</td>
<td>37.13</td>
<td>0.24</td>
<td>2.20</td>
<td>9.17</td>
<td>13</td>
</tr>
</tbody>
</table>

The retardation time (τ) is the time required for the Voigt element (viscoelastic component) to recover to 63.21% (or 1-1/e) of its total deformation. It is needed to calculate η₂ and was obtained using Equation 3.5. Blends displayed lower τ as dendrimer content was increased, suggesting an increase in solid-like behaviour. Similarly, recovery curves became flatter with increasing blend concentration, indicating the viscoelastic and elastic components experience faster recovery. Boltorn H40 blends exhibited shorter retardation times than those containing Boltorn H20; indicative of the influence dendrimer generation has on recovery and static mechanical properties. The calculated parameters accurately represent experimental data observed in the creep component and stress-strain analysis.
The KWW stretched exponential function was applied to the blends to interpret the recovery component. The results are summarised in Table 6.4. The pre-exponential constant (A) and relaxation time decreased with increasing blend concentration, corresponding to reduction in molecular mobility. The reduced relaxation time confirms the increase in solid-like behaviour with blend concentration and is in agreement with both the experimental creep component and four-element model parameters. Correspondingly, the shape fitting parameter β decreased with Boltorn content, indicating an increase in non-exponentiality. These observations strongly indicate that Boltorn and POSS impart considerable influence on the flow of linear TPU, the results of which extend to the mechanical-property response.

**Table 6.4** KWW parameters of PU-POSS-Boltorn blends

<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>β</th>
<th>τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>5.33</td>
<td>0.12</td>
<td>6.40</td>
</tr>
<tr>
<td>PU-H20 1</td>
<td>5.48</td>
<td>0.10</td>
<td>6.23</td>
</tr>
<tr>
<td>PU-H20 5</td>
<td>6.77</td>
<td>0.10</td>
<td>5.93</td>
</tr>
<tr>
<td>PU-H20 10</td>
<td>10.37</td>
<td>0.09</td>
<td>4.11</td>
</tr>
<tr>
<td>PU-H40 1</td>
<td>6.84</td>
<td>0.10</td>
<td>6.34</td>
</tr>
<tr>
<td>PU-H40 5</td>
<td>7.52</td>
<td>0.11</td>
<td>4.83</td>
</tr>
<tr>
<td>PU-H40 10</td>
<td>8.56</td>
<td>0.10</td>
<td>2.47</td>
</tr>
</tbody>
</table>

6.3.4.3 Modulated force – thermomechanometry

The storage moduli (E') of PU-POSS-Boltorn blends are presented in Figure 6.13 while E' values are summarised in Table 6.5. Pure TPU displayed an E' value of ~2.5 GPa at -80 °C. The addition of 1 % wt functionalised Boltorn had marginal impact on the storage modulus, resulting in E' values remaining at ~2.5 GPa. Increasing the POSS-dendrimer hybrid concentration increased the storage modulus, with PU-H20 5 and PU-H20 10 displaying E' values of ~2.8 and 3.3 GPa, respectively, at -80 °C. Similar behaviour was observed for blends containing Boltorn H40, with maximum modulus values recorded for PU-H40 10 (~3.8 GPa at -80 °C). The larger E' values indicate an increase in material strength with POSS-Boltorn content and correlate to stress-strain data. This increase in mechanical strength is facilitated by the restricted chain mobility and enhanced rigidity that were
imparted by the Boltorn and POSS, respectively. Boltorn H40 blends displayed larger $E'$ values than their Boltorn H20 counterparts for equal concentrations. This was attributed to the influence of dendrimer size and number of functional groups on mechanical properties [397], with blends displaying trends similar to those observed in stress-strain analysis.

**Figure 6.13** Storage ($E'$) moduli of PU-POSS-Boltorn blends

![Storage Moduli Graph](image)

Figure 6.14 displays the loss ($E''$) moduli of the blends while $T_g$ values are summarised in Table 6.5. Pure TPU displayed a $T_g$ of -47 °C. Increasing the blend concentration had a positive effect on the $T_g$, reaching maximum values of -37 (PU-H20 10) and -35 °C (PU-H40 10). This behaviour is in agreement with literature [413, 414], attributing the increased $T_g$ in linear-dendrimer blends to reduced free volume and restrictions imparted by the hyperbranched macromolecules on linear chain motions. These restrictions are usually facilitated through hydrogen bonding between the linear and dendritic polymers, causing an anti-plasticising effect. Within the PU-POSS-Boltorn blends, these hydrogen bonds can occur through the unreacted OH groups on Boltorn and C=O groups on the polyester (soft segment) component of linear TPU, increasing mechanical and $T_g$ properties. Furthermore, the $T_g$ of Boltorn (31 °C) [412] is considerably higher than linear TPU (-47 °C), allowing the dendrimer to remain solid-like and interact with linear chains.
while they experience \(T_g\) and eventually flow [415]. The rigid structure of POSS is also widely known to impart restrictions on polymer chains and increase the \(T_g\) of polyurethane [126, 416-419]. All blends displayed a single loss peak, corresponding to the \(T_g\) of linear TPU. This confirms that Boltorn dendrimer is miscible with TPU’s soft, polyester segments (refer Figure 6.7). In addition, the single maximum strongly suggests that functionalised Boltorn is primarily distributed throughout the soft segment within thermoplastic polyurethane.

![Figure 6.14 Loss (E’”) moduli of PU-POSS-Boltorn blends](image)

**Table 6.5** mf-TM data of PU-POSS-Boltorn blends

<table>
<thead>
<tr>
<th>Material</th>
<th>(E’”) peak (T_g) (°C)</th>
<th>Tan (δ) peak (T_g) (°C)</th>
<th>(E’) at -80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>-47</td>
<td>-31</td>
<td>2.5</td>
</tr>
<tr>
<td>PU-H20 1</td>
<td>-45</td>
<td>-28</td>
<td>2.5</td>
</tr>
<tr>
<td>PU-H20 5</td>
<td>-43</td>
<td>-26</td>
<td>2.8</td>
</tr>
<tr>
<td>PU-H20 10</td>
<td>-37</td>
<td>-20</td>
<td>3.3</td>
</tr>
<tr>
<td>PU-H40 1</td>
<td>-45</td>
<td>-28</td>
<td>2.4</td>
</tr>
<tr>
<td>PU-H40 5</td>
<td>-41</td>
<td>-25</td>
<td>3.1</td>
</tr>
<tr>
<td>PU-H40 10</td>
<td>-35</td>
<td>-19</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The addition of POSS-functionalised dendrimer increased the breadth of the \(E’”\) curves, with 10 %wt blends displaying the broadest peaks. This indicates the blends experienced glass-
rubber transition across a broader temperature range, with the POSS-Boltorn hybrid subsequently increasing the segmental relaxation time of the linear polyurethane matrix. Blends containing Boltorn H40 displayed higher \( T_g \) values than those composed of Boltorn H20, particularly at concentrations of 5 and 10 %·wt. Furthermore, Boltorn H40 blends yielded wider \( E'' \) curves. These results correlate with the observations of Carr et al [414] and Xu et al [413], who reported an increase in \( T_g \) values with dendrimer size in linear-dendrimer blends. They attributed the behaviour to increased chain entanglement density in blends containing larger dendrimers, shifting \( T_g \) towards higher temperatures. The more numerous hydroxyl groups on Boltorn H40 allow for an increased degree of interaction between the dendrimer and linear polymer, increasing the total amount and extent of chain restrictions. In addition, the large size of Boltorn H40 (compared with Boltorn H20) reduces the length of linear TPU chain segments between dendrimers, reducing the degree of rotation the segment can experience.

The loss tangent (\( \tan (\delta) \)) of the blends are presented in Figure 6.15. As with the \( E'' \) curves (refer Figure 6.14), a single peak is observed confirming adequate TPU-Boltorn interaction. The \( T_g \) values obtained from the loss tangent maximum were \(~16-17\) °C higher than those obtained from the \( E'' \) curve maxima. However, trends displayed in the \( \tan (\delta) \) curves were
similar to those in the loss modulus, with $T_g$ increasing with blend concentration and Boltorn H40 blends displaying the largest shift in $T_g$. The addition of Boltorn caused a reduction in peak height, indicative of diminished dampening ability. The dampening properties of a polymer become greater as the number of chain movements is increased. The incorporation of POSS and Boltorn reduce the number of chain motions and free volume, causing a reduction in dampening. The thermomechanical data showed that Boltorn H40 blends experienced the least amount of chain movement. As a result, these materials displayed poorer dampening properties than Boltorn H20 blends, indicative of the smaller tan (δ) peaks.

### 6.4 Conclusion

Boltorn hyperbranched aliphatic polyesters were functionalised with amino-treated isobutylPOSS and blended with linear thermoplastic polyurethane. Functionalisation was confirmed using FTIR. Agglomerate size and frequency amongst POSS increased with blend concentration, due to increased interparticle interaction. Blend morphology was primarily influenced by the Boltorn dendrimer, with minor contributions from POSS. The radius of gyration decreased and fractal dimensionality increased with functionalised dendrimer concentration. This indicated a reduction in free volume and increase compactness amongst polymer chains. Blends exhibited smaller d-spacing values, suggesting the Boltorn and POSS encourage enhanced miscibility and reduce phase separation.

Thermal stability increased with POSS-functionalised Boltorn content, due to restrictions on polymer chain vibration imparted by Boltorn and thermal shielding supplied by POSS. The tensile modulus and strength increased with blend concentration, while ductility decreased due to the rigid nature of the materials. Molecular restrictions imparted by the POSS-Boltorn hybrid reduced creep deformation and increased permanent strain with filler content. Storage modulus, loss modulus and glass transition temperature increased with blend concentration. Blends containing Boltorn dendrimers with a higher generation exhibited superior thermal and mechanical properties than those blended with lower generation Boltorn. This was attributed to the enhanced TPU-Boltorn interaction and restrictions imparted on linear polyurethane chains. Material properties were influenced by both the Boltorn dendrimer and POSS, indicating that blending with the functionalised
hyperbranched macromolecule provides a viable method of enhancing the thermal and mechanical properties of thermoplastic polyurethane.
CHAPTER 7: THERMOMECHANICAL AND MORPHOLOGICAL PROPERTIES OF ELASTOMER-POSS COMPOSITES*

7.1 Introduction
POSS substrates were functionalised with adipoyl or sebacoyl chloride to prepare telechelic (dumbbell)-shaped POSS structures that were subsequently incorporated into poly(styrene-\-butadiene-\-styrene) (SBS). This is in contrast to the previous chapter where POSS was used as a functional group to impart strength and thermal stability. The trisilanolPOSS starting material is an ideal substrate due to its nano-sized dimensions, compatibilising ‘R’ groups, high mechanical and thermal properties and silanol end groups which allow the molecule to react with functional groups. Although telechelic polymer structures with POSS attached to the end groups have been synthesised [154-156] these novel-structured POSS are yet to be incorporated as filler into a polymer matrix. Furthermore, no research has been conducted to optimise architecture, such as ‘barbell’ length or chain type. In order to preferably disperse throughout either the polybutadiene or polystyrene phase within SBS, POSS molecules contained isobutyl or phenyl ‘R’ compatibilising groups, respectively. The influence of telechelic-architecture and phase preference on the thermomechanical, thermal, optical and morphological properties is discussed.

7.2 Materials and methods
7.2.1 Materials, experimental details and nanocomposite nomenclature
Material information, functionalisation and compounding procedures and characterisation methods are detailed in Chapter 3. The nomenclature of the SBS-POSS nanocomposites is as

follows: SBS-xPOSS-y z; where x corresponds to the compatibilising ‘R’ groups on the POSS cage corners (ib = isobutyl, ph = phenyl), y is the diacyl chloride ‘barbell’ used to bridge the POSS molecules (adichl = adipoyl chloride, sebchl = sebacoyl chloride) and z is the concentration of functionalised POSS within the SBS matrix (1, 5, 10 or 20 %·wt).

7.2.2 Thermomechanical analysis

All materials were analysed in tensile mode. An Instron Universal Testing Instrument, Model 4465 was used to perform df-TM while a TA Instruments Q800 Dynamic Mechanical Analyser was used to perform sf-TM and mf-TM analysis. ASTM D638 – 97, specimen type IV test bars were utilised for df-TM while specimens prepared for sf-TM and mf-TM analysis were rectangular with average dimensions of ~12.80 x 4.00 x 0.70 mm³.

7.2.2.1 Stress-strain

A deformation rate of 50 mm·min⁻¹ was applied to each sample at ambient temperature for df-TM analysis. Results presented are the average of five measurements.

7.2.2.2 Creep-recovery

sf-TM analysis was performed by subjecting samples to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all the nanocomposites. Tests were conducted at ambient temperature (30 °C) and all results presented are the average of triplicate measurements.

7.2.2.3 Modulated force – thermomechanometry

Single frequency temperature scans were conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus (E’), loss modulus (E’’), loss tangent (tan δ) and associated T_g of the films were measured as a function of temperature from -100 to +110 °C at a heating rate of 2 °C·min⁻¹. Multi-frequency scans for subsequent time-temperature superposition analysis were performed by subjecting samples to frequencies of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 Hz across a temperature range of -100 to +110 °C. Data was collected at 10 °C intervals with a soak time of 5 min.
Chapter 7: Thermomechanical and Morphological Properties of Elastomer-POSS Composites

7.3 Results and discussion

7.3.1 Chemical structure of trisilanolPOSS and telechelic, functionalised POSS

FTIR spectroscopy was used to confirm the chemical structure formed by the reaction of POSS and the diacyl chlorides and to determine whether bonding between the respective molecules was achieved. The infrared spectra of the untreated POSS are shown in Figure 7.1a. The pure POSS show several bands characteristic of their structure: 3154 cm\(^{-1}\) (hydroxyl (OH) stretching vibrations), 1100 cm\(^{-1}\) and 890 cm\(^{-1}\) (Si-O-Si and SiOH stretching vibrations). TrisilanolphenylPOSS displays bands at 1594, 1490 and 1430 cm\(^{-1}\), corresponding to vibrational stretching of the C=C bonds within the phenyl ‘R’ groups. The three bands in this region confirm the presence of a conjugated phenyl system. Other bands corresponding to the trisilanolphenylPOSS structure include 3070 cm\(^{-1}\) (sp\(^2\) CH stretching vibrations), 696 cm\(^{-1}\) and 740 cm\(^{-1}\) (C-H bending vibrations). TrisilanolisobutylPOSS exhibits strong bands at 2950, 2900 and 2868 cm\(^{-1}\), corresponding to vibrational stretching of the CH\(_3\), CH\(_2\) and CH groups of the isobutyl ‘R’ groups. Other peaks specific to isobutyl include those at 1462, 1400, 1366 and 1328 cm\(^{-1}\), correlating to CH\(_2\) and CH\(_3\) bending vibrations and deformation.
Figure 7.1 (a) Infrared spectrographs of untreated POSS; (i) TrisilanolisobutylPOSS, (ii) TrisilanolphenylPOSS; (b) infrared spectrographs of functionalised POSS; (i) ibPOSS-adichl, (ii) ibPOSS-sebchl, (iii) phPOSS-adichl, (iv) phPOSS-sebchl

The infrared spectra of the functionalised dumbbell-POSS are shown in Figure 7.1b. For all functionalised POSS, a noticeable reduction in peak size is observed at 3154 cm\(^{-1}\). This indicates a reduction in the number of OH groups on the POSS molecules, confirming that bonding has occurred between the trisilanol group and 3-aminopropyltriethoxysilane used to treat the trisilanolPOSS. This was confirmed by the presence of new peaks at 3264 cm\(^{-1}\) (N-H vibrations). The formation of amide bonds between the amine-treated POSS and di-
acyl chlorides was confirmed by the presence of two peaks at 1638 and 1536 cm\(^{-1}\). These bands correspond to amide I (C=O stretching) and amide II (N-H bending) vibrations, respectively [420]. Dumbbell-phenylPOSS fillers displayed new peaks at 2902 and 2848 cm\(^{-1}\) that are attributed to CH\(_2\) vibrations of the alkane ‘barbell’ chains. These vibrations could also contribute to dumbbell-isobutylPOSS CH\(_2\) vibrations at 2950, 2900 and 2868 cm\(^{-1}\), in addition to isobutyl group contributions. The lack of new peaks at 800-700 cm\(^{-1}\) (C-Cl stretching) [421], 930 cm\(^{-1}\) (CO-Cl stretching) [422] or 1815-1770 cm\(^{-1}\) (acyl halide C=O vibrations) [421] demonstrates that there is no un-reacted sebacoyl or adipoyl chloride remaining and that reactions occurred at both acyl chloride groups. These observations strongly encourage that sufficient interaction and bonding has occurred between the treated trisilanol POSS and diacyl chlorides and that the desired dumbbell-shaped molecule was formed.

**7.3.2 Morphology of SBS-dumbbell POSS nanocomposites**

**7.3.2.1 Scanning electron microscopy**

Scanning electron microscopy (SEM) was employed to investigate the morphology and extent of filler dispersion within the nanocomposites. The micrographs are presented in Figure 4. Incorporation of up to 5 %·wt POSS into the SBS resulted in a relatively uniform distribution of filler throughout the matrix, with POSS clustering into small agglomerates with an average diameter of ~0.5-1.5 μm. As the concentration of POSS increased, so did the occurrence of agglomeration, ranging from few small instances at 5 %·wt (Figure 7.2a) to the formation of large agglomerates at 20 %·wt with average diameters of ~11 μm (Figure 7.2b). Despite utilising ultrasonic disruption to discourage filler clustering and solvent precipitation to ‘suspend’ the filler in a desired spatial arrangement, the micrographs indicate that at POSS concentrations greater than 5 %·wt, interactions between the functionalised POSS nanoparticles are quite strong and can withstand physical methods used to encourage particle separation. These interactions are usually in the form of Coulombic and van der Waals forces.
Figure 7.2 Scanning electron micrographs of SBS-POSS nanocomposites; (a) SBS-ibPOSS-adichl 5, (b) SBS-ibPOSS-adichl 20, (c) SBS-ibPOSS-sebchl 10 (d) SBS-phPOSS-sebchl 10

Figure 7.2c and 7.2d display the micrographs of SBS-ibPOSS-sebchl 10 and SBS-phPOSS-sebchl 10, respectively. Incorporation of 10 %·wt ibPOSS-sebchl gave an even distribution of filler throughout the matrix, with small clusters of ~2-3 μm. Conversely, addition of phenylPOSS at the same concentration and functionalised with the same diacyl chloride leads to an increase in the development of agglomeration, with larger clusters of ~5-8 μm occurring. This behaviour is attributed to the corner ‘R’ groups on the silsesquioxane cages, which determine phase compatibility and, therefore, morphology. The bulk of the SBS
matrix used consists of polybutadiene (~70.5 %·wt), providing isobutylPOSS groups a relatively large volume to disperse throughout and occupy. This was in contrast to phenylPOSS, which by comparison has a significantly smaller volume of polymer (styrene phase) to occupy, leading to increased interactions between the POSS molecules due to their proximity. This leads to the formation of larger agglomerates within the fewer styrene domains available. Adipoyl and sebacoyl chloride-functionalised POSS exhibited similar distribution behaviour, with the degree of aggregation and particle diameter being primarily influenced by the phase throughout which the fillers were dispersed (via the corner ‘R’ groups).

7.3.2.2 Small angle X-ray scattering

Figure 7.3 shows the one-dimensional small angle X-ray scattering (SAXS) profiles of SBS and selected nanocomposites, while material characteristics derived from SAXS data are summarised in Table 7.1. The relative intensity was plotted against the magnitude of the scattering vector (q). As shown in Figure 3.3a, the scattering pattern of pure SBS displayed three distinct maxima ($q_{\text{max}}$) at $q = 0.026$, $0.042$ and $0.069$ nm$^{-1}$ that were denoted $q_1$ (primary peak), $\sqrt{3}q_1$, and $\sqrt{7}q_1$, respectively. This sequence of Bragg peaks is typical of a hexagonally-packed cylinder morphology (refer Figure 2.13), which was expected of SBS with a polystyrene concentration of 29.5 %·wt [216]. The hexagonal-cylinder structure of SBS is shown in Figure 7.4. Incorporation of ibPOSS into the SBS matrix had no influence on the location of the primary peak at $q = 0.026$ nm$^{-1}$, with the SBS-ibPOSS composites exhibiting a similar d-spacing value as SBS of ~241 nm ($d = 2\pi/q_{\text{max}}$). This indicates that ibPOSS does not change the cylindrical structure of SBS. Although peak location remained fairly constant, peak intensity decreased with filler concentration. This was especially noticeable at filler loadings of 10 and 20 %·wt, where the peaks at 0.042 and 0.069 nm$^{-1}$ become broader and tapered. Fu et al [216] observed a similar decrease in peak intensity and lack-of-change in peak location in SBS composites grafted with isobutylPOSS. The behaviour was attributed to isobutylPOSS inhibiting the long-range order of polystyrene domains, restricting their packing ability. Conversely, phenylPOSS composites experienced a $q_1$ shift toward smaller angles (larger d-spacing values) with increasing concentration,
exhibiting maximum d-spacing values at concentrations of 10 %·wt. This behaviour is indicative of an increase in the interdomain distance between polystyrene domains.

In order to quantify this behaviour, the interdomain distance (D) was calculated using Equation 7.1 [423];

\[ D = \frac{4}{3} \cdot d_{100} \]  

Figure 7.3 One-dimensional SAXS profiles; (a) SBS and SBS-ibPOSS-adichl composites, (b) 10 %·wt filled composites. Spectra have been shifted for clarity.
where \( d_{100} \) corresponds to the \( d \) spacing value of the primary peak. Pure SBS yielded an interdomain distance of 278 nm. As summarised in Table 7.1, isobutylPOSS composites displayed little variation in \( D \) while materials reinforced with phenylPOSS exhibited an increase in \( D \) with filler content, reaching maximum values of 329 and 340 nm for SBS-phPOSS-adichl 10 and SBS-phPOSS-sebchl 10, respectively. Incorporation of phenylPOSS into SBS leads to the fillers dispersing throughout the polystyrene domains, facilitated by the phenyl compatibilising groups. This results in expansion of the cylindrical polystyrene domains, leading to the centres of the cylinders becoming further apart from one another.

\[
R_{\text{cylinders}} = \left[ d_{100} \left( \frac{3^{1/2} \phi_B}{2\pi} \right)^{1/2} \right] \tag{7.2}
\]

where \( \phi_B \) is the volume fraction of the minor phase. IsobutylPOSS exhibited relatively little influence on \( R_{\text{cylinders}} \), while the incorporation phenylPOSS expanded the radius of the polystyrene domains. However, at filler loadings of 20 %\text{-}wt \( d \) spacing, \( D \) and \( R_{\text{cylinders}} \) decreased. Given the limited volume available for phenylPOSS to disperse throughout, higher filler loadings will increase the probability of phenylPOSS dispersing in polybutadiene domains and forming agglomerates. Therefore, we can conclude that at filler concentrations up to and including 10 %\text{-}wt, phenylPOSS expands the cylindrical polystyrene domains, resulting in the interdomain distance increasing. As filler loading is increased past 10 %\text{-}wt, phenylPOSS is likely to be dispersed throughout both
polybutadiene and polystyrene phases, leading to a reduction in interdomain distance, cylinder radius and subsequent segregation between hard and soft domains.

**Table 7.1** SAXS data of SBS and SBS-POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>d-spacing (nm)</th>
<th>D (nm)</th>
<th>R_{cylinders} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>241</td>
<td>278</td>
<td>328</td>
</tr>
<tr>
<td>ibPOSS-adichl 1</td>
<td>253</td>
<td>292</td>
<td>345</td>
</tr>
<tr>
<td>ibPOSS-adichl 5</td>
<td>253</td>
<td>292</td>
<td>345</td>
</tr>
<tr>
<td>ibPOSS-adichl 10</td>
<td>245</td>
<td>283</td>
<td>334</td>
</tr>
<tr>
<td>ibPOSS-adichl 20</td>
<td>245</td>
<td>283</td>
<td>334</td>
</tr>
<tr>
<td>ibPOSS-sebchl 1</td>
<td>245</td>
<td>283</td>
<td>334</td>
</tr>
<tr>
<td>ibPOSS-sebchl 5</td>
<td>253</td>
<td>292</td>
<td>345</td>
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<tr>
<td>ibPOSS-sebchl 10</td>
<td>250</td>
<td>289</td>
<td>341</td>
</tr>
<tr>
<td>ibPOSS-sebchl 20</td>
<td>253</td>
<td>292</td>
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</tr>
<tr>
<td>phPOSS-adichl 1</td>
<td>253</td>
<td>292</td>
<td>345</td>
</tr>
<tr>
<td>phPOSS-adichl 5</td>
<td>268</td>
<td>310</td>
<td>365</td>
</tr>
<tr>
<td>phPOSS-adichl 10</td>
<td>285</td>
<td>330</td>
<td>389</td>
</tr>
<tr>
<td>phPOSS-adichl 20</td>
<td>276</td>
<td>318</td>
<td>375</td>
</tr>
<tr>
<td>phPOSS-sebchl 1</td>
<td>261</td>
<td>301</td>
<td>355</td>
</tr>
<tr>
<td>phPOSS-sebchl 5</td>
<td>275</td>
<td>318</td>
<td>375</td>
</tr>
<tr>
<td>phPOSS-sebchl 10</td>
<td>295</td>
<td>340</td>
<td>401</td>
</tr>
<tr>
<td>phPOSS-sebchl 20</td>
<td>285</td>
<td>330</td>
<td>389</td>
</tr>
</tbody>
</table>

All composites displayed peak broadening with increasing filler concentration. Among the factors which influence peak breadth is polydispersity [215], however the difference in peak breadth of the composites is most likely due to variances in structural domain size due to changes in packing ability caused by the introduction of functionalised POSS. As shown in Figure 7.3b, phenylPOSS composites exhibited broader primary peaks (q₁) than their isobutylPOSS counterparts, in particular at filler loadings of 10 and 20 %·wt. As mentioned previously, POSS inhibits the long-range order of polystyrene domains, restricting their packing ability. The increased domain radii and interdomain distance due to the incorporation of phenylPOSS will increase the difficulty of achieving hexagonal-close
packing, reducing material regularity. At concentrations of 20 %·wt, segments of phenylPOSS within the polybutadiene phase may further hinder the packing process. Hence, phenylPOSS composites displayed broader peaks than their isobutyl counterparts.

### 7.3.3 Optical properties of SBS-dumbbell POSS nanocomposites

The influence of the functionalised-POSS fillers on optical properties was analysed using UV-visible spectroscopy. In addition to thermal resistance and softness, optical clarity is a crucial property of developmental thermoplastic elastomers [200]. The incorporation of micro-sized particles as fillers into a polymer matrix absorbs and scatters light, reducing optical clarity [425]. Scattering can be reduced by encouraging particle dispersion and matrix-filler interaction, with the optimum filler diameter being ~200 nm (half the wavelength of visible light). The absorbance spectra of 5 %·wt-filled POSS nanocomposites are shown in Figure 7.5a. Incorporating POSS within the SBS matrix caused an increase in absorbance, which continued to rise with filler concentration. PhenylPOSS composites displayed higher absorbance values than their isobutylPOSS counterparts for the same concentration. Although all materials were subjected to ultrasonic disruption in an attempt to achieve this level of dispersion, the effect of phase preference needs to be considered. The SBS matrix is a block copolymer composed of approximately 70.5 %·wt polybutadiene and 29.5 %·wt polystyrene. Since the amount of butadiene (continuous, rubbery block) phase is significantly higher than styrene (glassy block), isobutylPOSS particles with an affinity for the rubber phase have greater volume for dispersion. In contrast, POSS with a preference for the polystyrene domains have a more constrained local environment to disperse throughout and will increase the likelihood of aggregates remaining. This contrast in dispersion and subsequent light scattering properties compliment the SEM observations (refer Figure 7.2).
Figure 7.5 Absorbance spectra of SBS-dumbbell POSS composites; (a) 5 %·wt filled POSS composites, (b) ibPOSS-sebchl composites

The UV-visible absorbance spectra of SBS-ibPOSS-sebchl nanocomposites are shown in Figure 7.5b. The intensity of the UV-visible absorbance increased with POSS concentration, correlating to the increase in filler-agglomerates and number of POSS particles available to scatter UV-visible light. Minimal differences were observed between composites containing adipoyl and sebacoyl chloride-functionalised POSS, due to scattering being influenced greater by the degree of dispersion rather than particle geometry/flexibility [426]. The
addition of functionalised-POSS caused the absorption spectra to shift towards longer wavelengths, with the inflection onset shifting towards longer wavelengths with concentration. This suggests that POSS reduces the amount of effective energy within the polymer, shifting the spectra [427].

7.3.4 Thermal stability of SBS-dumbbell POSS nanocomposites

The mass loss versus temperature curves of pure SBS and ibPOSS-adichl nanocomposites are shown in Figure 7.6. The decomposition of SBS shows one degradation step at ~467 °C. The thermal degradation mechanism of SBS consists of two main processes, namely chain scission and crosslinking [428]. As seen in Figure 7.5, incorporation of functionalised POSS into the SBS matrix increased the temperature at which the maximum rate of degradation occurs (T_d), with SBS-ibPOSS-adichl 1 POSS yielding T_d values of 468 °C. T_d continued to increase with filler content, reaching a maximum of 478 °C in SBS-ibPOSS-adichl 20. As displayed in Figure 7.5b, the mass loss rate maximum decreased with increasing filler content, ranging from 58 (pure SBS) to 42 %·min^{-1} (ibPOSS-adichl 20). This behaviour is characteristic of the thermal stability of POSS which stems from its silicon-oxygen structure. A proposed mechanism of thermal reinforcement is that POSS molecules restrict polymer chain motions, due to polymer-filler interactions or by the large inertia exhibited by segments of polymer containing POSS [147, 409]. The compatibilising organic groups on the POSS encourage this interfacial interaction, allowing thermal reinforcement to be achieved. The POSS can provide the most ‘torturous path’ for thermal degradation, lengthening the degradation process and increasing thermal stability. Following degradation, all materials displayed mass values corresponding to their respective filler concentrations.
At filler concentrations of 1-5 %·wt (agglomerate diameter generally < 2 μm), nanocomposites containing isobutylPOSS showed higher $T_d$ values than their phenylPOSS counterparts. The thermal stability of SBS is dependent on the sensitivity of the double bonds within the continuous, butadiene phase [208, 428]. When dispersed throughout the rubber phase, POSS imparts added stiffness into the matrix by acting as crosslink points and reducing chain mobility [429, 430]. This provides thermal stability to the phase upon
which the thermal degradation mechanism is dependent. At higher filler loadings (10 and 20 %·wt), phenylPOSS composites were observed to be more thermally stable than those containing isobutylPOSS. This is attributed, in part, to the difference in thermal stability between the phenyl and isobutyl ‘R’ compatibilising groups, with the former possessing greater intrinsic thermal stability [431, 432], displayed in Figure 7.7. A proposed mechanism is that at filler concentrations of 10 %·wt and higher, phenyl ‘R’ groups are more effective at reinforcing or ‘shielding’ the butadiene domains than isobutyl groups. Another possibility is that at higher filler loadings, phenylPOSS segments may be present within the polybutadiene phase.

Figure 7.7 Adipoyl chloride-functionalised POSS with varying ‘R’ groups; (a) phenyl, (b) isobutyl; grey = carbon, red = oxygen, purple = silicon, blue = nitrogen; hydrogens removed for clarity

Figure 7.8 shows that composites containing POSS functionalised with adipoyl chloride exhibited greater thermal stability than those functionalised with sebacoyl chloride. Several authors have observed similar behaviour for materials containing diacyl chlorides with different 'bridge' lengths (succinyl, adipoyl, sebacoyl, etc) [433-435], with thermal stability being inversely proportional to alkane chain length. Adipoyl chloride contains a
butane 'bar' connecting the two amide groups while sebacoyl chloride contains an octane linkage. As alkane chain length is increased, the amount of organic fuel for combustion increases [436, 437], leading to reduced thermal stability. Therefore, the relatively rigid butane linkage of adipoyl chloride will provide greater thermal stability and be less susceptible to thermal degradation than the octane 'bar' of sebacoyl chloride.

Figure 7.8 TGA curves of 20 %·wt-filled nanocomposites; (a) mass loss, (b) derivative mass
Chapter 7: Thermomechanical and Morphological Properties of Elastomer-POSS Composites

Table 7.2 $E_a$ values of SBS-dumbbell POSS nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_a$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>116</td>
</tr>
<tr>
<td>ibPOSS-adichl 1</td>
<td>116</td>
</tr>
<tr>
<td>ibPOSS-adichl 5</td>
<td>121</td>
</tr>
<tr>
<td>ibPOSS-adichl 10</td>
<td>124</td>
</tr>
<tr>
<td>ibPOSS-adichl 20</td>
<td>127</td>
</tr>
<tr>
<td>ibPOSS-sebchl 1</td>
<td>115</td>
</tr>
<tr>
<td>ibPOSS-sebchl 5</td>
<td>119</td>
</tr>
<tr>
<td>ibPOSS-sebchl 10</td>
<td>122</td>
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<td>ibPOSS-sebchl 20</td>
<td>125</td>
</tr>
<tr>
<td>phPOSS-adichl 1</td>
<td>110</td>
</tr>
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<td>phPOSS-adichl 5</td>
<td>118</td>
</tr>
<tr>
<td>phPOSS-adichl 10</td>
<td>129</td>
</tr>
<tr>
<td>phPOSS-adichl 20</td>
<td>132</td>
</tr>
<tr>
<td>phPOSS-sebchl 1</td>
<td>109</td>
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<td>118</td>
</tr>
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<td>126</td>
</tr>
<tr>
<td>phPOSS-sebchl 20</td>
<td>130</td>
</tr>
</tbody>
</table>

The Coats and Redfern model (Equation 3.11) was applied to determine the activation energy of degradation ($E_a$) of SBS-dumbbell POSS nanocomposites. The $E_a$ values are summarised in Table 7.2. Pure SBS exhibited an $E_a$ value of 116 kJ·mol$^{-1}$. The incorporation of functionalised POSS had a positive effect on $E_a$, with maximum values obtained for phPOSS-adichl 20 (132 kJ·mol$^{-1}$) and phPOSS-sebchl 20 (130 kJ·mol$^{-1}$). The increase in $E_a$ implies that functionalised POSS enhances the thermal stability of SBS, increasing the energy barrier required for thermal degradation to occur. Furthermore, maximum $E_a$ values observed for phPOSS-adichl 20 and phPOSS-sebchl 20 nanocomposites are in agreement with the highest thermal stability being observed for materials containing 10 and 20 %·wt functionalised POSS. Composites containing POSS functionalised adipoyl
chloride displayed higher $E_a$ values their sebacoyl chloride counterparts, correlating to experimentally observed trends.

7.3.5 Thermomechanical properties of SBS-dumbbell POSS nanocomposites

7.3.5.1 Stress-strain

The stress-strain curves of SBS and SBS-ibPOSS composites are presented in Figure 7.9, while the tensile properties are summarised in Table 7.3. All composites exhibited stress-strain curves with similar features. Application of load caused an initial linear increase in strain, due to the occurrence of elastic deformation. This extension continued until reaching a maximum at the yield stress, most notably with increasing ibPOSS-adichl concentration. Increasing the stress past yield caused a brief plateau in strain as the composites enter the non-linear region and experience viscoelastic flow. Further increase in stress imparted strain hardening into the composites, as strain continued to increase with applied load. Pure SBS displayed a tensile modulus ($E$) of 26.9 MPa and strength of 3.0 MPa. Addition of POSS had a positive effect on $E$ and strength, reaching maximum values at filler loadings of 20 %·wt. The increase is characteristic of the reinforcement ability of POSS. The applied stress was transferred from the SBS matrix to the POSS filler resulting in increased strength and stiffness. This stress-transfer process was aided by sufficient interfacial adhesion between the matrix and filler, achieved through compatibilising ‘R’ groups on the POSS molecules. Furthermore, effective dispersion of the filler throughout the SBS matrix, produced by ultrasonic disruption during composite preparation and confirmed by SEM (refer Figure 7.2), contributed to the improved mechanical properties. Filler dispersion promotes an even transfer of stress from the matrix to the reinforcement and prevents the formation of stress concentrations. This mechanism is crucial for enhancing mechanical properties within filler-dispersed composites.
Figure 7.9 (a) stress-strain curves of SBS-ibPOSS-adichl nanocomposites, (b) elastic deformation component of SBS-ibPOSS-sebchl nanocomposites, showing the influence of filler concentration
Table 7.3 Tensile mechanical properties of SBS-dumbbell POSS nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile modulus (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Strain hardening modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>26.9</td>
<td>3.0</td>
<td>5.9</td>
</tr>
<tr>
<td>ibPOSS-adichl 1</td>
<td>43.7</td>
<td>3.6</td>
<td>6.9</td>
</tr>
<tr>
<td>ibPOSS-adichl 5</td>
<td>78.6</td>
<td>4.1</td>
<td>7.2</td>
</tr>
<tr>
<td>ibPOSS-adichl 10</td>
<td>86.3</td>
<td>4.5</td>
<td>5.9</td>
</tr>
<tr>
<td>ibPOSS-adichl 20</td>
<td>137.1</td>
<td>5.0</td>
<td>7.8</td>
</tr>
<tr>
<td>ibPOSS-sebchl 1</td>
<td>41.1</td>
<td>3.4</td>
<td>6.1</td>
</tr>
<tr>
<td>ibPOSS-sebchl 5</td>
<td>80.5</td>
<td>4.0</td>
<td>8.0</td>
</tr>
<tr>
<td>ibPOSS-sebchl 10</td>
<td>83.7</td>
<td>4.1</td>
<td>7.1</td>
</tr>
<tr>
<td>ibPOSS-sebchl 20</td>
<td>115.5</td>
<td>4.8</td>
<td>7.6</td>
</tr>
<tr>
<td>phPOSS-adichl 1</td>
<td>37.8</td>
<td>3.1</td>
<td>6.5</td>
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<tr>
<td>phPOSS-adichl 5</td>
<td>62.3</td>
<td>3.5</td>
<td>6.9</td>
</tr>
<tr>
<td>phPOSS-adichl 10</td>
<td>74.3</td>
<td>3.8</td>
<td>7.0</td>
</tr>
<tr>
<td>phPOSS-adichl 20</td>
<td>94.1</td>
<td>4.5</td>
<td>8.6</td>
</tr>
<tr>
<td>phPOSS-sebchl 1</td>
<td>32.3</td>
<td>3.1</td>
<td>8.5</td>
</tr>
<tr>
<td>phPOSS-sebchl 5</td>
<td>51.0</td>
<td>3.2</td>
<td>8.3</td>
</tr>
<tr>
<td>phPOSS-sebchl 10</td>
<td>59.7</td>
<td>3.5</td>
<td>7.8</td>
</tr>
<tr>
<td>phPOSS-sebchl 20</td>
<td>80.1</td>
<td>4.2</td>
<td>9.1</td>
</tr>
</tbody>
</table>

IsobutylPOSS composites exhibited the greatest modulus and strength values. This was attributed to the dispersion of POSS within the polybutadiene (rubber) phase of the SBS, facilitated by the isobutyl ‘R’ groups on the POSS molecule. The styrene domains within SBS act as cross-links, restricting the flow of the rubber phase and providing strength and durability. Incorporating POSS into the rubber phase provides additional reinforcement, allowing for greater amounts of stress to be transferred from the polybutadiene. The $E$ increased with filler content, ranging from 43.7 and 41.1 MPa for 1 %·wt composites of isobutylPOSS-adichl and isobutylPOSS-sebchl, respectively, to 137.1 and 115.5 MPa for their respective 20 %·wt counterparts. As shown in Figure 7.10a, phenylPOSS composites exhibited lower $E$ and yield strength values than composites containing isobutylPOSS, due
to the phenyl ‘R’ groups on the POSS molecules which provide an affinity towards the glassy, polystyrene segments within the SBS. This reduces the chance of POSS being dispersed throughout the continuous polybutadiene phase and providing adequate reinforcement. Additionally, POSS functionalised with adipoyl chloride had a greater influence on modulus and yield strength than their sebacoyl chloride counterparts. This was attributed to the difference in ‘dumbbell’ length of the two molecules. POSS molecules functionalised with adipoyl chloride are bridged by a shorter, less-flexible and more constrained butane chain segment. This provides greater rigidity and reinforcement than the longer, more-flexible octane chain segment of sebacoyl chloride.

All composites exhibited strain hardening past the yield, due to deformation of the hard (polystyrene) domains and alignment of polymer chains in both segments [438]. Within elastomers, the glassy components contribute to strain hardening by providing rigidity [439]. The strain hardening modulus was calculated from the slope of the stress-strain curves following the onset of strain-hardening. As shown in Figure 7.10b, phenylPOSS composites displayed higher strain hardening moduli than isobutylPOSS (refer Table 7.3) and supported greater stress levels past the yield. Introducing phenylPOSS into the SBS matrix provides additional styrene (hard) domains which increase “hinge length” (the length of rigid-chain units between flexible linkages) [440]. IsobutylPOSS composites also exhibited greater strain hardening than pure SBS due to the fillers acting as crosslinks, increasing network density and encouraging strain delocalisation [441]. The tensile results indicate that isobutylPOSS is most effective for improving tensile modulus and strength while phenylPOSS allows for support of greater stress levels following plastic deformation.
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7.3.5.2 Creep-recovery

The creep-recovery curves of SBS and nanocomposites are shown in Figure 7.11. Several distinctive regions can be observed in the creep-recovery curve of pure SBS with the application and removal of load. The first is the instantaneous increase in strain, due to the elastic response of the butadiene phase. This is followed by the viscoelastic response, where time-dependent molecular rearrangement occurs. In elastomers, molecular motions

**Figure 7.10** Stress-strain curves of 20 %wt filled composites; (a) elastic deformation component, (b) total curves
involve chain sliding mechanisms, except at entanglements and crosslinks [442].

Increasingly along the load application period, viscous flow of the polymer is observed. Although the styrene domains provide some resistance against creep deformation, these crosslinks may undergo bond cleavage and deformation at sufficient stress levels over extended periods of time [443]. Removal of the load results in a rapid drop in strain response, which is equal to the initial elastic response. The recovery period involves time-dependent molecular relaxations as the polymer attempts to regain original dimensions [297, 298]. Since SBS exhibited viscous flow, full recovery is unattainable leaving a permanent deformation.

Creep deformation decreased with increasing POSS content, as displayed in Figure 7.11a. This was expected of an elastomer filled with rigid reinforcement. Due to its ceramic silica structure, the presence of POSS imparts stiffness into the matrix and aids in restricting the molecular motions of the polybutadiene chains, resulting in a lower susceptibility to deform under a given load. Furthermore, the compatibilising organic groups on the POSS encourage interaction between the matrix and filler, contributing to nanocomposite resistance to deformation. At higher POSS loadings (10 and 20 %wt), nanocomposites exhibited flatter creep curves with a lower gradient, indicating a decrease of deformation of the viscous component. Nanocomposites containing isobutylPOSS exhibited less deformation than their phenylPOSS counterparts due to filler phase compatibility, which was in agreement with the stress-strain results. Since the polybutadiene chains, which makes up the rubbery continuous phase of SBS experience molecular rearrangement and motions under stress, it is more effective to disperse filler throughout this phase in order to reduce deformation and obtain dimensional stability.
When comparing the curves of the adipoyl and sebacoyl chloride POSS composites (Figure 7.11b), a significant difference in creep behaviour is evident. Nanocomposites containing POSS functionalised with adipoyl chloride showed considerably less creep behaviour and deformation than those functionalised with sebacoyl chloride. This occurrence can be attributed to the difference in ‘barbell’ length for the POSS molecules. The shorter, more-rigid butane ‘bar’ of adipoyl chloride provides greater...
resistance to creep and deformation, compared with its flexible octane (sebacoyl chloride) counterpart. This observation is in good correlation with the stress-strain results and suggests that the bridge length between two POSS molecules can impart some physical constraints to dimensional stability.

The parameters of the four-element model were calculated for the creep components of SBS and the nanocomposites, which are presented in Table 7.4. SBS exhibited the greatest strain response under load while the POSS nanocomposites were found to lessen the creep strain response, providing steric resistance to both elastic and viscous contributions. The Maxwell modulus ($E_1$) of SBS was 0.22 MPa, which was increased with POSS content particularly at higher contents (5-20 %·wt), confirming that the nano-sized particulate fillers influenced the flow characteristic of the SBS matrix. The Maxwell viscosity ($η_1$) followed similarly with an increase with POSS content. These results confirm the addition aids in restraining deformation, even more so at higher amounts of POSS. This is attributed to the dispersion of nano-particulates and phase compatibility with the isobutyl or phenyl functionalisation and phase preferentiation, even with the formation of aggregates at higher content. Nanocomposites containing ibPOSS exhibited larger Maxwell component ($E_1$ and $η_1$) values than their phenylPOSS counterparts functionalised with the same diacyl chloride. Similarly, composites with adipoyl chloride functionalised POSS yielded higher values than sebacoyl chloride functionalised POSS. All materials displayed a certain proportion of unrecovered strain that is characteristic of viscous, amorphous materials such as SBS. This is due to chain entanglement slippage and detachment of styrene domains from the polybutadiene rubber-phase that may occur during the application of load. Permanent deformation increased with POSS concentration, with nanocomposites containing adipoyl chloride-isobutylPOSS displaying the largest values. Higher concentrations of filler, such as POSS, restrict the relaxation of SBS chains, causing irreversible chain slippage and unraveling. The Voigt viscosity ($η_2$) was observed to increase with POSS content, suggesting an increase in resistance of the SBS chains to uncoil.
Table 7.4 Creep-recovery data of SBS-dumbbell POSS nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_1$ (MPa)</th>
<th>$\eta_1$ (MPa·s$^{-1}$)</th>
<th>$E_2$ (MPa)</th>
<th>$\eta_2$ (MPa·s$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>Permanent deformation (%)</th>
</tr>
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<tbody>
<tr>
<td>SBS</td>
<td>0.22</td>
<td>67.91</td>
<td>0.35</td>
<td>3.31</td>
<td>9.46</td>
<td>18</td>
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<tr>
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<td>0.25</td>
<td>60.16</td>
<td>0.44</td>
<td>3.60</td>
<td>7.78</td>
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<tr>
<td>ibPOSS-adichl 5</td>
<td>0.26</td>
<td>75.43</td>
<td>0.63</td>
<td>3.97</td>
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<tr>
<td>ibPOSS-adichl 10</td>
<td>0.42</td>
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<tr>
<td>phPOSS-adichl 10</td>
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<td>0.66</td>
<td>4.18</td>
<td>7.10</td>
<td>21</td>
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<tr>
<td>phPOSS-adichl 20</td>
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<td>0.69</td>
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<td>6.02</td>
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<td>phPOSS-sebchl 1</td>
<td>0.21</td>
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<td>3.07</td>
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<tr>
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<td>0.23</td>
<td>79.19</td>
<td>0.51</td>
<td>3.54</td>
<td>7.67</td>
<td>19</td>
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<tr>
<td>phPOSS-sebchl 20</td>
<td>0.36</td>
<td>85.36</td>
<td>0.60</td>
<td>4.07</td>
<td>6.00</td>
<td>18</td>
</tr>
</tbody>
</table>

In order to determine $\eta_2$, the retardation time ($\tau$) was calculated using Equation 3.5. It is the time required for the Voigt element (viscoelastic component) to recover to 63.21% (or 1-1/e) of its total deformation. Increasing the POSS content caused the $\tau$ to decrease, suggesting that the nanocomposites become more solid-like in behaviour at higher filler concentrations. Similarly, highly filled composites exhibited flatter recovery curves, indicating a faster recovery of the viscoelastic and elastic components. Nanocomposites containing phenylPOSS displayed slightly longer $\tau$ than their isobutylPOSS counterparts with the same 'barbell' length. When rubbery, polybutadiene chains are highly stretched under an applied load, phenylPOSS molecules can become detached from the glassy, styrene domains for which they have an affinity. This can lead to dissimilar block-mixing.
occurring in interfacial regions, causing an increase in permanent deformation [443]. This behaviour can be further complicated by the possible forced migration of phenylPOSS molecules under axial strain. Nanocomposites functionalised with adipoyl chloride yielded shorter $\tau$ than those functionalised with sebacoyl chloride. This was attributed to the increased restrictions placed on segmental motions for relaxation by the stiffer, butane bridge, causing the material to behave in a more solid-like nature. The bridge-lengths of phenylPOSS dumbbell structures are compared in Figure 7.12. These results correlate well to the behaviour observed in the creep component and stress-strain analysis.

Figure 7.12 PhenylPOSS-functionnalised with varying di-acyl chloride 'bridges'; (a) sebacoyl chloride, (b) adipoyl chloride; grey = carbon, red = oxygen, purple = silicon, blue = nitrogen; hydrogens removed for clarity

In order to further examine relaxation behaviour, the KWW stretched exponential function was applied to SBS and the nanocomposites. The results are presented in Table 7.5. In fitting the function, the pre-exponential constant ($A$) and relaxation time ($\tau$) decreased with increasing POSS content. This was to be expected since the relaxation provides an
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Indication of the degree of mobility that molecules within the polymer possess. The decreased relaxation time at higher POSS concentrations is indicative of the solid-like behaviour highly-filled nanocomposites exhibit and is in agreement with the creep data obtained using the four-element model. Correspondingly, the shape fitting parameter $\beta$ changed with POSS content. These observations strongly suggest that the nanocomposites experience restricted flow, attributed to the incorporation of functionalised-POSS.

Table 7.5 KWW parameters of SBS-dumbbell POSS nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
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<th>$\beta$</th>
<th>$\tau$ (s)</th>
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<tbody>
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<td>9.51</td>
</tr>
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<td>0.04</td>
<td>6.33</td>
</tr>
<tr>
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<td>0.09</td>
<td>30.11</td>
</tr>
<tr>
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<td>0.07</td>
<td>22.78</td>
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<td>0.05</td>
<td>17.70</td>
</tr>
<tr>
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<td>0.12</td>
<td>12.44</td>
</tr>
<tr>
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<td>0.09</td>
<td>32.98</td>
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<tr>
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</tr>
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<td>0.05</td>
<td>11.77</td>
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<tr>
<td>phPOSS-sebchl 20</td>
<td>2.40</td>
<td>0.10</td>
<td>12.63</td>
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</tbody>
</table>

7.3.5.3 Modulated force – thermomechanometry

Figure 7.13 shows the storage modulus ($E'$) of SBS and nanocomposites filled with 20 %wt functionalised POSS. At temperatures below -100 °C the SBS was in a glassy state, with the modulus remaining fairly constant at ~2.0 GPa. The modulus began to decrease as it approached the $\alpha$ glass-rubber transition of the rubbery, butadiene phase. Heating above
the glass transition temperature ($T_g$) provides sufficient activation energy for rotation about bonds in segments of the polymer, causing a loss in material rigidity. Following this transition, the modulus of SBS briefly plateaued at -30 °C, maintaining a E’ value of ~0.03 GPa. Increasing the temperature caused a second drop in modulus as the glassy, styrene phase of SBS underwent the β glass-rubber transition (88 °C). At higher temperatures (>110 °C), the styrene segments flow after undergoing the transition and are unable to continue to provide the SBS with structural integrity and reinforcement. As a result, the polymer lacks rigidity, exhibiting very viscous and liquid-like properties.

Figure 7.13 Storage modulus (E’) curve across the polybutadiene glass-rubber transition of SBS and 20 %·wt filled composites

The E’ values of nanocomposites at various temperatures are summarised in Table 7.6. Nanocomposites containing POSS displayed higher E’ values than pure SBS, increasing with POSS concentration, indicative of the increased stiffness attained with the addition of nanoparticles in the matrix. As shown in Figure 7.13, the E’ modulus reached a maximum at POSS concentrations of 20 %·wt, with SBS-ibPOSS-adichl 20 and SBS-ibPOSS-sebchl 20 exhibiting E’ values of 5.3 and 5.0 GPa at -90 °C, respectively. Similar observations were recorded at the plateau before the polystyrene transition, with maximum E’ values of 0.24 and 0.21 GPa for SBS-ibPOSS-adichl 20 and SBS-ibPOSS-sebchl 20, respectively at 10 °C. The highest modulus values were exhibited by composites containing isobutylPOSS
Chapter 7: Thermomechanical and Morphological Properties of Elastomer-POSS Composites

Functionalised with adipoyl chloride, attributed to influence of phase preference and filler stiffness, respectively. This influence of filler structure on mechanical properties is in agreement with behaviour observed in creep-recovery analysis. At temperatures above the \( \alpha \) (butadiene) transition, the relative decrease in \( E' \) modulus was reduced when compared with pure SBS, while an increase in the \( E' \) reduction rate was observed at temperatures above the \( \beta \) (styrene) transition. A significant shift in \( E' \) \( \alpha \)-transition was observed for ibPOSS, which is further discussed below.

<table>
<thead>
<tr>
<th>Material</th>
<th>( E' ) (MPa)</th>
<th>( T_g ) from ( E'' ) max (°C)</th>
<th>( T_g ) from tan (δ) max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-90 °C</td>
<td>10 °C</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>SBS</td>
<td>2.0</td>
<td>0.03</td>
<td>-75</td>
</tr>
<tr>
<td>ibPOSS-adichl 5</td>
<td>3.2</td>
<td>1.4</td>
<td>-72</td>
</tr>
<tr>
<td>ibPOSS-adichl 20</td>
<td>5.3</td>
<td>0.24</td>
<td>-64</td>
</tr>
<tr>
<td>ibPOSS-sebchl 5</td>
<td>3.0</td>
<td>1.3</td>
<td>-73</td>
</tr>
<tr>
<td>ibPOSS-sebchl 20</td>
<td>5.0</td>
<td>0.21</td>
<td>-65</td>
</tr>
<tr>
<td>phPOSS-adichl 5</td>
<td>2.9</td>
<td>1.1</td>
<td>-74</td>
</tr>
<tr>
<td>phPOSS-adichl 20</td>
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<td>-78</td>
</tr>
<tr>
<td>phPOSS-sebchl 5</td>
<td>2.5</td>
<td>0.09</td>
<td>-75</td>
</tr>
<tr>
<td>phPOSS-sebchl 20</td>
<td>4.4</td>
<td>0.20</td>
<td>-77</td>
</tr>
</tbody>
</table>

The loss modulus (\( E'' \)) of SBS and nanocomposites is shown in Figure 7.14, while \( T_g \) values are summarised in Table 7.6. The \( T_g \) is determined by the peak of the \( E'' \) curve (\( E''_{\text{max}} \)), since that is where maximum heat dissipation occurs. Pure SBS displays two peaks in the \( E'' \) curve, located at -75 and 88 °C. These peaks correspond to the \( T_g \) of the butadiene and styrene phases, respectively. Addition of POSS caused the \( T_g \) to increase, reaching a maximum at 20 %·wt. The increase in glass transition temperature is attributed to the ability of the functionalised-POSS to restrict molecular motions of the polymer chains, causing the material to become less flexible. In addition, composites exhibited glass transitions over a larger temperature range, as indicated by the broader \( E'' \) peaks. The increase in peak breadth is attributed to an increase in the distribution of segmental
relaxation times of the matrix [356]. Peak breadth was observed to increase with POSS concentration, reaching maximum values at loadings of 10 and 20 %·wt, indicating an increase in the relaxation time required due to segmental constraints, including polymer chain coupling/entanglements and polymer-POSS interactions.

![Figure 7.14](image)

**Figure 7.14** Loss modulus (E”) curve across the polybutadiene glass-rubber transition of SBS and 20 %·wt filled composites

As summarised in Table 7.6, composites containing isobutylPOSS displayed the greatest increase in \( T_g \) for the butadiene phase, with ibPOSS-adichl 20 and ibPOSS-sebchl 20 yielding \( T_g \) values of -65 and -64 °C, respectively. Similarly, materials filled with phenylPOSS exhibited higher \( T_g \) values for the polystyrene transition than their isobutylPOSS counterparts. This behaviour suggests that the compatibilising groups are providing an affinity for their corresponding phases, allowing the POSS to disperse throughout and entangle within a particular phase within the SBS. At concentrations of 10 and 20 %·wt phenylPOSS slightly reduced the \( T_g \) of polybutadiene. Due to the limited volume of polymer available for the phenylPOSS to disperse throughout, at higher filler loadings (10 and 20 %·wt) small fractions of phenylPOSS may be present within the soft, polybutadiene domains, reducing the \( T_g \) [214]. Composites functionalised with adipoyl chloride displayed higher \( T_g \) values than those treated with sebacoyl chloride. This was due
to the structure of adipoyl chloride’s butane chain segment, which allows for additional restraint on molecular motions.

The loss tangent (tan (δ)) of SBS and several nanocomposites is shown in Figure 7.15. The maximum of the tan (δ) curve can also be used to determine $T_g$, although the $E''$ maximum is shown to be more consistent with other determinations of $T_g$. The tan (δ) were ~6-8 °C higher than $T_g$ obtained from loss modulus curves (refer Table 7.6). The glass transition temperatures obtained from the loss tangent maximum displayed similar trends to those obtained from $E''_{\text{max}}$. Nanocomposites containing isobutylPOSS showed a reduction in butadiene-phase peak height, with 20%·wt exhibiting the greatest reduction. Conversely, increasing the isobutylPOSS concentration caused an increase in the styrene-phase peak. The amplitude of the tan (δ) peak provides an indication of the number of kinetic units mobile enough to contribute to the glass transition [357]. The decrease in peak intensity indicates that isobutylPOSS molecules restrict motions of polymer chains within the butadiene phase, as indicated by the isobutylPOSS nanocomposites displaying $T_g$ values higher than SBS. The increase peak height of the styrene phase suggests an increase in free volume and plasticising effect on the glassy domains, leading to composites displaying $T_g$ values lower than SBS. These observations correlate to SAXS results (refer Section 7.3.2) which revealed larger d-spacing values within phenylPOSS composites. This less-effective packing leads to additional pockets of free volume remaining, giving polymer chains more room for segmental motions resulting in reduced $T_g$ values. The addition of phenylPOSS similarly caused a decrease in the butadiene-phase peak, which was expected since the styrene domains within SBS provide the polymer with rigidity and structure.
Adipoyl chloride composites exhibited slightly lower tan(δ) peak heights than their sebacoyl chloride counterparts. This was attributed to composites containing stiffer, adipoyl chloride-functionalised POSS behaving more solid-like than those with sebacoyl chloride POSS, resulting in decreased dampening properties. The damping ability of a filled polymer system is believed to be influenced by two factors; (a) the amount of free volume, (b) internal friction between the filler and matrix and between the filler particles themselves across the glass transition region [444]. The latter increases as the number of chain movements become greater, leading to an increase in damping ability. Composites containing sebacoyl chloride-functionalised POSS are able to experience greater chain motion due to the flexible-bridge structure of the filler, experiencing greater internal friction than their adipoyl chloride counterparts and subsequently exhibiting enhanced dampening properties. As with the $E''$ curves, peak broadening of the tan(δ) curves was observed at higher filler loadings. Since the peak breadth is an indication of structural heterogeneity, the wider peaks suggest an increase in segmental relaxation time due to increased SBS-POSS interactions. The broader peaks are also indicative of the aforementioned increase in damping and internal friction.
7.4 Conclusion

SBS-dumbbell POSS nanocomposites were prepared via physical blending. Prior to their dispersion throughout the polymer matrix, POSS molecules were successfully functionalised with adipoyl and sebacoyl chloride as indicated by FTIR, creating dumbbell-shaped POSS. Agglomerate size increased with filler content, due to increased interactions between the POSS particles. The morphology of the nanocomposites was dependent on the organic substituent groups on the POSS cages, with the amount of filler agglomeration being dependent on the relative volume of butadiene or styrene phase to disperse throughout. IsobutylPOSS was observed to be confined within the polybutadiene domains and did not change the cylinder morphology of SBS. The increased d-spacing values of phenylPOSS composites suggests the filler expands polystyrene domains within the matrix, leading to an increase in interdomain distance.

IsobutylPOSS had the greatest influence on thermal stability at filler loadings of 1-5 %wt, due to its incorporation into the thermally-sensitive polybutadiene phase. At concentrations of 10 and 20 %wt, phenylPOSS composites exhibited greater thermal stability, corresponding to the increased presence of more-stable phenyl groups. POSS functionalised with adipoyl chloride exhibited greater influence on thermal stability than its sebacoyl chloride counterpart, due to the butane 'barbell' (alkane chain length) being less susceptible to thermal degradation than octane. The tensile modulus (E), yield strength and strain hardening of the nanocomposites increased with filler content. Creep deformation decreased and permanent strain increased with POSS content, due to the restricted molecular motions caused by filler. Incorporation of POSS increased the storage modulus (E’), loss modulus (E”) and glass transition temperature (T_g). Three factors contributed to the mechanical properties of the nanocomposites; (a) POSS concentration, (b) the phase which the POSS was dispersed throughout, (c) the architecture of the dumbbell-shaped POSS, specifically the 'barbell' length. The study demonstrates the versatility of POSS, being applicable as a filler core and functional group (refer Chapter 6).
CHAPTER 8: DYE-FUNCTIONALISED POSS ELASTOMER COMPOSITES*

8.1 Introduction

Coloured polymers are utilised in a variety of applications, particularly consumer products, packaging and building materials, due to improved appearance and aesthetic value. The traditional method of producing coloured polymer materials involves directly adding the dye or pigment into the polymer; however this process has several drawbacks. Conventionally coloured polymers can fade, lose colour or experience unexpected colour changes. Dyes may leach from the polymer matrix, lose intensity or bleach due to external factors, such as ultraviolet light, radiation and thermal degradation [445]. To further complicate matters, dispersion of dyes throughout a polymer is difficult, leading to observable swirling and variation in colour. Poor dispersion can lead to poor mechanical properties. Although compatibilisers have been used to aid with dye/pigment dispersion, they are expensive and can also be detrimental to mechanical and thermal properties. One solution is to covalently bond the dye to a stable media and disperse the dye-functionalised particles throughout the polymer. Functionalised-nanoparticles have been prepared by bonding reactive dyes with alumina [445] and silica [446, 447], although polymer composites containing dye-functionalised fillers have not been reported in literature, hence providing a novel opportunity to pursue.

In the previous chapter, POSS were successfully functionalised with di-acyl chlorides and exhibited phase selectivity following compounding into SBS. This chapter investigates the functionalisation of trisilanolPOSS with dichlorotriazine reactive dyes and their subsequent incorporation into SBS. These hybrid structures were chosen as an example of

Chapter 8: Dye-Functionalised POSS Elastomer Composites

Functionalisation of POSS with a large complex molecule, of which the concept could be extended to fluorescent, compatibilising and magnetic grafting species. The colour can be considered as a visual and measureable marker/probe. By preparing dye-functionalised POSS and dispersing them throughout SBS, the POSS can provide enhanced mechanical and thermal properties and overcome compatibility issues via its compatibilising ‘R’ groups. Simultaneously, the dye maintains its functionality, colouring the polymer matrix. The influence of dye structure and phase preference on the colourimetric/optical, thermal stability and thermomechanical properties of the composites is determined.

8.2 Materials and methods

8.2.1 Materials, experimental details and nanocomposite nomenclature

Material information, functionalisation and compounding procedures and characterisation methods are detailed in Chapter 3. The nomenclature for the nanocomposites is SBS-\(x\)POSS-\(y\)\(z\), where \(x\) corresponds to the functional groups on the POSS (\(ph = \)phenyl, \(ib = \)isobutyl), \(y\) is the dye that POSS was reacted with (blue or red) and \(z\) equals the amount of POSS or functionalised POSS within the composite by %·wt.

8.2.2 Thermomechanical analysis

A TA Instruments Q800 Dynamic Mechanical Analyser was used for df-TM and sf-TM analysis while mf-TM analysis was performed using a Perkin Elmer Diamond DMA. All analyses were conducted in tensile mode. df-TM and sf-TM test specimens had average dimensions of df-TM and sf-TM \(~12.80 \times 4.00 \times 0.70 \text{ mm}^3\) while materials analysed by mf-TM displayed average dimensions of \(~10.00 \times 4.00 \times 0.70 \text{ mm}^3\).

8.2.2.1 Stress-strain

Stress-strain (dynamic force-thermomechanometry, df-TM) analysis was performed using an initial force of 10 mN followed by an applied force increasing at a rate of \(1 \text{ N·min}^{-1}\), reaching a maximum of 18 N. Tests were conducted under ambient conditions (30 °C) to determine the linear viscoelastic region and elastic modulus. Results presented are the average of triplicate measurements.
8.2.2.2 Creep-recovery

Creep-recovery (static force-thermomechanometry, sf-TM) analysis was performed by subjecting films to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all the nanocomposites. Tests were conducted at ambient temperature (30 °C) and all results presented are the average of triplicate measurements.

8.2.2.3 Modulated force – thermomechanometry

Modulated force-thermomechanometry (mf-TM) analysis was conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus ($E'$), loss modulus ($E''$), loss tangent (tan δ) and associated glass transition (Tg) temperatures of the films were measured as a function of temperature from -100 to 110 °C at a heating rate of 2 °C·min⁻¹.

8.3 Results and discussion

8.3.1 Chemical structure of dye-functionalised POSS

FTIR spectroscopy was used to confirm the chemical structure formed by the reaction of POSS and the reactive dyes, to determine whether bonding between the respective molecules was achieved. The infrared spectra of the untreated POSS and dyes are shown in Figure 8.1a. The structure and characteristic bands of the trisilanolPOSS are discussed in Section 7.3.1 of Chapter 7. The reactive dyes (refer Chapter 3 for structure) exhibited several bands indicative of the functionality/segments common in both structures; 3436 cm⁻¹ (N-H stretching vibrations), 3064 cm⁻¹ (C-N symmetric stretching), 2924 cm⁻¹ (C-N asymmetric stretching), 1212 cm⁻¹ (C-N stretching vibrations), 1042 cm⁻¹ (S=O stretching vibrations) and 678 cm⁻¹ (C-Cl stretching). CI Reactive Blue 4 displays additional bands specific to its structure at 3258 cm⁻¹ (N-H stretching vibrations for secondary amines), 1538 cm⁻¹ (NH₂ scissoring), 1718 cm⁻¹ (C=O stretching for saturated ketones) and 1404 cm⁻¹ (SO₃H stretching vibrations). CI Reactive Red 2 displayed additional characteristic peaks at 1534 cm⁻¹ (N=N stretching of the azo group), 862 and 964 cm⁻¹ (NH₂ and NH wagging – shifts on H-bonding).
Figure 8.1 (a) Infrared spectrographs of raw materials; (i) TrisilanolphenylPOSS, (ii) TrisilanolisobutylPOSS, (iii) CI Reactive Red 2, (iv) CI Reactive Blue 4, (b) infrared spectrographs of functionalised POSS; (i) ibPOSS-blue, (ii) ibPOSS-red, (iii) phPOSS-blue, (iv) phPOSS-red

The infrared spectrographs of the dye-functionalised POSS nanoparticles are shown in Figure 8.1b. For all nanoparticles, a noticeable reduction in peak size is noticed at 3154 cm\(^{-1}\). This indicates a reduction in the number of OH groups on the POSS molecules, suggesting that bonding has occurred with the reactive dyes. Strong peaks are observed at 1100 cm\(^{-1}\), confirming the presence of Si-O bonds. Both isobutylPOSS pigments display bands at 2950 and 2868 cm\(^{-1}\), confirming the presence of isobutyl groups. Similarly,
phenylPOSS pigments displayed characteristic peaks at 3044 cm\(^{-1}\) (CH stretching vibrations) and 1580, 1554 and 1542 cm\(^{-1}\) (C=C vibrational stretching of phenyl groups). The presence of the reacted dyes was confirmed by the occurrence of several characteristic peaks in all functionalised POSS; 3296 cm\(^{-1}\) (NH stretching vibrations), 1558 cm\(^{-1}\) (NH\(_2\) scissoring), 1546 cm\(^{-1}\) (NH bending vibrations) and 700 cm\(^{-1}\) (C-Cl stretching). These observations strongly encourage that sufficient interaction and bonding has occurred between the amino-treated trisilanolPOSS and reactive dyes.

### 8.3.2 Morphology of SBS-dye functionalised POSS composites

Scanning electron microscopy (SEM) was employed to investigate the morphology of the nanocomposites. The micrographs are presented in Figure 8.2. Incorporation of up to 5 %·wt POSS into the SBS resulted in a relatively uniform distribution of filler throughout the matrix, with POSS clustering into small agglomerates with an average diameter of \(~0.08-0.1\) μm. As the concentration of POSS increased, so too did the occurrence of aggregation, ranging from few small instances at 5 %·wt (Figure 8.2a) to the formation of large agglomerates at 20 %·wt with average diameters of \(~0.6-0.7\) μm (Figure 8.2b). Despite utilising ultrasonic disruption to discourage filler clustering and polymer precipitation to ‘trap’ the filler in place, the micrographs indicate that at POSS concentrations greater than 5 %·wt, interactions between the functionalised POSS nanoparticles are quite strong and can withstand physical methods used to encourage particle separation. These interactions are usually in the form of Coulomb and van der Waals forces.
Figure 8.2 Scanning electron micrographs of SBS-dye functionalised POSS composites; (a) ibPOSS-blue 5, (b) ibPOSS-blue 20, (c) ibPOSS-red 5 (d) phPOSS-red 5

Figure 8.2c and 8.2d display the micrographs of SBS-ibPOSS-red 5 and SBS-phPOSS-red 5, respectively. Incorporation of 5% wt red-functionalised isobutylPOSS gives an even distribution of filler throughout the matrix, with small clusters of ~0.1-0.2 μm. Conversely, addition of phenylPOSS at the same concentration and functionalised with the same dye leads to an increase in the development of agglomeration, with larger clusters of ~0.4-0.6 μm occurring. This behaviour is attributed to the corner ‘R’ groups on the silsesquioxane cages, which determine phase compatibility and, therefore, morphology. As
Chapter 8: Dye-Functionalised POSS Elastomer Composites

noted previously, the bulk of the SBS matrix used consists of polybutadiene (~70.5 %·wt), providing POSS cages with isobutyl ‘R’ groups a relatively large volume to disperse throughout and occupy. This was in contrast to phenylPOSS, which by comparison has a significantly smaller volume of polymer (styrene phase) to occupy, leading to increased interactions between the POSS molecules due to their proximity. This leads to the formation of larger agglomerates within the fewer styrene domains available and correlates to observations in SBS-dumbbell POSS composites. These observations are consistent with the isobutylPOSS and phenylPOSS composites discussed in Chapter 7. This provides complimentary details reinforcing the phase preference behaviour is still being maintained, even with the addition of dichlorotriazine reactive dyes.

8.3.3 Optical properties of SBS-dye functionalised POSS composites

8.3.3.1 Colourimetric properties of SBS-dye functionalised POSS composites

Figure 8.3 demonstrates the basic principles of how dyes and pigments produce their colour. Incident light interacts with the dye/pigment, of which some light becomes scattered, transmitted or reflected (Figure 8.3a), providing the chromophore its characteristic colour. When light of a certain energy wavelength is absorbed a change in structure within the molecule occurs, whereby electrons are promoted to higher energy levels (Figure 8.3b). Both dyes utilised in these SBS nanocomposites have an extended conjugated system, enabling the capture of photons of energy. Quantised molecular electronic energy levels are closer together in these systems. Systems composed of less than eight conjugated double bonds absorb only in the ultraviolet region and are colourless to the human eye. With every double bond added, the system absorbs photons of longer wavelength (and lower energy). Bonding various autochromes (halogens, OH, NH$_2$) to the chromophore can modify the colour, due to these molecules changing the delocalised electron density. Within dyes with an azo (–N=N–) group (such as CI Reactive Red 2), this linkage is part of an extended delocalised electron system involving the aromatic rings of the chromophore.
Figure 8.3 (a) how light interacts with a dye/pigment, (b) excitation and promotion of coloured and colourless compounds, adapted from [448]

The CIELAB (L*, a*, b*) colour space coordinates of SBS and the dye-functionalised nanocomposites are presented in Table 8.1. The L* coordinate represents the whiteness of the material (0 = black, 100 = white). Pure SBS displayed an L* value of 94.13, indicative of its transparency. The nanocomposites became more translucent and intense in colour with increasing functionalised-POSS content, which was characterised by a decrease in the value of L*. This was expected since a higher filler concentration causes an increase in the number of bound-dye molecules dispersed throughout the polymer. IsobutylPOSS nanocomposites yielded lower L* than their phenylPOSS counterparts at the same concentration, attributed to the dispersion of POSS (and dye) throughout the continuous, polybutadiene phase. The a* coordinate provides an indication of the colour’s position between red and green (negative = green, positive = red) while the b* coordinate gives the position between blue and yellow (negative = blue, positive = yellow), as shown in Figure 8.4. Nanocomposites containing POSS functionalised with CI Reactive Blue 4 displayed a* values which gradually became more positive with filler content and b* values which rapidly became negative. This correlated well with the increasing intensity of blue colour which developed throughout the polymer with the increase in functionalised-POSS concentration. Materials containing CI Reactive Red 2 functionalised-POSS yielded a* and b* values which both became positive. As with their blue dye counterparts, this behaviour was
accompanied by an increase in colour intensity with filler content. In particular, $b'$ values leveled-off at higher filler loadings, due to limited dispersion throughout the SBS matrix.

**Table 8.1** CIELAB colour space co-ordinates of SBS-dye-functionalised POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>94.13</td>
<td>0.00</td>
<td>2.74</td>
</tr>
<tr>
<td>ibPOSS-blue 1</td>
<td>82.49</td>
<td>0.36</td>
<td>-10.78</td>
</tr>
<tr>
<td>ibPOSS-blue 5</td>
<td>44.43</td>
<td>6.49</td>
<td>-32.94</td>
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<td>ibPOSS-blue 10</td>
<td>34.94</td>
<td>9.50</td>
<td>-36.42</td>
</tr>
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<td>14.23</td>
<td>-37.78</td>
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<td>-4.73</td>
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</table>

**Figure 8.4** CIELAB colour space co-ordinates
Composites with filler loadings of 1 and 5 \%\text{-}wt visually displayed a uniform and even distribution of colour. As the concentration increased to 10 and 20 \%\text{-}wt, the quality of colourimetric properties began to decline, with pigment specks and minor swirling being observed. This deterioration in visual appearance was more evident in phenylPOSS composites than those containing isobutylPOSS and can be attributed to the degree of filler dispersion. Furthermore, interactions between autochromes (NH$_2$, SO$_3$H and C=O on CI Reactive Blue 4, SO$_3$Na and OH on CI Reactive Red 2) may result in filler agglomeration.

Colour-producing ability is proportional to the amount of pigment surface that can interact with light. Thus, the ability of a pigment to selectively absorb specific wavelengths of light increases with decreasing particle size, reaching optimal values when the particle is completely penetrated by light [449]. Due to the structural composition of SBS, POSS containing isobutyl ‘R’ compatibilising groups have greater phase volume to disperse throughout compared with phenylPOSS. This greater degree of volume reduces the probability of agglomerate formation, particularly at higher filler loadings (10 and 20 \%\text{-}wt). The “dye-functionalised POSS chromophores” are not transparent (the pure POSS particles are white) and lack optimal light-absorption properties, due to their tendency to cluster at higher filler loadings. The chromophores were not surface-treated for two reasons; (1) to leave the visual properties of the dye unchanged and (2) to not compromise the mechanical or thermal properties of the composite. The colourimetric results indicate that although the colour intensity can be increased, consistency and uniformity decrease at dye-functionalised POSS concentrations past 5 \%\text{-}wt.

8.3.3.2 UV-visible spectroscopy

The UV absorbance spectra of various SBS-POSS nanocomposites are shown in Figure 8.5. Nanocomposites containing CI Reactive Red 2-functionalised POSS (Figure 8.5a) displayed absorption spectra indicative of a red dye/pigment, with strong peaks at ~520 and 550 nm (green absorption) and a weaker band at ~370 nm (violet absorption). Little-to-no absorbance was observed across the red wavelength region (620-750 nm), indicative of the reflectance of red light by the chromophore. Absorbance intensity increased with filler concentration, due to the increased number of dye-functionalised POSS segments able to absorb and reflect light. The incorporation of CI Reactive Blue 4-functionalised POSS into
SBS yielded strong peaks at ~600 and 630 nm (absorption of orange/red), with an additional weaker wavelength band at ~375 nm (violet absorption), as shown in Figure 8.5b. A large trough was observed at ~450 nm, indicating the reflectance of blue light. The intensity of the UV absorbance increased with filler concentration, which correlated with the increase in colour intensity observed at higher filler concentrations (refer Section 8.3.3.1).
A significant difference in the absorbance properties of both blue- and red-dye functionalised materials was clearly observed in the nanocomposites derived from isobutylPOSS and phenylPOSS. Composites prepared with isobutylPOSS exhibited greater absorbance peaks compared with phenylPOSS, this behaviour attributed to the compatibility and dispersion of the respective functionalised fillers within SBS. Although ultrasonic disruption was used in an attempt to obtain a full dispersion of particles throughout the matrix, specific interactions between particles and phase preference limited the ability to obtain the optimal level of dispersion desired. Ideally, when adding dyes or pigments into a polymer, the goal is to achieve full dispersion of particles throughout the matrix, since this gives the highest possible colour strength [450].

In Chapter 7, isobutylPOSS was observed to exhibit a stronger affinity to disperse throughout the butadiene phase, due to compatibility of the POSS ‘R’ groups, greater phase volume for dispersion and reduced probability of agglomerate formation. Here, similar behaviour of phase selectivity manifested, resulting in the UV-visible characteristics shown in Figure 8.5c. Materials containing dye-functionalised isobutylPOSS (both red and blue) exhibited greater absorbance intensity because of the smaller particle domains being
dispersed within the main phase of SBS, allowing for a greater amount of light absorption. This yielded films with a fuller, more intense colour. In contrast, due-functionalised phenylPOSS, with a preference for the styrene phase, have a more constrained local environment to disperse the particles and may increase the likelihood of aggregate formation, leading to inferior light-absorption properties. Interactions between chromophores may also lead to filler clustering. The UV-visible spectroscopy results correlate to the increase in colour intensity observed using colourimetry and reiterate that filler dispersion is the primary factor which dictates visual properties.

8.3.4 Thermal properties of SBS-dye functionalised composites

The mass loss versus temperature curves of pure SBS and nanocomposites are shown in Figure 8.6. The decomposition of SBS shows one degradation step at \( \sim 454 \, ^\circ\text{C} \). The thermal degradation mechanism of SBS consists of two main processes, namely chain scission and crosslinking [428]. As listed in Table 8.2, incorporation of functionalised POSS into the SBS matrix increased the temperature at which the maximum rate of degradation occurs (\( T_d \)), with nanocomposites containing 1 \%·wt isobutylPOSS yielding \( T_d \) values ranging from 455-456 \( ^\circ\text{C} \). \( T_d \) continued to increase with filler content, reaching a maximum of 463 \( ^\circ\text{C} \) in SBS-ibPOSS-blue-20. This behaviour is characteristic of the thermal stability of POSS which stems from its silicon-oxygen structure. A proposed mechanism of thermal reinforcement is that POSS molecules restrict polymer chain motions, due to polymer-filler interactions or by the large inertia exhibited by segments of polymer containing POSS [147, 409]. The compatibilising ‘R’ groups on the POSS encourage this interfacial interaction, allowing thermal reinforcement to be achieved. This is especially important given the organic nature of the reactive dyes, which undergo thermal degradation at temperatures well below that of SBS. The improved thermal stability despite the presence of ‘volatile’ reactive dyes suggests effective matrix-POSS interactions and adequate thermal reinforcement by POSS molecules.
Negligible differences were observed between nanocomposites containing isobutylPOSS and phenylPOSS at concentrations of 1-5 %·wt. At filler concentrations of 10 and 20 %·wt, isobutylPOSS nanocomposites exhibited slightly higher $T_d$ values than their phenylPOSS counterparts, as shown in Figure 8.6b. The behaviour is attributed to the dispersion of POSS within a particular phase of the SBS matrix. The thermal stability of SBS is dependent on the sensitivity of the double bonds within the continuous, butadiene phase [208, 428]. When dispersed throughout the rubber phase, POSS imparts added stiffness into the matrix.
by acting as crosslink points and reducing chain mobility [429, 430]. This provides thermal stability to the phase upon which the thermal degradation mechanism is dependent. Similarly, little difference was observed between materials containing blue and red dye-functionalised POSS at concentrations of 1-5 %·wt. However, at higher filler loadings (10 and 20 %·wt), nanocomposites containing POSS functionalised with CI Reactive Blue 4 displayed $T_d$ values ~2-3 °C higher than their CI Reactive Red 2 counterparts. Although TGA precision may account for the difference in thermal stability at higher filler concentrations, chromophore structures of the reactive dyes may also be a factor. The chromophore of CI Reactive Blue 4 is based on anthracene which is known to be quite thermally stable [451, 452]. In contrast, CI Reactive Red 2 contains a less-stable, naphthalene-based chromophore, which experiences thermal degradation at lower temperatures. These results indicate that thermal degradation behaviour is dependent on both the phase in which the POSS is dispersed and the structure of the bonded reactive dyes.
Table 8.2 $T_d$ values of SBS-dye functionalise POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>454</td>
</tr>
<tr>
<td>ibPOSS-blue 1</td>
<td>454</td>
</tr>
<tr>
<td>ibPOSS-blue 5</td>
<td>458</td>
</tr>
<tr>
<td>ibPOSS-blue 10</td>
<td>461</td>
</tr>
<tr>
<td>ibPOSS-blue 20</td>
<td>462</td>
</tr>
<tr>
<td>ibPOSS-red 1</td>
<td>455</td>
</tr>
<tr>
<td>ibPOSS-red 5</td>
<td>456</td>
</tr>
<tr>
<td>ibPOSS-red 10</td>
<td>458</td>
</tr>
<tr>
<td>ibPOSS-red 20</td>
<td>460</td>
</tr>
<tr>
<td>phPOSS-blue 1</td>
<td>456</td>
</tr>
<tr>
<td>phPOSS-blue 5</td>
<td>457</td>
</tr>
<tr>
<td>phPOSS-blue 10</td>
<td>457</td>
</tr>
<tr>
<td>phPOSS-blue 20</td>
<td>460</td>
</tr>
<tr>
<td>phPOSS-red 1</td>
<td>455</td>
</tr>
<tr>
<td>phPOSS-red 5</td>
<td>455</td>
</tr>
<tr>
<td>phPOSS-red 10</td>
<td>457</td>
</tr>
<tr>
<td>phPOSS-red 20</td>
<td>458</td>
</tr>
</tbody>
</table>

8.3.5 Thermomechanical properties of SBS-dye functionalised POSS composites

8.3.5.1 Stress strain analysis

The elastic moduli (E) of SBS and nanocomposites are presented in Figure 8.7. The matrix of SBS exhibited an E of 189 Pa. Addition of POSS had a positive effect on E, which increased with filler concentration, reaching a maximum at 5 %·wt POSS content. The increase is characteristic of the reinforcement ability of POSS. The applied stress was transferred from the SBS matrix to the POSS filler resulting in increased strength and stiffness. This stress-transfer process was aided by sufficient interfacial adhesion between the matrix and filler, achieved through compatibilising ‘R’ groups on the POSS molecules. Furthermore, the
dispersion obtained for these low filler nanocomposites throughout the SBS matrix contributed to the improved mechanical properties.

![Figure 8.7 Elastic moduli of SBS-dye functionalised POSS composites](image)

Higher POSS concentrations (10 and 20 %·wt) caused a decrease in $E$ values. There are several possible reasons for the mechanical $E$ reduction in higher filled nanocomposites. Verker et al [453] and Zhao and Schiraldi [454] attributed similar behaviour to a disruption of the polymer molecular (chain) structure brought on by POSS concentrations above 5 %·wt. Liu and Zheng [137] suggested this observation is caused by a decrease in material density, due to an increase in nanocomposite porosity [455, 456]. Additionally, the crosslinking densities per unit volume can decrease with increasing POSS content, compromising the reinforcement mechanism as a consequence. The observed reduction in modulus is most probably caused by such reasons, that may be induced by filler agglomeration affecting the SBS-filler mechanisms that would normally provide good reinforcement. The agglomeration of pigment-pigment clusters, along with reduced effective crosslinking densities and potential voids deteriorate the mechanical properties, resulting in decreased modulus values [457, 458]. Furthermore, agglomerated pigment clusters can act as stress concentrators, causing premature mechanical failure. This
correlates to the deterioration in optical properties associated with clustering at filler loadings above 5 %·wt. (refer Section 8.3.3.1).

IsobutylPOSS composites yielded the greatest modulus values (Figure 8.7). This was attributed to the dispersion of POSS within the polybutadiene (rubber) phase of the SBS, facilitated by the isobutyl ‘R’ groups on the POSS molecule. The styrene domains within SBS act as cross-links, restricting the flow of the rubber phase and providing strength and durability. Incorporating POSS into the rubber phase provides additional reinforcement, allowing for greater amounts of stress to be transferred from the polybutadiene. The E increased with filler content, ranging from 278 and 283 Pa for 1 %·wt composites of isobutylPOSS-blue and isobutylPOSS-red, respectively, to 570 and 549 Pa for their respective 5 %·wt counterparts. PhenylPOSS composites exhibited lower modulus values than composites containing isobutylPOSS, due to the phenyl ‘R’ groups on the POSS molecules which provide an affinity towards the glassy, polystyrene segments within the SBS. This reduces the chance of POSS being dispersed throughout the continuous polybutadiene phase and providing adequate reinforcement. No clear distinction between the effects of the two dyes was observed.

Figure 8.8 shows the tensile strength at yield of the nanocomposites. Similar trends were observed as per the elastic modulus, with the tensile strength at yield reaching a maximum value at 5 %·wt for all nanocomposites. POSS concentrations up to and including 5 %·wt provide enhanced toughness and strength by allowing sufficient stress transfer to occur. At higher concentrations, aggregation amongst the POSS particles occurred. This resulted in the possible formation of voids within the SBS-POSS interface and the reduction in tensile strength [183]. Composites containing isobutylPOSS exhibited slightly higher values than their phenylPOSS equivalents, due to the increased reinforcement ability when POSS was dispersed throughout the continuous phase of the SBS. As a consequence of the higher modulus, elongation at yield (Figure 8.9) decreased with increasing POSS content for all nanocomposites. The incorporation of rigid nanoparticles into an elastomer imparts stiffness, decreasing the elasticity and ductility.
8.3.5.2 Creep-recovery analysis

The creep-recovery curves of SBS and ibPOSS-red filled composites are shown in Figure 8.10. Creep deformation decreased with increasing POSS content. This was expected of an elastomer filled with rigid reinforcement. Due to its ceramic silica structure, the presence
of POSS imparts stiffness into the matrix. This restricts the molecular motions of the polybutadiene chains, resulting in less deformation. Furthermore, the compatibilising organic groups on the POSS encourage further interaction and adhesion between the matrix and filler, allowing for the nanocomposites to withstand greater levels of stress without experiencing deformation. At higher POSS loadings (10 and 20 %-wt), nanocomposites exhibited flatter creep curves with a lower viscosity component, indicating a decrease of deformation of the elastic component. Nanocomposites containing isobutylPOSS exhibited less deformation than their phenylPOSS counterparts, which was in agreement with the stress-strain results. Since the polybutadiene chains which comprise the rubbery, continuous phase experience molecular rearrangement and motions under stress, it is more effective to disperse filler throughout this phase in order to reduce deformation.

![Creep-recovery curves of ibPOSS-red composites](image)

**Figure 8.10** Creep-recovery curves of ibPOSS-red composites

When comparing the curves of the blue and red dye-nanocomposites (Figure 8.11), a significant difference in creep behaviour is evident. Nanocomposites containing POSS functionalised with CI Reactive Blue 4 showed considerably less creep and deformation than those containing CI Reactive Red 2. This occurrence can be attributed to the difference in chromophore structure of the dyes, as shown in Figure 8.12. The anthracene-based chromophore of CI Reactive Blue 4 is considerably bulkier and extends further from the
dichlorotriazine reactive group than the naphthalene-based chromophore of CI Reactive Red 2. These features provide additional restraints on molecular motions, resulting in the matrix exhibiting less creep and deformation. Hence the dye can impart some physical constraints to dimensional stability.

The parameters of the four-element model were calculated for the creep component of SBS and the nanocomposites, which is presented in Table 8.3. The Maxwell modulus ($E_1$) was observed to increase with POSS content, confirming that the nano-sized fillers influence the flow of the SBS matrix. This behaviour correlates to an increase in Maxwell viscosity ($\eta_1$), which indicates improved resistance to deformation. Nanocomposites containing isobutylPOSS displayed larger $E_1$ and $\eta_1$ values than their phenylPOSS counterparts treated with the same dye. Similarly, composites with CI Reactive Blue 4-functionalised POSS yielded higher values than those functionalised with CI Reactive Red 2. These parameters provide an accurate representation of what was observed experimentally. All materials displayed a certain proportion of unrecovered strain that is characteristic of viscoelastic materials such as SBS. This is due to irreversible chain entanglement slippage and detachment of styrene domains from the polybutadiene rubber-phase which occurs during the application of load. Permanent deformation increased with POSS concentration, with nanocomposites containing blue-functionalised isobutylPOSS displaying the largest values.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{creep_recovery_curves.png}
\caption{Creep-recovery curves of 10 \% wt filled composites}
\end{figure}
Higher concentrations of filler, such as POSS, restrict the relaxation of SBS chains, causing irreversible chain slippage and unravelling. The Voigt viscosity ($\eta_2$) was observed to increase with POSS content, suggesting an increase in resistance of the SBS chains to uncoiling.

Increasing the POSS content caused the $\tau$ to decrease, suggesting that the nanocomposites become more solid-like in behaviour at higher filler concentrations. Similarly, highly filled composites exhibited flatter recovery curves, indicating a faster recovery of the viscoelastic component. Nanocomposites containing phenylPOSS displayed slightly longer $\tau$ than their isobutylPOSS counterparts treated with the same-coloured dye. When rubbery, polybutadiene chains are highly stretched under an applied load, phenylPOSS molecules can become detached from the glassy styrene domains for which they have an affinity. This can lead to dissimilar block-mixing occurring in interfacial regions, causing an increase in permanent deformation [443]. Nanocomposites functionalised with CI Reactive Blue 4 yielded shorter $\tau$ than those functionalised with CI Reactive Red 2. This was once again attributed to the increased restrictions placed on segmental motions for relaxation by the bulkier, blue-coloured chromophore, causing the material to behave in a more solid-like nature. These results correlate well to the behaviour observed in the creep component and

**Figure 8.12** Structure of dichlorotriazine reactive dyes; (a) CI Reactive Blue 4, (b) CI Reactive Red 2; light grey = carbon, blue = nitrogen, red = oxygen, orange = sulphur, green = chlorine, dark grey = sodium
stress-strain analysis, with the time scale allowing the more subtle effects of phase preference, filler concentration and chromophore structure to become observable.

Table 8.3 Creep-recovery data of SBS-dye functionalised POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_1$ (MPa)</th>
<th>$\eta_1$ (MPa·s$^{-1}$)</th>
<th>$E_2$ (MPa)</th>
<th>$\eta_2$ (MPa·s$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>Permanent deformation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>0.22</td>
<td>67.91</td>
<td>0.35</td>
<td>3.31</td>
<td>9.46</td>
<td>18</td>
</tr>
<tr>
<td>ibPOSS-blue 1</td>
<td>0.26</td>
<td>77.04</td>
<td>0.74</td>
<td>6.17</td>
<td>8.33</td>
<td>23</td>
</tr>
<tr>
<td>ibPOSS-blue 5</td>
<td>0.34</td>
<td>85.06</td>
<td>1.24</td>
<td>8.79</td>
<td>7.09</td>
<td>29</td>
</tr>
<tr>
<td>ibPOSS-blue 10</td>
<td>0.57</td>
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<td>6.94</td>
<td>33</td>
</tr>
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<td>2.48</td>
<td>16.37</td>
<td>6.60</td>
<td>37</td>
</tr>
<tr>
<td>ibPOSS-red 1</td>
<td>0.22</td>
<td>72.77</td>
<td>0.65</td>
<td>5.70</td>
<td>8.77</td>
<td>23</td>
</tr>
<tr>
<td>ibPOSS-red 5</td>
<td>0.26</td>
<td>78.84</td>
<td>0.87</td>
<td>7.03</td>
<td>8.08</td>
<td>25</td>
</tr>
<tr>
<td>ibPOSS-red 10</td>
<td>0.47</td>
<td>91.32</td>
<td>1.08</td>
<td>8.53</td>
<td>7.90</td>
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<tr>
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<td>138.25</td>
<td>1.62</td>
<td>11.43</td>
<td>7.05</td>
<td>34</td>
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<tr>
<td>phPOSS-blue 1</td>
<td>0.20</td>
<td>73.61</td>
<td>0.71</td>
<td>6.09</td>
<td>8.58</td>
<td>20</td>
</tr>
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<td>phPOSS-blue 5</td>
<td>0.31</td>
<td>80.81</td>
<td>1.14</td>
<td>8.53</td>
<td>7.48</td>
<td>28</td>
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<td>phPOSS-blue 10</td>
<td>0.43</td>
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<td>1.47</td>
<td>10.66</td>
<td>7.25</td>
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</tr>
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<td>phPOSS-blue 20</td>
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<td>145.64</td>
<td>2.16</td>
<td>14.95</td>
<td>6.92</td>
<td>34</td>
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<td>0.48</td>
<td>4.35</td>
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<td>6.58</td>
<td>9.01</td>
<td>21</td>
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<td>1.33</td>
<td>10.97</td>
<td>8.24</td>
<td>29</td>
</tr>
</tbody>
</table>

In order to further examine relaxation behaviour, the KWW stretched exponential function was applied to SBS and the nanocomposites. The results are presented in Table 8.4. In fitting the function, the pre-exponential constant and relaxation time decreased with increasing POSS content. This was to be expected since the relaxation provides an indication of the degree of mobility molecules within the polymer possess. The decreased relaxation time at higher POSS concentrations is indicative of the solid-like behaviour highly-filled nanocomposites exhibit and is in agreement with the creep data obtained using the four-element model. Correspondingly, the shape fitting parameter $\beta$ changed with POSS content. The value of $\beta$ is influenced by various factors, including structure, the
presence of fillers, crosslinks and crystallinity [355]. These observations strongly suggest that the nanocomposites experience restricted flow, attributed to the incorporation of functionalised-POSS.

Table 8.4 KWW parameters of SBS-dye functionalised POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Lambda$</th>
<th>$\beta$</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>3.18</td>
<td>0.14</td>
<td>35.74</td>
</tr>
<tr>
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<td>2.36</td>
<td>0.09</td>
<td>30.84</td>
</tr>
<tr>
<td>ibPOSS-blue 5</td>
<td>1.91</td>
<td>0.04</td>
<td>24.97</td>
</tr>
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<tr>
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<td>0.07</td>
<td>24.6</td>
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<td>24.7</td>
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<td>20.4</td>
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<td>0.02</td>
<td>17.6</td>
</tr>
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<td>phPOSS-red 1</td>
<td>2.94</td>
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<td>31.5</td>
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<td>phPOSS-red 5</td>
<td>2.31</td>
<td>0.09</td>
<td>27.9</td>
</tr>
<tr>
<td>phPOSS-red 10</td>
<td>1.77</td>
<td>0.06</td>
<td>23.0</td>
</tr>
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<td>phPOSS-red 20</td>
<td>1.29</td>
<td>0.04</td>
<td>17.8</td>
</tr>
</tbody>
</table>

8.3.5.3 Modulated temperature – thermomechanometry

Figure 8.13 shows the storage modulus ($E''$) of SBS and selected nanocomposites. Nanocomposites containing POSS displayed higher $E''$ values than pure SBS. The $E''$ modulus reached a maximum at POSS concentrations of 5 %·wt, with SBS-ibPOSS-blue 5 and SBS-ibPOSS-red 5 exhibiting $E''$ values of 3.1 and 2.8 GPa at -90 °C, respectively. Similar observations were recorded before the styrene transition at 10 °C, with maximum $E''$ values of 0.11 and 0.10 GPa for SBS-ibPOSS-blue 5 and SBS-ibPOSS-red 5, respectively. These results are indicative of the additional stiffness imparted by POSS. As filler content was
increased past 5 %·wt, the modulus began to decrease, suggesting that after a critical concentration (~5 %·wt), POSS begins to lose reinforcing ability in this nanocomposites system. Filler agglomeration at higher concentrations reduces the particle surface area available to interact with the polymer, resulting in less-effective reinforcement. Zucchi et al. [459] attributed this reduction in elastic modulus to a decrease in the cohesive energy density caused by higher POSS concentrations. POSS functionalised with blue dye and containing isobutyl compatibilising groups exhibited the highest modulus values, attributed to the influence of dye structure and phase preference, respectively, on mechanical properties. This influence of dye-structure on mechanical properties is in agreement with behaviour observed in creep-recovery analysis. At temperatures above the α (butadiene) transition, composites displayed higher E’ values compared to pure SBS, while an increase in E’ reduction rate was observed at temperatures above the β (styrene) transition.

![Figure 8.13](image.png)

**Figure 8.13** Storage modulus (E’) curves across the polybutadiene glass-rubber transition of SBS and ibPOSS-filled composites

The loss modulus (E”) of SBS and nanocomposites is shown in Figure 8.14, while T_g values are summarised in Table 8.5. The T_g is determined by the peak of the E” curve (E”_max), since that is where maximum heat dissipation occurs. The curve of pure SBS displays two peaks, at -75 and 88 °C. These peaks correspond to the T_g of the butadiene and styrene phases,
respectively. Addition of POSS caused the \( T_g \) to increase in both phases, reaching a maximum at 5 \%·wt, before decreasing at higher concentrations. The initial increase in glass transition temperature is attributed to the ability of the functionalised-POSS to restrict molecular relaxation motions and bond rotations of the polymer chains. The decrease in loss (and storage) modulus and \( T_g \) at higher POSS concentrations has been observed previously [138, 457] and can be attributed to increased filler agglomeration leaving larger pockets of polymer to undergo relaxation and experience segmental motion.

![Figure 8.14](image)

**Figure 8.14** Loss modulus \((E'')\) curves across the polybutadiene glass-rubber transition of SBS and ibPOSS-filled composites

As displayed in Table 8.5, composites containing isobutylPOSS displayed the greatest increase in \( T_g \) for the butadiene phase, with ibPOSS-blue 5 and ibPOSS-red 5 yielding \( T_g \) values of -70 and -71 °C, respectively. Similarly, materials filled with phenylPOSS exhibited higher \( T_g \) values in the styrene phase than their isobutylPOSS counterparts. This behaviour suggests that the compatibilising groups are providing an affinity for their corresponding phases, allowing the POSS to disperse throughout and entangle within a particular phase within the SBS. Despite being dispersed throughout the rubbery phase, isobutylPOSS increased the styrene phase \( T_g \) at concentrations up to 5 \%·wt, before decreasing with additional POSS content. Fu et al [216] observed similar results, attributing the behaviour to an equal distribution of stress across both domains at temperatures near the styrene
phase $T_g$ (~88 °C). This arises from the similar behaviour of the butadiene and styrene phases at this temperature, allowing the POSS molecules to act as physical crosslinks and reduce segmental relaxation. PhenylPOSS showed a similar, although less intense influence over the butadiene phase.

### Table 8.5 $E'$ values and $T_g$ data of SBS-dye functionalised POSS composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ from $E'$ max (°C)</th>
<th>$T_g$ from $tan(\delta)$ max (°C)</th>
<th>$E'$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$A$</td>
</tr>
<tr>
<td>SBS</td>
<td>-75</td>
<td>88</td>
<td>-67</td>
</tr>
<tr>
<td>ibPOSS-blue 5</td>
<td>-70</td>
<td>89</td>
<td>-62</td>
</tr>
<tr>
<td>ibPOSS-blue 20</td>
<td>-73</td>
<td>85</td>
<td>-64</td>
</tr>
<tr>
<td>ibPOSS-red 5</td>
<td>-71</td>
<td>88</td>
<td>-63</td>
</tr>
<tr>
<td>ibPOSS-red 20</td>
<td>-72</td>
<td>86</td>
<td>-64</td>
</tr>
<tr>
<td>phPOSS-blue 5</td>
<td>-73</td>
<td>93</td>
<td>-65</td>
</tr>
<tr>
<td>phPOSS-blue 20</td>
<td>-76</td>
<td>90</td>
<td>-68</td>
</tr>
<tr>
<td>phPOSS-red 5</td>
<td>-73</td>
<td>92</td>
<td>-66</td>
</tr>
<tr>
<td>phPOSS-red 20</td>
<td>-76</td>
<td>91</td>
<td>-69</td>
</tr>
</tbody>
</table>

Nanocomposites functionalised with CI Reactive Blue 4 displayed slightly higher $T_g$ values than those treated with CI Reactive Red 2. This was due to the bulkier structure of the blue-dye chromophore which allows for additional restraints on molecular motions. Nanocomposites exhibited glass transitions over a larger temperature range, as indicated by the broader $E''$ peaks. The increase in peak breadth is attributed to an increase in the segmental relaxation times of the matrix [356]. Peak breadth was observed to increase with POSS concentration, reaching maximum values at loadings of 10 and 20 %·wt, suggesting an increase in the relaxation time due to segmental constraints, including polymer chain coupling and polymer-POSS interactions.

The loss tangent ($tan(\delta)$) of SBS and several nanocomposites is shown in Figure 8.15. The maximum of the $tan(\delta)$ curve can be used to determine $T_g$, although the $E''$ maximum is shown to be more consistent with other determinations of $T_g$. The $tan(\delta)$ were ~6-9 °C higher than $T_g$ obtained from loss modulus curves (refer Table 6). The glass transition
temperatures obtained from the loss tangent maximum displayed similar trends to those obtained from $E''_{\text{max}}$.

Figure 8.15 Loss tangent ($\tan(\delta)$) of SBS and 5 %·wt filled composites

Nanocomposites containing isobutylPOSS showed a reduction in butadiene-phase peak height, with 5 %·wt exhibiting the greatest reduction. At concentrations above 5 %·wt, the peaks began to increase towards the initial location of SBS. Conversely, the addition of isobutylPOSS caused an increase in the styrene-phase peak, reaching a maximum at 5 %·wt before reducing at higher loadings. The amplitude of the $\tan(\delta)$ peak provides an indication of the number of kinetic units mobile enough to contribute to the glass transition [357]. The decrease in peak intensity indicates that isobutylPOSS molecules restrict motions of polymer chains within the butadiene phase, as indicated by the isobutylPOSS nanocomposites displaying $T_g$ values higher than SBS. The increase peak height of the styrene phase indicates isobutylPOSS exerts a plasticising effect on the glassy domains, leading to composites displaying similar or lower $T_g$ values than SBS. PhenylPOSS-blue nanocomposites experienced an increase in styrene-phase peak intensity, while a decrease was observed in phenylPOSS-red nanocomposites. This was particularly interesting since the blue-functionalised materials exhibited the greatest increase in $T_g$, which is usually characterised by a reduction in $\tan(\delta)$ peak intensity. The damping ability of a filled polymer system is believed to be influenced by two factors; (a) the amount of free
Chapter 8: Dye-Functionalised POSS Elastomer Composites

volume, (b) internal friction between the filler and matrix and between the filler particles themselves across the glass transition region [444]. The latter increases as the number of chain movements become greater, leading to an increase in damping ability. PhenylPOSS functionalised with bulkier CI Reactive Blue 4 experienced a greater amount of internal friction within the SBS matrix than its CI Reactive Red 2 counterpart, resulting in greater damping ability and internal friction.

The addition of phenylPOSS caused no increase in the butadiene-phase peak, which was expected since the styrene domains within SBS provide the polymer with rigidity and structure. As with the E” curves, peak broadening of the tan (δ) curves was observed at higher filler loadings. Since the peak breadth is an indication of structural heterogeneity (β parameter in KWW equation), the wider peaks suggest an increase in segmental relaxation time due to increased SBS-POSS interactions. The broader peaks are also indicative of the aforementioned increase in damping and internal friction.

8.4 Conclusion

POSS molecules were successfully functionalised with dichlorotriazine reactive dyes as indicated by FTIR and incorporated into SBS via physical blending. Aggregate size and frequency increased with filler content, due to increased inter-POSS and inter-chromophore interactions. The morphology of the nanocomposites was dependent on the R groups on the POSS cages, with the amount of filler aggregation being dependent on the relative volume of butadiene or styrene phase to disperse throughout. Colour intensity was able to be controlled by altering the functionalised POSS concentration. Films displayed uniform and smooth colour distribution at concentrations up to and including 5 %·wt. Higher filler loadings resulted in colour swirling and fleck formation, due to increased filler diameters. Functionalised isobutylPOSS provided the greatest uniformity of colour, due to the greater amount of polymer (polybutadiene phase) which the POSS can be dispersed throughout. The use of dye-functionalised POSS as a pigment displayed limited success; at concentrations greater than 5 %·wt surface treatment of the chromophore or further processing (shear, greater ultrasonication, etc) are required to prevent filler agglomeration.
The thermal stability of SBS was enhanced by the addition of functionalised POSS. IsobutylPOSS had the greatest influence on thermal stability, due to its incorporation into the thermally-sensitive polybutadiene phase. POSS functionalised with CI Reactive Blue 4 exhibited a marginally better influence on thermal stability than its CI Reactive Red 2 counterpart, due to the thermal stability of the anthracene-based chromophore of CI Reactive Blue 4. The tensile modulus ($E$) of the nanocomposites increased with filler content, reaching a maximum at 5 %·wt. Creep deformation decreased and permanent strain increased with POSS content, due to the restricted molecular motions caused by filler. Incorporation of POSS increased the storage modulus ($E'$), loss modulus ($E''$) and glass transition temperature ($T_g$), all reaching maximum values at filler concentrations of 5 %·wt. The decrease in mechanical properties at POSS concentrations above 5 %·wt was attributed to a disruption of the polymer molecular structure due to excess filler loading and reduction in material density. Three factors contributed to the mechanical properties of the nanocomposites; (a) POSS concentration, (b) the phase which the POSS was dispersed throughout, (c) chemical structure of the dye. The optimal POSS concentration was deemed to be 5 %·wt.
CHAPTER 9: MAGNETITE-FUNCTIONALISED CARBON NANOTUBE POLYURETHANE COMPOSITES

9.1 Introduction
Magnetite (Fe$_3$O$_4$) is one of the best-studied and highly utilised magnetic materials, due to its simple synthesis techniques, low cost and unique properties, including superparamagnetism [460] and having the highest Curie temperature for a half-metal (~858 K) [461]. This versatility has led to Fe$_3$O$_4$ finding use in applications including sealants, information storage and electronics [15]. Furthermore, the push for novel materials has encouraged the incorporation of Fe$_3$O$_4$ into polymer matrices [462-464], showing potential for use as magnetorheological elastomers [465], electromagnetic wave-absorbing materials [466], medical devices [467], recording media and insulators [463]. Several authors have documented that increasing magnetic particle content within an elastomer increased magnetic properties, at the expense of mechanical properties [468-470]. This was attributed to poor matrix-filler adhesion and filler agglomeration. One possible solution is to bind the magnetic particles to another nano-filler substrate and disperse the hybrid magnetic filler throughout the matrix. The presence of the nano-substrate will encourage interaction between the polymer and filler, effectively compatibilising the magnetite. In addition, a rigid inorganic substrate will provide additional mechanical strength and thermal stability to the polymer composite. An ideal candidate for a nano-substrate is carbon nanotubes (CNTs), due to their low cost and unique properties. Although CNTs have been functionalised with Fe$_3$O$_4$ [471-473] (Figure 9.1), these hybrid fillers are yet to be incorporated into a polymer matrix.

Filler dispersion is a critical issue concerning property enhancement in polymer composites, particularly when nano-sized dispersion is desired. Differences in polarity between the matrix and filler can provide further complications by limiting the interaction between the composite constituents [474]. These issues can result in polymer composites displaying inferior or insufficient mechanical, thermal and optical properties. In addition,
materials such as iron oxides require adequate interparticle space, critical particle-size and favourable matrix-filler interactions to maximise intrinsic properties, including superparamagnetism and electromagnetic wave absorption [14-16]. Several methods are available to encourage filler dispersion and prevent cluster formation, the most common being chemical modification of the filler surface [17, 18]. Other techniques available, specifically for composites prepared by physical blending, include ultrasonic disruption and shear during mixing. These methods of filler deagglomeration are particularly useful when preparing large volumes of material and when an unchanged filler surface is desired. In addition, physical blending provides a convenient option when functionalised-fillers have been prepared with the intention of being incorporated into a polymer matrix with the surface functionality intact.

This chapter focuses on magnetic elastomers consisting of a thermoplastic polyurethane (TPU) matrix reinforced with magnetite-functionalised multi-walled carbon nanotubes (CNTs). The CNTs provide partial compatibility with the polyurethane matrix and impart additional mechanical strength and thermal stability into the composite. Two physical blending techniques, melt-mixing and solvent dispersion, were utilised to uniformly distribute the functionalised-filler throughout the polymer matrix while leaving the magnetic functionality of the nanoparticles intact. Based on the processing limitations encountered in Chapter 8, melt-mixing is expected to provide additional shear and encourage filler cluster deagglomeration. The influence of filler content and processing technique on thermal stability, thermomechanical and magnetic properties is examined.
9.2 Materials and methods

9.2.1 Materials, experimental details and nanocomposite nomenclature

Material information, functionalisation and compounding procedures and characterisation methods are detailed in Chapter 3. TPU composites filled with magnetite-functionalised CNTs are referred to as Mix x or Sol x, where ‘Mix’ or ‘Sol’ corresponds to the compounding method (Mix = melt-mixing, Sol = solution dispersion/ultrasonication) and ‘x’ refers to the concentration (%·wt) of functionalised CNTs added to the TPU matrix (1, 5 or 10 %·wt).

9.2.2 Thermomechanical analysis

All materials were analysed in tensile mode. An Instron Universal Testing Instrument, Model 4465 was used to perform df-TM while a TA Instruments Q800 Dynamic Mechanical Analyser was used to perform sf-TM. mf-TM analysis was performed using a Perkin Elmer Diamond DMA. ASTM D638 – 97, specimen type IV test bars were utilised for df-TM while specimens prepared for sf-TM and mf-TM analysis were rectangular with average dimensions of \( \approx 12.80 \times 4.00 \times 0.70 \text{ mm}^3 \) and \( \approx 10.00 \times 4.00 \times 0.70 \text{ mm}^3 \), respectively.

9.2.2.1 Stress-strain

A deformation rate of 50 mm·min\(^{-1}\) was applied to each sample at ambient temperature. Results presented are the average of five measurements.

9.2.2.2 Creep-recovery

Creep-recovery (static force – thermomechanometry, sf-TM) analysis was performed by subjecting films to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all polymer films. Tests were conducted at 30 °C and all results presented are the average of triplicate measurements.

9.2.2.3 Modulated force – thermomechanometry

Single frequency temperature scans were conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus (\( E' \)), loss modulus
(E”), loss tangent (tan δ) and associated T_g of the films were measured as a function of temperature from -80 to +110 °C at a heating rate of 2 °C·min⁻¹.

9.3 Results and discussion

9.3.1 Morphology of magnetite-functionalised CNTs and PU-CNT-Fe_3O_4 composites

9.3.1.1 Microscopy

The transmission electron microscope (TEM) images of magnetite-functionalised carbon nanotubes are displayed in Figure 9.2. Fe_3O_4 particles are present throughout the entangled web of nanotubes, both inside and outside the CNTs. Interactions between the CNTs and Fe_3O_4 are in the form of non-covalent bonds, namely van der Waals forces [475]. Magnetite primary particles were observed to have average dimensions of ~7-8 nm, although clustering is evident due to strong interparticle attractions. The images confirm successful functionalisation of CNTs.

![TEM image of Fe_3O_4-functionalised CNTs](image)

**Figure 9.2** TEM image of Fe_3O_4-functionalised CNTs

SEM images of PU-CNT-Fe_3O_4 composites are presented in Figure 9.3. Both composite sets displayed similar dispersion behaviour following the incorporation of 1 %·wt CNT-Fe_3O_4. As shown in Figure 9.3a and 9.3b, Mix 1 and Sol 1 exhibited an even distribution of CNTs, with filler clusters displaying an average dimension of ~1 μm. Minimal occurrence of larger aggregates was observed. This indicates that at lower filler loadings, ultrasonic disruption
for solvent dispersion and melt-mixing both encouraged a similar degree of filler distribution. Filler dispersion is composed of two distinct elements; (1) disentanglement of CNTs, (2) uniform distribution of filler particles throughout the polymer matrix [476]. As the concentration is increased, differences in dispersion were observed for solvent dispersed and melt-mixed composites. In both blend sets, agglomerate size and frequency increased with filler content, due to van der Waals forces between nanotubes (and surface magnetite). However, Mix 10 (Figure 9.3c) yielded aggregates with average dimensions of ~2 μm, in contrast to Sol 10 (Figure 9.3d) with ~4-5 μm diameter aggregates. Furthermore, agglomerate frequency appeared greater for Sol 10 than Mix 10.

Figure 9.3 SEM images of PU-CNT-Fe₃O₄ composites; (a) Mix 1, (b) Sol 1, (c) Mix 10, (d) Sol 10
Chapter 9: Magnetite-Functionalised Carbon Nanotube PU Composites

The difference in filler distribution and dispersion at higher CNT concentrations can be attributed to processing technique. During melt-mixing applied stresses act on the nanotubes, mechanically fracturing/breaking the tubes and reducing their size. Furthermore, if polymer melt can infiltrate the filler clusters, agglomerate strength and packing structure can be disrupted and the cohesive forces binding smaller aggregates with larger agglomerates weakened [477]. This weakens aggregates/agglomerates, reducing the shear force and energy required to break up the filler particles. Although ultrasonication-solvent dispersion may break-up segments of filler clusters, particles may re-aggregate/re-agglomerate prior to polymer precipitation or while excess solvent is being removed. Furthermore, matrix viscosity during composite preparation is an important factor when nanotubes are entangled. Low matrix viscosity during solvent dispersion requires an extremely high shear rate to effectively break-up filler clusters. Reduced viscosity can also lead to voids remaining between filler agglomerates, compromising the mechanical properties of the composite [478]. In contrast, high matrix viscosity, such as that during melt-mixing, enables a shear/mixing force to be high even at a low rate. This provides more effective filler deagglomeration and distribution. The SEM images indicate that melt-mixing is more effective at dispersing CNTs at higher filler concentrations than ultrasonication.

9.3.1.2 Small angle X-ray scattering

The one dimensional SAXS profiles of PU-CNT-Fe$_3$O$_4$ composites are presented in Figure 9.4, while the SAXS data is summarised in Table 9.1. Both melt-mixed and solvent dispersed PU matrices displayed similar profiles, with maxima at $q = 0.0130$ and 0.0190 nm$^{-1}$. These peaks are due to segregation of hard, polyurethane segments within the TPUs, leading to the formation of hard domains. Segmented polyurethanes, such as TPUs, generally exhibit a lamellar morphology, with alternating layers of hard and soft domains [479]. Incorporation of Fe$_3$O$_4$-functionalised CNTs caused a sharp increase in peak intensity, reaching maximum values at filler concentrations of 10 %∙wt. Several authors have observed similar behaviour in PU composites [396, 480]. A probable explanation is that CNTs increase the scattering contrast between the hard and soft domains [394].
Figure 9.4 One dimensional SAXS profiles of PU-CNT-Fe$_3$O$_4$ composites; (a) melt-mixed, (b) solvent dispersed

At concentrations of 5 and 10 %·wt, solvent dispersed composites exhibited larger peak intensities than their melt-mixed counterparts. Buffa et al [481] observed differences in scattering intensity when comparing functionalised and unfunctionalised CNTs dispersed throughout polyurethane, attributed to the magnitude of electron and mass density. Similarly, Li et al [482] attributed increased scattering intensity to ordering within hard domains, increasing the electron density contrast between hard and soft segments.
Table 9.1 SAXS data of PU-CNT-Fe$_3$O$_4$ composites

<table>
<thead>
<tr>
<th>Material</th>
<th>d-spacing (nm)</th>
<th>$R_g$ (nm)</th>
<th>$D_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU Mix</td>
<td>483</td>
<td>10.1</td>
<td>2.33</td>
</tr>
<tr>
<td>Mix 1</td>
<td>491</td>
<td>10.7</td>
<td>1.93</td>
</tr>
<tr>
<td>Mix 5</td>
<td>503</td>
<td>11.7</td>
<td>1.24</td>
</tr>
<tr>
<td>Mix 10</td>
<td>524</td>
<td>14.0</td>
<td>1.23</td>
</tr>
<tr>
<td>PU Sol</td>
<td>480</td>
<td>8.6</td>
<td>2.52</td>
</tr>
<tr>
<td>Sol 1</td>
<td>495</td>
<td>9.2</td>
<td>2.25</td>
</tr>
<tr>
<td>Sol 5</td>
<td>507</td>
<td>12.8</td>
<td>1.66</td>
</tr>
<tr>
<td>Sol 10</td>
<td>551</td>
<td>14.6</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Peak breadth remained relatively constant for melt-mixed composites, indicating little change in polymer morphology. In contrast, peak breadth increased in solvent dispersed composites with filler concentration. Abouzahr et al [483] related the behaviour to changes in shape of the hard domains or a significant change in morphology, such as increased interconnectivity between hard segments. It is evident that processing technique (and filler dispersion) had an influence on material morphology. To determine the extent of this influence, the interdomain distance (d-spacing) was calculated and is summarised in Table 9.1. PU Mix and PU Sol displayed d-spacing values of 483 and 480 nm, respectively ($d = 2\pi/q_{\text{max}}$). Incorporation of filler caused peak maxima to shift to lower $q$ values, subsequently increasing the d-spacing. Composites containing 10 %·wt filler displayed the largest d-spacing values of 524 (Mix 10) and 551 nm (Sol 10). The increase in d-spacing is associated with greater phase separation within TPU [484].

The presence of functionalised CNTs within the polymer matrix leads to an increase in the distance between hard and soft domains. Solvent dispersed composites exhibited larger d-spacing values than melt-mixed composites. This was particular evident when comparing materials with the highest filler concentration (Mix 10 and Sol 10). The SEM micrographs (refer Figure 9.2) confirmed that solvent dispersed composites possessed larger filler aggregates than their melt-mixed counterparts. The larger filler clusters impart greater separation between the phases, in particular if the CNTs have an affinity for the
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hard domains. Dispersion of CNT aggregates throughout the hard, polyurethane domains leads to the growth of these segments, increasing both the segment interconnectivity and distance between the hard-phase centres. This accounts for the increased scattering contrast between hard/soft domains and broader peaks of solvent dispersed composites observed in Figure 9.4.

Figure 9.5 Guinier plots of PU-CNT-Fe₃O₄ composites; (a) melt-mixed, (b) solvent dispersed

The radii of gyration (R_g) of the composites were obtained by constructing Guinier plots, to determine the size of the scattering “particles” following the introduction of filler. The
Guinier plots are shown in Figure 9.5. Using the slope obtained from plotting ln(I) vs. q^2, R_g was determined from Equation 3.14. R_g values of the composites are summarised in Table 9.1. PU Mix displayed an R_g value of 10.1 nm. Addition of functionalised CNTs caused the R_g to increase to 10.7 (Mix 1), 11.7 (Mix 5) and 14.0 nm (Mix 10). Similar behaviour was observed for solvent dispersed composites, with R_g increasing from 8.6 (PU Sol) to 14.6 nm (Sol 10). Similar results were reported by Chen et al [485], who observed an increase in R_g with filler concentration in titania-filled polyurethane composites. The behaviour was attributed to the growth of titania-rich domains, due to interparticle interactions. Similarly, increasing the CNT concentration within the polyurethanes increases the likelihood of filler agglomeration. If the nanotubes have an affinity for the hard phase within polyurethane and begin to cluster, hard segments will grow in size and increase their scattering contribution (increase R_g). Due to the expanded dimensions, hard domains centres will move further apart, indicative of the larger d-spacing values (refer Table 9.1). Solvent dispersed composites displayed larger R_g values than their melt-mixed counterparts, particularly at filler concentrations of 5 and 10 %·wt. This was due to greater filler agglomeration within solvent dispersed composites.

Porod plots of PU-CNT-Fe_3O_4 composites are displayed in Figure 9.6, while fractal dimension (D_f) values are summarised in Table 9.1. PU Mix and PU Sol exhibited D_f values of 2.33 and 2.52, respectively. D_f values between 2 and 3 are characteristic of polymer networks, indicating the systems are mass fractals. The incorporation of functionalised CNTs caused D_f to decrease, with Mix 10 and Sol 10 reaching minimum values of 1.23 and 1.02, respectively. Fractal dimension values of ~1 indicate that scattering is obtained from rigid rods. The reduced D_f values indicate that CNT-rich domains within the blends (particularly the hard segments) display mass fractal geometry with an open, less-constrained structure than pure TPU [485]. This is in agreement with increased d-spacing and R_g values, confirming that CNTs encourage domain growth and separation.
9.3.2 Magnetic properties of PU-CNT-Fe$_3$O$_4$ composites

Magnetite (Fe$_3$O$_4$), like other oxides, possesses a spinel (MgAl$_2$O$_4$) crystal structure, consisting of a cubic close-packed oxygen array and iron in tetrahedral or octahedral configuration [486]. The crystal structure and configurations are displayed in Figure 9.7a and 9.7b, respectively. This crystal structure leads to Fe$_3$O$_4$ exhibiting ferrimagnetic ordering. In ferrimagnetic materials, the magnetic structure consists of two opposed
sublattices (A and B) separated by oxygens. These oxygen anions govern exchange interactions, of which the strongest form causes anti-parallel alignment of spins between the A and B sublattice (Figure 9.7c). The tetrahedral and octahedral sites of magnetite form the A and B sublattices, respectively. The unequal magnetic moments of the A and B sublattices results in a net magnetic moment.

![Diagram](image)

Figure 9.7 (a) Face-centered cubic spinel structure of magnetite [487], (b) tetrahedral and octahedral sites sharing an oxygen atom [487], (c) ferrimagnetic coupling, with opposing A and B sublattices

The hysteresis curves of PU-CNT-Fe$_3$O$_4$ composites obtained at 25 °C are presented in Figure 9.8. All materials displayed narrow hysteresis curves, indicating that following the removal of an external magnetic field following saturation, a minimal amount of energy is required for remagnetisation. This behaviour is typical of ferrimagnetic materials [488]. Increasing the magnetic-filler content yielded larger hysteresis curves, due to increased interactions between magnetite particles. Processing technique was observed to influence the intensity of the curves, with melt-mixed composites displaying larger hysteresis loops than their solvent-dispersed counterparts. This was attributed to differences in the degree of filler dispersion throughout the TPU matrix. From the hysteresis loops, various parameters can be obtained regarding a material’s magnetic properties and potential applications. The method by which these parameters are derived is shown in Figure 9.9.
Figure 9.8 Hysteresis curves of PU-CNT-Fe₃O₄ composites measured at 25 °C

Figure 9.9 Hysteresis loop with various magnetic parameters

The magnetic properties of the PU-CNT-Fe₃O₄ composites obtained from the hysteresis loops are summarised in Table 9.2. Amongst a magnetic material’s most important characteristics are its saturisation magnetisation ($M_s$, the maximum induced magnetic
moment that can be obtained in a magnetic field) and remanent magnetisation ($M_R$, a material’s ability to retain residual magnetic field following removal of the external magnetic force after saturation). $M_S$ and $M_R$ values for composites prepared by both processing techniques increased with filler content, reaching maximum values at filler concentrations of 10 % wt. This is due to the effect of interparticle interactions on magnetic properties. As the concentration of Fe$_3$O$_4$-functionalised CNTs within the TPU increased, a corresponding increase in the degree of dipole-dipole and surface exchange interactions [489] between Fe$_3$O$_4$ nanoparticles occurred. This increased interaction restricted free rotation of magnetic particles in the polymer matrix.

<table>
<thead>
<tr>
<th>Material</th>
<th>$M_S$ (emu·g$^{-1}$)</th>
<th>$M_R$ (emu·g$^{-1}$)</th>
<th>$H_C$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 1</td>
<td>0.34</td>
<td>0.008</td>
<td>26.93</td>
</tr>
<tr>
<td>Mix 5</td>
<td>1.92</td>
<td>0.036</td>
<td>24.24</td>
</tr>
<tr>
<td>Mix 10</td>
<td>3.74</td>
<td>0.066</td>
<td>24.68</td>
</tr>
<tr>
<td>Sol 1</td>
<td>0.30</td>
<td>0.007</td>
<td>25.70</td>
</tr>
<tr>
<td>Sol 5</td>
<td>0.91</td>
<td>0.017</td>
<td>21.53</td>
</tr>
<tr>
<td>Sol 10</td>
<td>2.23</td>
<td>0.052</td>
<td>25.56</td>
</tr>
</tbody>
</table>

Both composites sets exhibited different values of $M_S$. The $M_S$ values for composites prepared using melt mixing were significantly higher than their solvent-dispersed counterparts at equal filler concentrations. Similarly, melt-mixed composites exhibited slightly larger $M_R$ values. This can be attributed to the different processing techniques that result in different degrees of dispersion of CNT-Fe$_3$O$_4$ particles. Magnetic nanoparticles have a tendency to agglomerate due to strong magnetic dipole-dipole attractions between particles [490]. The filler agglomerates exhibit a demagnetising effect due to random dipole–dipole interaction between particles, resulting in antiferromagnetic coupling (zero net magnetisation) [491, 492]. In addition, the size of iron oxides is crucial in determining their magnetic behaviour. Smaller particles (such as those obtained using melt-mixing) possess a single domain structure that includes groups of spins all pointing in the same direction and acting cooperatively [493]. In contrast, large particles possess a multi-domain structure composed of several single domains separated by domain walls. These
structures produce magnetic flux closures, rendering the bulk material macroscopically non-magnetic [494]. The coercivity ($H_C$) provides a measure of the intensity of the applied magnetic field required to reduce a material's magnetisation to zero following saturation. $H_C$ values for all materials were in the range of 20-26 G, as determined from the hysteresis loops. This indicated that the composites prepared were magnetically soft at room temperature. Magnetically soft materials possess a high flux density but experience little energy loss upon remagnetisation [495]. These parameters and narrow hysteresis loops indicate the PU-Fe$_3$O$_4$-CNT films could be utilised as microwave devices, recording heads, magnetic shielding or transformers [496]. The magnetometry data indicated that filler concentration and processing technique (filler dispersion) impart a significant influence on magnetic properties.

### 9.3.3 Thermal stability of PU-CNT-Fe$_3$O$_4$ composites

The mass loss and derivative mass loss curves of PU-CNT-Fe$_3$O$_4$ composites are presented in Figure 9.10a and 9.10b, respectively. Composites prepared via melt-mixing exhibited an increase in degradation temperature ($T_d$) with increasing filler concentration, with Mix 10 displaying $T_d$ values of 380 and 497 °C for the 1$^{st}$ and 2$^{nd}$ mass loss steps, respectively. Both degradation steps were observed to shift to higher temperatures, suggesting the functionalised CNTs interact with both hard and soft segments of the PU. Similarly, the derivative mass loss peaks diminished in height with increasing filler content, causing the rate of decomposition to decrease from -24 (Mix 1) to -22 %·min$^{-1}$ (Mix 10). A number of mechanisms have been proposed to describe the influence of CNTs on thermal stability. One mechanism notes that nanotubes may hinder the flux of degradation of the polymer, delaying the onset of degradation [165]. At high content and well dispersed nanoparticulates within a polymer matrix, polymer chain segments within close vicinity to the nanotubes may degrade more slowly due to the CNTs providing the “most torturous path” for degradation. Another proposed explanation is that the polymer-CNT composites exhibit superior thermal conductivity properties, facilitating better heat dissipation [497]. All composites displayed final residual masses corresponding to the amount of filler present, confirming the planned amount of functionalised-CNTs were incorporated during material preparation.
In contrast, the thermal stability of materials prepared using solvent dispersion decreased with the addition of filler, with the 10 %·wt composite displaying onset of degradation at the lowest temperature ($T_d = 330 \, ^\circ C$). The thermal stability of composites containing CNTs is influenced by the effectiveness of filler dispersion [165]. The observations in Figure 9.9 are particularly interesting, since the combination of ultrasonic disruption and rapid precipitation is arguably more effective at filler dispersion and deagglomeration than melt mixing. One probable explanation is that filler agglomeration can occur during solvent
evaporation, leading to inhomogeneous particulate distribution [165]. Kashiwagi et al [498] reported that poorly dispersed CNTs are likely to agglomerate into ‘islands’ of filler, compromising the thermal stability of the composite. In addition, well dispersed CNTs possess a larger surface area, increasing heat dissipation and thermal properties of the films. The results indicate that filler distribution and concentration are crucial factors that determine composite thermal stability.

9.3.4 Thermomechanical properties of PU-CNT-Fe$_3$O$_4$ composites

9.3.4.1 Stress strain

The stress-strain curves of melt-mixed and solvent dispersed PU-CNT-Fe$_3$O$_4$ composites are presented in Figure 9.11a and 9.11b, respectively, while the stress strain data is summarised in Table 9.3. PU Mix and PU Sol displayed tensile moduli (E) of 28.0 and 19.2 MPa, respectively. Incorporation of CNT-Fe$_3$O$_4$ increased E values, reaching maximum values of 36.0 (Mix 10) and 29.0 MPa (Sol 10) at filler concentrations of 10 %·wt. Accompanying the increase in modulus with filler loading was an increased yield strength. The strength ranged from 17.9 (PU Mix) to 20.5 MPa (Mix 10) and 11.6 (PU Sol) and 12.7 MPa (Sol 10). The enhanced static-mechanical properties are characteristic of the reinforcing nature of carbon nanotubes. Upon application of load, the soft segments within TPU undergo deformation. As the applied stress increases, load is transferred to the hard segments and chain slippage between the hard domains occurs [499]. Addition of functionalised-CNTs allows for the transfer of stress during load application and restricts/hinders chain slippage [500], enhancing the strength and durability of the nanocomposite film. As expected, elongation at yield decreased with filler concentration, due to the reduced elasticity that accompanies the incorporation of CNTs, a rigid filler.
Figure 9.11 Stress-strain curves of PU-CNT-$\text{Fe}_3\text{O}_4$ composites; (a) melt-mixed, (b) solvent dispersed

Both sets of composites showed similar trends with regard to the effect of filler concentration, indicating that a degree of polymer-filler interaction is present. Differences between melt-mixed and solvent dispersed composites are evident. Composites prepared via melt-mixing exhibited higher modulus and strength values than composites prepared using solvent dispersion. Since differences were observed between the pure TPUs, this can be attributed to the influence of processing technique on the structural properties of the TPU [408]. Cooling from a critical order-disorder temperature can encourage phase
separation within TPUs via spinodal decomposition [501]. This allows the hard segments
to increase their contribution to the mechanical integrity of TPU, enhancing mechanical
properties [502, 503]. However, Joseph et al [504, 505] compared melt-mixed and solvent
dispersed polypropylene-sisal fibre composites, observing superior mechanical properties
in the former. The behaviour was attributed to differences in fibre dimensions and
dispersion achieved during melt-mixing. Therefore, processing technique influences
mechanical properties by altering filler dispersion and phase separation.

### Table 9.3 Stress-strain data of PU-CNT-Fe₃O₄ composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile modulus (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation at break (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU Mix</td>
<td>28.0</td>
<td>17.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Mix 1</td>
<td>29.9</td>
<td>18.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Mix 5</td>
<td>31.2</td>
<td>17.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Mix 10</td>
<td>36.0</td>
<td>20.5</td>
<td>3.8</td>
</tr>
<tr>
<td>PU Sol</td>
<td>19.2</td>
<td>11.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Sol 1</td>
<td>20.8</td>
<td>11.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Sol 5</td>
<td>24.6</td>
<td>11.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Sol 10</td>
<td>29.0</td>
<td>12.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Solvent dispersed composites displayed significantly lower elongation at break than their
melt mixed counterparts. This premature failure has been documented in other PU-CNT
composites [506, 507] and is attributed to the increased frequency of CNT aggregates. The
degree of filler dispersion and polymer-filler interaction is widely acknowledged as being
crucial for enhanced mechanical properties in polymer-CNT composites [476, 477, 508,
509]. Adequate dispersion increased the amount of filler surface available to interact with
the matrix [476]. This allowed for a greater, more-even transfer of load during
deformation. Furthermore, well-dispersed CNTs promote a high interfacial stiffness and
static adhesion strength [500], which is necessary to obtain any reinforcing effect. In
contrast, CNT aggregates have considerably less surface area available to interact with a
polymer matrix, leading to weaker interfacial adhesion. The aggregated nanotubes behave
as ‘holes’ or nano-sized defects within the matrix, introducing stress concentrations and
negating any benefit in mechanical properties [510].
9.3.4.2 Creep-recovery

Figure 9.12 shows the creep-recovery curves of PU-CNT-Fe₃O₄ composites. Increasing functionalised CNT content reduced creep deformation. The stiff nanotubes provide stiffness and rigidity to the TPU matrix, restricting molecular motions of the soft, polyester segments and preventing chain slippage [511]. As the filler concentration increased and approached 10 %·wt, composites exhibited flatter creep curves with a lower gradient, indicating a decrease of deformation of the viscous component. The difference in creep deformation magnitude between melt-mixed and solvent dispersed composites is attributed to processing technique-induced structural difference between the composite sets. The results are in agreement with the stress-strain data (refer Section 9.3.4.1).

![Creep-recovery curves of PU-CNT-Fe₃O₄ composites](image)

The four-element model was applied to the creep component of the PU-CNT-Fe₃O₄ composites, to describe the deformation behaviour. The calculated parameters are presented in Table 9.4. PU Mix and PU Sol displayed Maxwell moduli (E₁) of 0.26 and 0.16 MPa, respectively. E₁ values increased with CNT concentration, reaching maximum levels at filler loadings of 10 %·wt. and confirming that flow behaviour of the TPU matrix is restricted by the presence of rod-shaped nanofillers. A similar increase in Maxwell viscosity (η₁) followed with increasing functionalised CNT concentration. The increase in E₁ and η₁ values with higher filler loadings confirms that the degree of deformation restriction
increases with CNT concentration. All materials displayed a proportion of unrecovered strain that is characteristic of viscous elastomers, including TPU. This behaviour is due to permanent slippage of chain entanglements and unraveling during load application. Permanent deformation increased with Fe$_3$O$_4$-CNT concentration, with 10 %·wt-filled composites displaying the greatest deformation (16 and 15 % for Mix 10 and Sol 10, respectively). Rigid fillers, such as CNTs, restrict the relaxation of polymer chains, causing chain segment entanglements and unraveling that occur during load application to be irreversible.

Table 9.4 Creep-recovery data of PU-CNT-Fe$_3$O$_4$ composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_1$ (MPa)</th>
<th>$\eta_1$ (MPa·s$^{-1}$)</th>
<th>$E_2$ (MPa)</th>
<th>$\eta_2$ (MPa·s$^{-1}$)</th>
<th>$\tau$ (s)</th>
<th>Permanent deformation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU Mix</td>
<td>0.26</td>
<td>28.04</td>
<td>0.75</td>
<td>2.58</td>
<td>3.24</td>
<td>11</td>
</tr>
<tr>
<td>Mix 1</td>
<td>0.26</td>
<td>30.31</td>
<td>0.86</td>
<td>2.66</td>
<td>3.09</td>
<td>12</td>
</tr>
<tr>
<td>Mix 5</td>
<td>0.30</td>
<td>31.48</td>
<td>1.00</td>
<td>2.79</td>
<td>2.79</td>
<td>15</td>
</tr>
<tr>
<td>Mix 10</td>
<td>0.31</td>
<td>33.18</td>
<td>1.18</td>
<td>3.02</td>
<td>2.56</td>
<td>16</td>
</tr>
<tr>
<td>PU Sol</td>
<td>0.16</td>
<td>15.77</td>
<td>0.44</td>
<td>1.08</td>
<td>2.93</td>
<td>11</td>
</tr>
<tr>
<td>Sol 1</td>
<td>0.16</td>
<td>19.18</td>
<td>0.47</td>
<td>1.20</td>
<td>2.53</td>
<td>12</td>
</tr>
<tr>
<td>Sol 5</td>
<td>0.18</td>
<td>19.94</td>
<td>0.58</td>
<td>1.43</td>
<td>2.47</td>
<td>13</td>
</tr>
<tr>
<td>Sol 10</td>
<td>0.19</td>
<td>20.23</td>
<td>0.76</td>
<td>1.80</td>
<td>2.38</td>
<td>15</td>
</tr>
</tbody>
</table>

The Voigt viscosity ($\eta_2$) was observed to increase with functionalised-CNT content, indicating that polymer chains within the composites exhibit an increased resistance to uncoiling. Mix-melted composites displayed larger four-element model parameters than solvent dispersed materials, due to differences in material morphology. Additionally, enhanced filler dispersion achieved using melt-mixing leading to more effective reinforcement (filler has greater amount of surface volume to interact with polymer) could contribute to the increased parameters. Increasing the Fe$_3$O$_4$-CNT concentration caused the $\tau$ to decrease, suggesting that the nanocomposites become more solid-like in behaviour at higher filler concentrations. Similarly, highly filled composites exhibited flatter recovery curves, indicating a faster recovery of the viscoelastic and elastic components.
The KWW stretched exponential function was applied to composites, in order to describe the relaxation behaviour. The parameters are summarised in Table 9.5. The pre-exponential constant and relaxation time (τ) decreased with increasing CNT-Fe₃O₄ content. The relaxation time provides an indication of the potential mobility of chain segments within the polymer. Shorter relaxation times at higher filler loadings indicate the polymer becomes more solid-like in nature following the introduction of functionalised CNTs. This is in agreement with the creep data obtained using the four-element model. The shape fitting parameter β decreased with increasing filler content, corresponding to an increase in non-exponentiality. This confirms CNTs-Fe₃O₄ impart restrictions on the relaxation process. Solvent dispersed composites displayed lower β and τ values than their melt-mixed counterparts, arising from the different material morphologies created during processing. The lower β values indicate the ‘Sol’ set of composites are more solid-like in nature, with polymer chains being more constricted. This reasoning is supported by stress-strain analysis and experimental creep-recovery data. The KWW parameters confirm that the composites experience restricted flow due to the incorporation of functionalised CNTs.

Table 9.5 KWW parameters of PU-CNT-Fe₃O₄ composites

<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>β</th>
<th>τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU Mix</td>
<td>5.42</td>
<td>0.8</td>
<td>12.13</td>
</tr>
<tr>
<td>Mix 1</td>
<td>4.49</td>
<td>0.8</td>
<td>8.39</td>
</tr>
<tr>
<td>Mix 5</td>
<td>4.09</td>
<td>0.7</td>
<td>5.92</td>
</tr>
<tr>
<td>Mix 10</td>
<td>3.07</td>
<td>0.6</td>
<td>3.33</td>
</tr>
<tr>
<td>PU Sol</td>
<td>6.90</td>
<td>0.2</td>
<td>6.94</td>
</tr>
<tr>
<td>Sol 1</td>
<td>6.57</td>
<td>0.1</td>
<td>4.59</td>
</tr>
<tr>
<td>Sol 5</td>
<td>4.89</td>
<td>0.09</td>
<td>3.41</td>
</tr>
<tr>
<td>Sol 10</td>
<td>4.33</td>
<td>0.06</td>
<td>1.92</td>
</tr>
</tbody>
</table>

9.3.4.3 Modulated-force thermomechanometry

The storage moduli (E’) of 1 and 10 %wt filled PU-CNT-Fe₃O₄ composites are displayed in Figure 9.13, while the Tₘ and E’ data is summarised in Table 9.6. All composites displayed higher modulus values than their pure TPU matrices. E’ values increased with the incorporation of functionalised CNTs ranging from 2.6 (Mix 1) to 5.5 GPa (Mix 10) and
1.8 (Sol 1) to 2.3 GPa (Sol 10) for melt-mixed and solvent dispersed composites, respectively. This indicates that CNTs-Fe$_3$O$_4$ strengthen and reinforce the polyurethane, allowing the polymer to endure greater applied stresses, especially at higher filler concentrations. Melt-mixed composites yielded higher E' values than their solvent dispersed counterparts, which was attributed to differences in material morphology due to processing technique, as previously discussed. However, the magnitude of change in E' with functionalised CNT content was greater following melt-mixing rather than solvent dispersion.

![Figure 9.13 Storage (E') modulus curves of PU-CNT-Fe$_3$O$_4$ composites](image)

This difference in dynamic mechanical behaviour can be attributed to the effective degree of filler dispersion within the composite films. Increasing the dispersion of CNTs increases the filler-rubber interface [512], providing the material with enhanced stiffness and more-effective reinforcement. Additionally, sufficient filler deagglomeration increases the aspect ratio of the functionalised CNTs, increasing the volume of filler surface available to interact with the polymer. As noted previously (refer 9.3.1.2), CNTs can compact the structure of polyurethane, reducing free volume and encouraging phase separation. These changes in mobility and morphology can lead to an increase in bound rubber [480]. These trapped polymer chains are shielded from deformation by the CNTs–Fe$_3$O$_4$ and act as part of the
Chapter 9: Magnetite-Functionalised Carbon Nanotube PU Composites

filler rather than the matrix. Trends observed in the $E'$ curves are in correlation with stress-strain data (refer 9.3.4.1).

**Table 9.6** $E'$ and $T_g$ data of PU-CNT-Fe$_3$O$_4$ composites

<table>
<thead>
<tr>
<th>Material</th>
<th>$E''$ peak $T_g$ (°C)</th>
<th>Tan ($\delta$) peak $T_g$ (°C)</th>
<th>$E'$ (GPa) at -80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU Mix</td>
<td>-47</td>
<td>-36</td>
<td>2.4</td>
</tr>
<tr>
<td>Mix 1</td>
<td>-46</td>
<td>-35</td>
<td>2.6</td>
</tr>
<tr>
<td>Mix 5</td>
<td>-43</td>
<td>-33</td>
<td>3.9</td>
</tr>
<tr>
<td>Mix 10</td>
<td>-39</td>
<td>-30</td>
<td>5.5</td>
</tr>
<tr>
<td>PU Sol</td>
<td>-47</td>
<td>-36</td>
<td>1.6</td>
</tr>
<tr>
<td>Sol 1</td>
<td>-46</td>
<td>-35</td>
<td>1.8</td>
</tr>
<tr>
<td>Sol 5</td>
<td>-45</td>
<td>-34</td>
<td>2.1</td>
</tr>
<tr>
<td>Sol 10</td>
<td>-42</td>
<td>-33</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 9.14 displays the loss moduli ($E''$) of the composites. The melt-mixed and solvent dispersed PU composites containing 1 %·wt filler exhibited $T_g$ values of -46 °C. Increasing filler content raised the $T_g$, reaching a maximum value of -39 (Mix 10) and -42 °C (Sol 10) at filler loadings of 10 %·wt. The increase in $T_g$ attributed to the ability of functionalised CNTs to restrict molecular motions of the polymer chains. Composites experienced glass-rubber transition over a larger temperature range, as indicated by broader $E''$ peaks. This corresponds to an increase in the segmental relaxation times of the matrix. As the loading of CNTs-Fe$_3$O$_4$ reached and exceeded 5 %·wt, melt-mixed composites displayed higher $T_g$ values than solvent dispersed composites of equal filler concentration. This increase in $T_g$ at higher filler content is attributed to the degree of filler distribution and effectiveness at which segmental chain motions can be suppressed. The superior distribution and dispersion of CNTs-Fe$_3$O$_4$ achieved using melt-mixing results in a greater amount of filler interacting with the polymer matrix (greater surface-to-volume ratio) [419] and promotes a larger polymer-filler interface. A greater quantity of nanotubes distributed throughout the PU via melt-mixing are able to restrict chain rotation more-uniformly during the glass-rubber transition, increasing the $T_g$. In contrast, the ineffective distribution and agglomerate/aggregate formation observed in solvent dispersed composites results in less filler surface being available to come into contact and bond/interact with the polymer. This
leads to inefficient polymer-filler interactions and less effective enhancement of material mechanical properties.

![Figure 9.14 Loss (E'') modulus curves of PU-CNT-Fe$_3$O$_4$ composites](image)

**Figure 9.14** Loss (E'') modulus curves of PU-CNT-Fe$_3$O$_4$ composites

The loss tangent (tan(δ)) of the composites is shown in Figure 9.15. The $T_g$ values obtained from the loss tangent maximum were ~9-11 °C higher than those obtained from the E' curve maxima, however similar trends were displayed by both sets of composites. PU-CNT-Fe$_3$O$_4$ composites exhibited a decrease in tan(δ) peak height with filler concentration, indicating diminished damping ability. As with the E'' curves, peak broadening of the tan(δ) curves was observed at higher filler loadings. Melt-mixed films exhibited slightly taller peaks than their solvent dispersed counterparts, while composites prepared using solvent dispersion yielded broader peaks. This suggests the damping properties of the materials are primarily determined by two different mechanisms; increased relaxation times in solvent dispersed films and greater internal friction between the filler and matrix and between the filler particles across the glass transition region in the melt-mixed films [444].
9.4 Conclusion

TPU composites containing Fe$_3$O$_4$-functionalised CNTs were prepared using two different physical blending methods; melt-mixing and solvent dispersion. TEM confirmed successful functionalisation of the CNTs, with Fe$_3$O$_4$ nanoparticles being present on the surface and inside the nanotubes. SEM indicated that shear forces at temperatures above the $T_g$ during melt-mixing was more effective at breaking-up CNT-Fe$_3$O$_4$ agglomerates than ultrasonication and solvent dispersion. The addition of functionalised CNTs encouraged localised phase separation of TPU and increased the radius of gyration ($R_g$) as filler particles began to agglomerate and reduce unoccupied volume. Fractal dimension ($D_f$) decreased with increasing filler concentration, due to the increase in the number of rod-like scattering objects (nanotubes). Films exhibited more magnetic behaviour at higher filler concentrations, as the number of interactions between Fe$_3$O$_4$ particles increased. Solvent dispersed composites displayed inferior magnetic properties than their melt-mixed counterparts, due to clusters of magnetic filler reducing the net magnetisation. The composites were magnetically soft materials.

Melt-mixed composites displayed superior thermal properties to their solvent-dispersed counterparts, which became less stable with increasing filler concentration. Ineffective filler distribution and increased agglomeration compromised composite thermal stability.
Tensile modulus and strength increased with filler concentration while elongation decreased as films became less ductile. Composites displayed reduced creep deformation and permanent strain compared to pure TPU, due to restrictions imparted on chain motions by the CNTs-Fe$_3$O$_4$. The storage modulus ($E'$), loss modulus ($E''$) and glass transition temperature ($T_g$) increased with functionalised-CNT content, reaching maximum values at filler concentrations of 10 %·wt. Composites prepared via melt-mixing displayed more dramatic changes in material properties and were generally superior than their solvent dispersed counterparts. Preparing composites using two different physical blending techniques highlights the dependency of material properties and magnetic functionality on filler dimensions, dispersion, TPU phase behaviour and structural morphology.
CHAPTER 10: CONCLUSIONS AND FURTHER WORK

10.1 Conclusion
Several functionalised polymer composites and blends were successfully prepared. Functionalised particles incorporated into amorphous polymer matrices included those exhibiting novel architecture (CCS polymers, POSS-functionalised dendrimers, telechelic POSS), colour (dye-functionalised POSS) and magnetism (Fe$_3$O$_4$-functionalised CNTs). Materials exhibited enhanced mechanical and thermal properties, while functional group properties were evident and controlled by adjusting filler concentration. The particle-particle and particle-matrix interactions were apparent and relationships discussed for the respective systems investigated. Various models (eg. Maxwell/Kelvin-Voigt for creep, KWW equation for recovery and relaxation) were applied to some of the data to reaffirm/compliment the experimental observations.

Incorporating CCS polymers into linear PS and PMMA increased the $T_g$ and decreased $\Delta H$ relaxation (Chapter 4). This was attributed to reduced unoccupied volume within the blends and segmental restrictions imparted on linear chains by CCS polymer ‘arms’. Sub-$T_g$ isothermal annealing increased $T_g$ and $\Delta H$, with both parameters exhibiting maximum values at the longest $t_a$ (100 h). This was due to the reduction in mobility and free volume that occurs as the polymer undergoes relaxation. Heat loss during annealing increased with $t_a$, as the materials equilibrated at a faster rate following heating through and above $T_g$. Linear-CCS polymer blends continued to exhibit higher $T_g$ and lower $\Delta H$ values than pure, linear matrices for identical $t_a$. This confirms that CCS polymers continue to restrict chain segment motion during structural relaxation, acting in a similar manner to physical crosslinks.

The linear coefficient of thermal expansion and material shrinkage decreased with increasing CCS polymer content, attributed to restrictions imparted on matrix flow and conformational motions that govern expansion. Below $T_g$, $\alpha$ values decreased as $t_a$ increased, due to expansion ability being inhibited by reduced free volume. $\alpha$ values above $T_g$ increased with $t_a$, attributed to the greater expansion rate required to regain free volume.
lost during annealing/structural relaxation. Volume relaxation during annealing was successfully observed using mT-TM, the phenomenon displaying non-linear and non-exponential behaviour. The rate of relaxation during annealing increased with cooling rate, due to the faster equilibration allowed by greater amounts of ‘entrapped’ free volume. Non-linearity and relaxation times increased with CCS polymer content, indicating the hyperbranched macromolecules restrict molecular motions and retard the relaxation process. The results demonstrated the suitability of mT-TM as a method of analysing structural relaxation.

The thermal and thermomechanical properties of linear-CCS polymer blends were characterised in Chapter 5. PS-CCS polymer blends exhibited minimal changes in thermal stability. In contrast, blending PMMA with CCS polymer enhanced thermal stability, due to CCS polymer ‘arm’ structure. Blending caused polymer chains to become more constrained and contorted, as indicated by the reduced radii of gyration and increased fractal dimension. Tensile modulus and strength increased with CCS polymer content while elongation at break decreased, indicating the ability of hyperbranched polymers to reinforce linear chains. Similarly, creep deformation decreased and permanent strain increased with CCS polymer content due to restrictions on molecular motions. Storage modulus and loss modulus increased with the addition of CCS polymers, while dampening ability decreased as the blends became more rigid. Master curves shifted to lower frequencies as CCS polymer content increased, with segmental relaxation occurring across a broader time scale. CCS polymers increased dynamic fragility and apparent activation energy while decreasing fractional free volume and the free volume expansion coefficient, confirming that free volume is reduced within the blends.

The data indicates that CCS polymer ‘arms’ entangle and interpenetrate within the linear chains, reducing unoccupied volume and restricting segmental motions of linear chains. This is achieved due to one end of the ‘arm’ being tethered to the CCS polymer ‘core’, leaving the other end free to interact with surrounding polymer chains. The results compliment the enthalpic and volumetric data presented in Chapter 4 and indicate the suitability of CCS polymers as effective ‘fillers’ for linear matrices.
In Chapter 6, Boltorn hyperbranched aliphatic polyesters were functionalised with aminotreated isobutylPOSS and blended with linear thermoplastic polyurethane. The morphology of the blends was primarily influenced by the Boltorn dendrimer, with minor contributions from POSS. The radius of gyration decreased and fractal dimensionality increased with functionalised dendrimer concentration, indicating a reduction in free volume and increased compactness amongst polymer chains. Incorporating Boltorn-POSS into thermoplastic polyurethane enhanced miscibility and reduced phase separation, as indicated by the reduced d-spacing values. Both Boltorn and POSS contributed to the enhanced thermal stability exhibited by the blends; Boltorn imparted restrictions on polymer chain vibrations while POSS shielded segments of polymer chain from thermal degradation. Blends became more rigid in behaviour, displaying enhanced tensile modulus and strength. Molecular restrictions imparted by the POSS-Boltorn hybrid reduced creep deformation and increased permanent strain. Storage modulus, loss modulus and $T_g$ increased with blend concentration. Blends containing higher generation Boltorn displayed superior thermal and mechanical properties than blends lower generation Boltorn. This was attributed to the increased degree of linear-dendrimer polymer interactions which accompany an increase in dendrimer generation. Both Boltorn and POSS imparted influence on material properties, indicating the suitability of the functionalised dendrimer as reinforcement or ‘toughener’.

Telechelic (dumbbell-shaped) POSS were prepared by functionalised POSS molecules with adipoyl or sebacoyl chloride (Chapter 7). The novel fillers were subsequently incorporated into SBS to observe the influence of filler architecture and phase preference on material properties. Interactions between POSS molecules encouraged increased aggregation with larger filler concentrations. Composite morphology was dependent on the organic substituent groups on the POSS cages, with the volume of butadiene or styrene available for POSS to disperse through influencing filler aggregation. Composites displayed increased polydispersity. IsobutylPOSS remained confined within polybutadiene domains and did not change the cylinder morphology of SBS. PhenylPOSS composites exhibited increased d-spacing values due to expanded polystyrene domains and greater interdomain distance.
IsobutylPOSS had the greatest influence on thermal stability at filler loadings of 1-5 %·wt, due to its incorporation into the thermally-sensitive polybutadiene phase. At concentrations of 10 and 20 %·wt, phenylPOSS composites exhibited greater thermal stability, corresponding to the increased presence of more-stable phenyl groups. ‘Barbell’ length influenced thermal stability, with adipoyl chloride composites displaying superior thermal properties to their sebacoyl chloride counterparts. This was attributed to the butane 'barbell' (alkane chain length) being less susceptible to thermal degradation than octane. Dumbbell-shaped POSS enhanced tensile modulus, strength and strain hardening, while reducing creep deformation. Incorporation of POSS increased the storage modulus, loss modulus, and T\textsubscript{g}. Composites reinforced with adipoyl-chloride functionalised isobutylPOSS exhibited the greatest enhancement in mechanical properties due to the filler being; (a) smaller and more-rigid in nature, (b) its incorporation into the continuous (polybutadiene) phase. Three factors contributed to the mechanical properties of the nanocomposites; (a) POSS concentration, (b) the phase which the POSS was dispersed throughout, (c) the architecture of the dumbbell-shaped POSS, specifically the ‘barbell’ length. The versatility of POSS was highlighted, proving the molecule could find application as a filler core as well as a functional group.

POSS molecules were successfully functionalised with dichlorotriazine reactive dyes (Chapter 8) and incorporated into SBS. Aggregate size and frequency increased with filler content, due to increased inter-POSS and inter-chromophore interactions. As with the telechelic POSS composites prepared in Chapter 7, material morphology was dictated by the compatibilising ‘R’ groups on the POSS cages. By altering the functionalised POSS concentration, colour intensity was able to be controlled. At filler concentrations up to and including 5 %·wt, films displayed uniform and smooth colour distribution. Increasing the dye-POSS concentration past 5 %·wt increased filler diameters due to aggregation, resulting in swirling and fleck formation. The greatest uniformity of colour was reported in isobutylPOSS composites, due to the larger volume of polymer (polybutadiene) that the POSS will preferentially disperse throughout.
The thermal stability of SBS was enhanced by the addition of functionalised POSS, with phase preference and chromophore structure influencing thermal behaviour. IsobutylPOSS had the greatest influence on thermal stability, due to its incorporation into the thermally-sensitive polybutadiene phase, while CI Reactive Blue 4 exhibited a marginally better influence on thermal properties than CI Reactive Red 2 counterpart, due to the thermal stability of its anthracene-based chromophore. Tensile properties, storage modulus, loss modulus and $T_g$ reached maximum values at filler loadings of 5 %·wt. Creep deformation decreased and permanent strain increased with POSS content, due to the restricted molecular motions caused by filler. The decrease in mechanical properties at POSS concentrations above 5 %·wt was due to a disruption of the polymer molecular structure due to excess filler loading and reduction in material density. Filler concentration, phase preference and chromophore structure all contributed to the material properties. The study highlighted the limitations of functionalised polymer composites and sole reliance on processing technique to disperse and distribute filler.

TPU composites containing Fe$_3$O$_4$-functionalised CNTs were prepared using two different physical blending methods; melt-mixing and solvent dispersion (Chapter 9). Fe$_3$O$_4$ nanoparticles were present on the surface and inside the carbon nanotubes. SEM confirmed that shear at temperatures above the $T_g$ during melt-mixing was more effective at breaking-up CNT agglomerates than ultrasonication and solvent dispersion. Phase separation and the radius of gyration increased with filler content, as agglomeration occurred and unoccupied volume decreased. Magnetic properties increased with functionalised-CNT concentration, as the number of interactions between Fe$_3$O$_4$ particles increased. Solvent dispersed composites displayed inferior magnetic properties than their melt-mixed counterparts, due to clusters of magnetic filler reducing the net magnetisation.

Melt-mixed composites displayed superior thermal properties to their solvent-dispersed counterparts, which decreased in thermal stability with the addition of filler. The poor thermal properties were attributed to ineffective filler distribution and greater occurrence of agglomeration. Composites were less ductile and more rigid in behaviour, displaying enhanced tensile modulus and strength values. Creep deformation decreased and
permanent strain increased as functionalised-CNTs loading increased. Storage modulus, loss modulus and \( T_g \) values increased with functionalised-CNT content, reaching maximum values at filler concentrations of 10 %·wt. Composites prepared via melt-mixing displayed more dramatic changes in material properties and were generally superior than their solvent dispersed counterparts. Preparing composites using two different physical blending techniques highlights the dependency of material properties on filler dimensions and dispersion.

The research presents a broad range of functionalised polymer composites and blends, highlighting the versatility and practicality of these materials. The field of functionalised nanoparticles and polymer composites is constantly growing and evolving, providing a promising future. The preliminary results presented here provide a basis for further research into functionalised polymer nanocomposites, with the potential for these materials to find use in various practical applications.

10.2 Suggestions for further work

Chapter 4: The DSC and mT-DSC studies revealed much information regarding the glass transition and relaxation properties of the blends. Various CCS polymer characteristics, such as functionality, ‘arm’ length, ‘core’ size could be altered and the influence on \( T_g \)/relaxation properties determined. Rheological studies can be performed to further probe the relaxation properties of the materials. In addition, phenomenological models such as the Tool-Narayanaswamy-Moynihan (TNM) or Adam-Gibbs-Scherer (AGS) could be utilised to compare experimental and theoretical data. mT-TM provided an effective and novel method of characterising relaxation behaviour. The popularity of the technique is sure to increase as the applications and limitations of the instrument are determined.

Chapter 5: This chapter (in conjunction with Chapter 4) demonstrated how CCS polymers can be applied as additives to amorphous linear polymer matrices. CCS polymers could be incorporated into crystalline or semi-crystalline matrices, allowing the influence of crystallinity to be observed. Furthermore, CCS polymers may be utilised as potential unique nucleating agents. Blending CCS polymers with multi-phase polymers would enable the influence of selective dispersion and phase affinity on blend properties to be
The use of CCS polymers as functionalised additives has much potential. Functionalising the ‘core’ or ‘arms’ of the CCS polymer and incorporating it into a linear matrix can provide an effective method of introducing a specific functional group without compromising matrix properties.

Chapter 6: Bolton additives are used as tougheners in blends, with the materials presented in this chapter being no exception. The extent of the amorphous phase can be estimated using DSC, providing additional information regarding the degree of reinforcement. Although most hyperbranched aliphatic polyesters are amorphous, the introduction of crystalline segments may enhance mechanical properties within blends, including strength and rigidity. Similarly, the influence of POSS architecture is of consideration, with various cage sizes and shapes providing opportunity for modification of material properties and further functionalisation via reactive groups. Bolton dendrimers could be used to reinforce biopolymer matrices, creating potential for new environmentally friendly materials.

Chapter 7: There are numerous filler architectures and configurations that could be applied and characterised to determine how they affect polymer matrices. The dumbbell-POSS could be compounded with single phase polymers (in this case polystyrene or polybutadiene) to eliminate the influence of phase preference and gain further insight into architectural influences on material properties. The fraction of polymer chains constrained by the filler can be estimated via further mf-TM studies.

Chapter 8: This chapter highlighted the application and limitations of physically-blending organic substituents into a non-polar polymer. Capping the organic groups of the chromophore provides an alternative, although care must be taken to not significantly alter the characteristics of the dye or composite properties. Melt-mixing or extrusion can provide additional shear which may encourage superior dispersion of functionalised filler. Optical functional groups bonded to POSS can be expanded to include fluorescent molecules and liquid crystals. Additionally, azobenzene compounds could be used to control birefringence and dichroism, due to azobenzene derivatives undergoing trans-cis photoisomerisation by applying specific wavelengths of light or heat.
Chapter 9: Magnetically aligning the Fe$_3$O$_4$-functionalised CNTs within an elastomer allows for nanotube ‘channel’ formation. This enables the material to be utilised as a ‘switch’ or magnetorheological elastomer. Despite utilising shear and ultrasonication, agglomeration amongst the functionalised fillers occurred. Coating the functionalised nanotubes with a silane or alkyl group prior to compounding could be considered, allowing the influence on magnetic and mechanical properties to be characterised. Bi- and polymetallic complexes can experience ferromagnetic coupling, enhancing the magnetic moment of the materials. Various rare-earth magnetic materials have been developed with superior magnetic properties over ferrite or alnico magnets. These may provide suitable candidates for functional groups.
**GLOSSARY**

**Agglomerate:** A larger cluster of particulates, consisting of a cluster of aggregates.

**Aggregate:** A small cluster of primary particulates, formed due to inter-particle attractions.

**Annealing:** The process of holding a material at a constant temperature (annealing temperature, $T_a$) for a given length of time (annealing time, $t_a$). In the case of polymers, the $T_a$ is usually below the $T_g$, near the onset of glass transition.

**Coercivity:** A measure of the intensity of the applied magnetic field required to reduce a material’s magnetisation to zero following saturation. Abbreviated to $H_C$.

**Core cross-linked star polymer:** A type of star polymer, consisting of a ‘hard’ crosslinked core and ‘soft’ arms. Abbreviated to CCS polymer.

**Creep:** The long-term deformation of a polymer under a constant load.

**Dendrimer:** A multi-branched, large molecule, usually spherical in dimensions.

**Differential scanning calorimetry:** Abbreviated to DSC, a technique in which the difference in the amount of heat required to heat a sample and reference are measured as a function of temperature. Provides information regarding enthalpy, specific heat and thermal/phase transitions.

**Elastomer:** A polymer with the property of elasticity.

**Fictive temperature:** The temperature at which the glassy state of a polymer would be in thermal equilibrium. Obtained at the intersection of the extrapolated glassy line of the volume/enthalpy and equilibrium line.

**Filler:** The dispersed phase in a polymer composite. Called ‘reinforcement’ when the filler is used to improve mechanical properties.

**Filler network:** A three-dimensional interconnected structure formed by filler particulates within a polymer matrix.

**Free volume:** The collective name for hole/voids/vacancies within a polymer, necessary for segmental motion to occur.

**Functionality:** The number of polymeric arms attached to the core of a star polymer.

**Glass transition:** A pseudo second order phase transition during which a material in the glassy state transforms on heating into a supercooled liquid.
**Glass transition temperature:** The temperature at which polymer chains have sufficient energy for rotation about bonds. Abbreviated to $T_g$.

**Hyperbranched polymer:** A three-dimensional macromolecule with a high degree of branching.

**Loss modulus:** Abbreviated as $E''$, the loss modulus measures the unrecoverable energy dissipated by a material during flow.

**Magnetite:** A ferrimagnetic iron oxide with the chemical formula $\text{Fe}_3\text{O}_4$.

**Master curve:** A curve that shows the expanded time or frequency dependency of a material. Constructed by shifting data horizontally and vertically to superimpose on a reference curve.

**Matrix:** The continuous phase in a polymer composite. Usually, though not always, a polymer.

**Modulated force – thermomechanometry:** A technique in which an oscillating force is applied to a sample over a temperature range. The applied force is converted to stress and the sample's response to this response is measured, obtaining the storage modulus, loss modulus and tan delta. Abbreviated to mf-TM and is also known as dynamic mechanical spectroscopy (DMS).

**Modulated temperature – differential scanning calorimetry:** Thermal analysis technique where a low frequency sinusoidal or non-sinusoidal temperature program is applied over the linear temperature program. Unlike conventional DSC, components which are in-phase and out-of-phase with temperature modulation can be separated, as well as reversing and non-reversing thermal events. This provides additional information regarding time-dependent thermal events, kinetics and enthalpy evolution. Abbreviated to mT-DSC.

**Modulated temperature – thermomechanometry:** Thermomechanical technique involving the application of an oscillating temperature to a linear/isothermal underlying heating rate. The modulated temperature program induces a sinusoidal response in specimen dimension change that can be resolved into reversing (in-phase with $\Delta T$) and non-reversing (out-of-phase with $\Delta T$) components. Abbreviated to mT-TM.

**Nanocomposite:** A composite material where one of the components has at least one dimension in the nanometre range (1-100 nm).
**Nanometre**: A unit of length equal to one billionth of a metre (10\(^{-9}\) m).

**Physical ageing**: Changes in material properties due to structural relaxation/recovery.

**Polyhedral oligomeric silsesquioxanes**: A class of molecule comprised of a rigid inorganic core, most often made of 8, 10 or 12 silicon atoms linked by oxygen atoms. Each corner is attached to an organic group and the entire molecule is only 1-3 nm in size. Abbreviated to POSS.

**Remanent magnetisation**: A material’s ability to retain residual magnetic field following removal of the external magnetic force after saturation. Abbreviated to \(M_R\).


**Saturation magnetisation**: The maximum induced magnetic moment that can be obtained from a material in a magnetic field. Abbreviated to \(M_s\).

**Segmental motion**: Movement among polymer chain segments during glass-rubber transition or applied force/frequency. Motion can be in the form of stretching, bending or rotation.

**Single-phase polymer**: A polymer that consists of only one phase (amorphous or glass).

**Star polymer**: A class of hyperbranched macromolecule that consists of several linear polymer chains joined to a central core.

**Storage modulus**: Used to determine the stiffness of a material, the storage modulus (\(E'\)) is a measure of stored elastic energy.

**Structural relaxation**: The process by which thermodynamic variables, such as volume or enthalpy, evolve in an attempt to reach equilibrium. Also called structural recovery.

**Tan delta**: Also written as \(\tan \delta\), this is the ratio of loss modulus (\(E''\)) to storage modulus (\(E'\)) and is a measure of energy loss in relation to recoverable energy.

**Telechelic**: Used to describe a polymer that has functional groups as its end groups. Similar to a ‘dumbbell’ shape.

**Thermal expansion**: The tendency of a material to change in volume in response to a change in temperature. The ratio of the change in dimension to the change in temperature is referred to as the material’s coefficient of thermal expansion.
Glossary

**Thermogravimetry:** A technique in which the weight of a material is measured as a function of temperature. Abbreviated to TGA, it is useful in determining thermal degradation behaviour, material composition and thermal stability.

**Thermoplastic:** A polymer that can soften and melt upon the application of heat.

**Thermoplastic elastomer:** A polymer, generally a copolymer or blend, which contains reversible physical crosslinks, allowing the material to display both thermoplastic and elastic properties.

**Time-temperature superposition:** Method used to determine the temperature dependence of the rheological behaviour of a polymer liquid or to expand the time or frequency at a temperature at which the material is being characterised. It operates on the principle that low temperature corresponds to a high frequency response and vice-versa. Data is shifted horizontally and vertically to superimpose on the reference curve, creating an expanded master curve.

**Tortuosity:** The property of having many turns or being twisted.

**Two-phase polymer:** A polymer that contains both amorphous and glassy segments.
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APPENDICIES

APPENDIX A: Calculating the number of POSS molecules bonded to a single Boltorn dendrimer

FTIR absorbance spectra were utilised to determine the number of POSS molecules that reacted with hydroxyl groups on the Boltorn dendrimers following functionalisation, as shown in Figure A. Several POSS-functionalised Boltorn samples were prepared in different molar ratios as summarised in Table A.

Figure A Absorbance spectra of POSS-functionalised Boltorn H20. Spectra have been shifted 0.05 units vertically for clarity
Table A  Peak absorbance intensity and molar ratios of POSS-functionalised Boltorn samples

<table>
<thead>
<tr>
<th>Molar ratio (POSS:Boltorn)</th>
<th>mol of POSS / mol of Boltorn (x-axis)</th>
<th>Peak height at ~1100 cm(^{-1}) (POSS peak)</th>
<th>Peak height at ~1720 cm(^{-1}) (Boltorn peak)</th>
<th>POSS peak / Boltorn peak (y-axis)</th>
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<tr>
<td><strong>POSS-functionalised Boltorn H20</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.33</td>
<td>0.39</td>
<td>0.40</td>
<td>0.98</td>
</tr>
<tr>
<td>1:2</td>
<td>0.5</td>
<td>0.39</td>
<td>0.37</td>
<td>1.05</td>
</tr>
<tr>
<td>1:1</td>
<td>1</td>
<td>0.39</td>
<td>0.29</td>
<td>1.35</td>
</tr>
<tr>
<td>2:1</td>
<td>2</td>
<td>0.48</td>
<td>0.25</td>
<td>1.92</td>
</tr>
<tr>
<td>3:1</td>
<td>3</td>
<td>0.69</td>
<td>0.28</td>
<td>2.46</td>
</tr>
<tr>
<td><strong>POSS-functionalised Boltorn H40</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.33</td>
<td>0.53</td>
<td>0.49</td>
<td>1.08</td>
</tr>
<tr>
<td>1:2</td>
<td>0.5</td>
<td>0.48</td>
<td>0.43</td>
<td>1.12</td>
</tr>
<tr>
<td>1:1</td>
<td>1</td>
<td>0.49</td>
<td>0.40</td>
<td>1.23</td>
</tr>
<tr>
<td>2:1</td>
<td>2</td>
<td>0.66</td>
<td>0.46</td>
<td>1.43</td>
</tr>
<tr>
<td>3:1</td>
<td>3</td>
<td>0.72</td>
<td>0.42</td>
<td>1.71</td>
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<td><strong>POSS-functionalised Boltorn H20 used in blends:</strong></td>
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<tr>
<td></td>
<td>0.19</td>
<td></td>
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<td>1.19</td>
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<tr>
<td><strong>POSS-functionalised Boltorn H40 used in blends:</strong></td>
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<tr>
<td></td>
<td>0.15</td>
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<td>1.25</td>
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Figure B  Linear plot of absorbance peak ratio vs. molar ratio

\[
y = 0.5629x + 0.7824 \\
R^2 = 0.9998
\]
The ratio of the peak heights at \( \sim 1720 \text{ cm}^{-1} \) (C=O stretching within Boltorn) and \( \sim 1100 \text{ cm}^{-1} \) (Si-O stretching within POSS) was taken and plotted as a function of the molar ratio of POSS:Boltorn to yield a linear graph as shown in Figure B.

**Example calculation using POSS-functionalised Boltorn H20**

Boltorn H20 displayed an absorbance peak ratio of 0.19:0.16 or 1.19. Substituting 1.19 into the linear fit equation obtained from Figure B yields a molar fraction of 0.72. This corresponds to a molar ratio of 1:1.4 (POSS:Boltorn). Using these mol values, the mass of Boltorn and POSS were determined using Equation A:

\[
 n = \frac{\text{mass}}{\text{molar mass}}
\]  

(A)

**Boltorn H20:**

\[
 1.4 = \frac{\text{mass}}{2100}
\]

Mass = 2940 g

**POSS:**

\[
 1 = \frac{\text{mass}}{871.92}
\]

Mass = 871.92 g

To determine the number of POSS molecules bonded to one Boltorn dendrimer, Equation B was utilised:

\[
 \text{Number of molecules} = \frac{A_v}{(\text{mass} \times \text{molar mass})}
\]  

(B)

where \( A_v \) is Avagadro’s number.

**Boltorn H20:**

\[
 \text{Number of molecules} = \frac{6.022 \times 10^{23}}{(2940 \times 2100)}
\]

\[
= 9.75057 \times 10^{16}
\]
POSS:

Number of molecules = $6.022 \times 10^{23} / (871.92 \times 871.92)$

= $7.92114 \times 10^{17}$

Number of Boltorn H20 molecules: $9.75057 \times 10^{16} / 9.75057 \times 10^{16} = 1$

Number of POSS molecules: $7.92114 \times 10^{17} / 9.75057 \times 10^{16} = 8.1$

~8 POSS molecules attached to 1 Boltorn H20 dendrimer.

Similarly the molar ratio of POSS:Boltorn H40 was calculated to be 1:1, with ~31 POSS molecules attached to 1 Boltorn H40 dendrimer.
APPENDIX B: Enthalpy and volume relaxation of core-crosslinked star polystyrene/poly(methyl methacrylate) blends

Enthalpy and Volume Relaxation of Core-Crosslinked Star Polystyrene/Poly(methyl methacrylate) Blends

Steven Spoljaric,* Antonietta Genovese, Tor Kit Goh, Anton Blencowe, Greg G. Qiao, Robert A. Shanks

Blends of linear and core-crosslinked star (CCS) polymers are prepared. The relaxation and thermal properties of the blends are determined using conventional and modulated-temperature DSC and modulated-temperature thermomechanometry. Addition of CCS polymers increases the glass transition temperature while decreasing the enthalpy and the linear coefficient of thermal expansion, suggesting that the hyperbranched polymers restrict matrix chain motions. Isothermal annealing increased the $T_g$ and $\Delta H$ and decreased sub-$T_g \alpha$ due to the reduced free volume and mobility within the polymer films. Volume relaxation during annealing is observed using $m$-T-M, while a stretched-exponential function is utilised to interpret the data.

Introduction

Core-crosslinked star (CCS) polymers are unique three-dimensional macromolecules that consist of a ‘hard’ crosslinked core surrounded by numerous ‘soft’ linear arms. These polymers are generally synthesised using living radical polymerisation techniques which allow for a high degree of structural control and narrow molecular weight distribution. These techniques include nitroxide-mediated radical polymerisation (NMP) atom-transfer radical polymerisation (ATRP) and reverse addition/fragmentation chain transfer (RAFT). Despite exhibiting a very high molecular weight, CCS polymers display solubility and viscosity parameters similar to linear and branched polymers of low-molecular weight. This combination of unique intrinsic properties and polymerisation techniques, allowing for high structural control, has led to significant interest in CCS polymers. Furthermore, these macromolecules show potential for use in various applications, including drug delivery, paint additives and membrane formation.

Despite the wide scale academic and industrial attention star polymers have received, the bulk of available literature concerns synthesis techniques and rheological properties, with practically no research performed regarding structural relaxation, physical ageing or the glass transition properties of CCS polymers and/or blends with linear polymers. In particular, no studies have been performed using thermal analysis methods including DSC (both conventional and modulated techniques) or thermomechanometry. CCS polymers generally exhibit a single glass transition.
APPENDIX C: Thermal, optical and static/dynamic mechanical properties of linear-core crosslinked star polymer blends

Thermal, Optical, and Static/Dynamic Mechanical Properties of Linear-core Crosslinked Star Polymer Blends

Steven Spoljaric,* Tor Kit Goh, Anton Blencowe, Greg G. Qiao, Robert A. Shanks

Core crosslinked star (CCS) polymers are synthesized and blended with linear polymers. Constrained mobility is revealed by an increase in modulus and strength with CCS polymer concentration, while creep deformation decreases and permanent strain increases. Storage modulus, loss modulus, and glass transition temperature increase with CCS polymer concentration due to miscibility and linear-CCS polymer “arm” interactions. Master curves shift to lower frequencies with blends that experience segmental relaxation across a broader time scale due to a range of molecular environments from linear to maximum constraints in the vicinity of the crosslinked cores. Fracture and apparent activation energy increase with CCS polymer content, while fractional free volume and volume expansion decrease.

Introduction

Core crosslinked star (CCS) polymers are three-dimensional macromolecules comprised of a “hard” crosslinked polymer core surrounded by numerous “soft” linear arms. Also referred to as star microgels or star nanogels, these polymers are generally synthesized using living radical polymerization techniques that allow a high degree of structural control and narrow molecular weight (M) distribution, including nitroxide-mediated radical polymerisation (NMP), atom transfer radical polymerisation (ATRP) and reverse addition-fragmentation chain transfer (RAFT). One particular feature which distinguishes CCS polymers from conventional star polymers is that the former are traditionally synthesised using the arms-first approach. In this approach, a living macroinitiator (the arm) is reacted with a vinyl crosslinker to form a highly crosslinked core from which the arms protrude. In contrast, the “core-first approach” involves the use of a...
APPENDIX D: Novel-elastomer-dumbbell functionalized POSS composites: Thermomechanical and morphological properties

Novel Elastomer-Dumbbell Functionalized POSS Composites: Thermomechanical and Morphological Properties

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ABSTRACT: Nanocomposites consisting of poly(styrene-1-butadiene-1-styrene) (SBS) and polyhedral oligomeric silsesquioxanes (POSS) were prepared using a solvent dispersion method. Dumbbell-shaped POSS fillers were prepared using diaclyl chlorides to bridge the POSS molecules. Fourier-transform infrared spectroscopy confirmed functionalization. Scanning electron microscopy revealed an increase in filler aggregation with concentration, with preferential phase selectivity. Polydispersity increased with filler concentration while $d$ spacing was influenced by phase selectivity and domain-filler compatibility. Functionalized POSS improved thermal stability by imparting restrictions of SBS chain motions. Tensile stress–strain analysis revealed an increase in modulus, yield strength, and strain hardening with filler concentration, while creep deformation decreased and permanent strain increased with POSS content. Storage modulus, loss modulus, and glass transition temperature increased with filler content due to effective SBS–POSS interactions. Nanocomposite properties were influenced by filler concentration, the phase of the filler was dispersed throughout and the length of the alkyl “barbell” on the dumbbell-shaped POSS. © 2011 Wiley Periodicals, Inc.

Keywords: POSS; thermomechanical; functionalization; elastomer

INTRODUCTION

Functionalization involves the introduction of chemical functional groups onto a surface or substrate. Various chemical groups, including organic compounds, fluorescent materials, reactive dyes, metals, and magnetic compounds, have been bonded to surfaces such as carbon black, fumed silica, montmorillonite clays, and alumina. These hybrid materials show much potential for incorporation into polymer composites as a novel class of filler. By controlling the specific functionality of the bonded chemical groups with the mechanical, thermal, or additional intrinsic properties of the surface/substrate, functionalized fillers provide potential for new materials and properties. One particular class of filler suitable for functionalization are polyhedral oligomeric silsesquioxanes (POSS), empirical formula $RSiO_x$.

These hybrid molecules consist of a rigid inorganic core consisting of 8, 10, or 12 silicon atoms linked by oxygen atoms, with organic substituents attached at the corners of the silica cage. The central core is ceramic in nature, providing thermal stability and rigidity, while the organic groups compatibilize the molecule. First synthesized in 1946 by Scott, POSS have begun to attract serious attention as a filler material within the last 10–15 years, encouraged by the significant improvement in composite properties the fillers provide.

A variety of functional groups have been bonded directly onto POSS molecules, including organic groups, 
and fluorescent emitters. The possibility of introducing these molecules is encouraged by the commercial availability of POSS with pre-existing reactive groups, such as trisilanol or amines. In addition, POSS molecules with various architectures and molecular shapes have been prepared, including pendant, bead, and starlike structures. Several of these shape-functionalized POSS have been incorporated into network structures or grafted onto polymer chains to prepare nanocomposites with noticeable enhancements in glass transition temperature, thermal stability, and mechanical properties. Another specific architectural structure is dumbbell-shaped (telechelic) POSS, consisting of two POSS “weights” connected chemically by an alkyl, polymer, or similar chain “barbell.” These structures have received relatively little attention, despite exhibiting enhanced thermal stability, solubility, and film-forming properties. Mather and coworkers have synthesized telechelic polymers consisting of a poly(ethylene glycol) bridges with POSS bonded to the chain end groups, observing...
APPENDIX E: Poly(styrene-b-butadiene-b-styrene) – dye-coupled polyhedral oligomeric silsesquioxanes

Poly(styrene-b-butadiene-b-styrene) – Dye-coupled Polyhedral Oligomeric Silsesquioxanes

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Abstract: Dye-coupled polyhedral oligomeric silsesquioxane (POSS) were prepared and the coloured POSS particles were ultrasonically solution dispersed in poly(styrene-b-butadiene-b-styrene) (SBS). POSS molecules contained either isobutyl or phenyl groups to provide selective compatibility with either the soft (butadiene) or hard (styrene) phase within the block copolymer. The composition and thermal stability were characterised using thermogravimetry. Colour coordinates were measured. Tensile mechanical properties, creep and recovery were determined. Creep was modeled using the 4-element model of Maxwell and Kelvin-Voigt, while recovery correlated with the stretched-exponential function of Kohlrausch, Williams and Watts.

Introduction

POSS are hybrid molecules consisting of a rigid inorganic core composed of 8, 10 or 12 silicon atoms linked by oxygen atoms, with organic substituents attached at the corners of the silica cage. First synthesized in 1946 [1], POSS have begun to attract serious attention as a filler constituent within the last 10 to 15 years, due to the enhanced mechanical and thermal properties these nanosized materials provide. POSS with various reactive groups (–OH, –NH₂, –CN, –COOH) have been prepared, allowing functional groups to be bonded to the molecule. Functionalisation of POSS enables the introduction of substituent molecules (metals, organic groups, fluorescent emitters, polymer chains) [2-4] while ensuring polymer-filler compatibility and not compromising the mechanical integrity of the polymer matrix. The combination of POSS thermal and mechanical properties with the specific unit of a functional molecule results in a new class of hybrid fillers, with potential for unique materials and applications.

The aim was to synthesis SBS-POSS nanocomposites via a physical blending process, where the POSS will favor a specific phase of the polymer matrix and enhance composite properties, while the functionality of the dye remains intact. Objectives included functionalising the POSS molecules with dichlorotriazine reactive dyes, preparing SBS-POSS nanocomposites using a solvent dispersion technique and characterizing the thermal, colorimetric and mechanical properties of the nanocomposites.

Experimental

Materials: SBS was Kraton D-1102 (Kraton Polymers LLC). It is a pure, linear triblock copolymer with 29.5 % wt bound styrene and a density of 0.938 g cm⁻³. Two types of POSS were used as fillers; Trisilanolpheny1POSS and TrisilanolisobutsylPOSS. (Hybrid Plastics Inc.) Two varieties of dichlorotriazine dye were reacted with the POSS molecules; CI Reactive Blue 4 (Procion Blue MX-R) and CI Reactive Red 2 (Procion Red MX-B5), obtained from Kraft Kolour Pty Ltd., Whittlesea, Australia. 3-aminopropyltrimethoxysilane and diisopropylethyamine were obtained from Aldrich Chemical Co., Milwaukee, USA. All chemicals were used as received.