MOLECULAR STRUCTURE AND RHEOLOGY OF
POLYPROPYLENE IN BLOWN FILM PROCESSING

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DECLARATION

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

[Ivan Ivanov]

06/08/2003

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SUMMARY

Polypropylene (PP) is one of the most important polymers in use. It is a cheap commodity plastic, yet useful for manufacturing a range of versatile products. One of the prominent applications of PP is the production of biaxially oriented PP film (BOPP), which became an irreplaceable material for food and tobacco packaging and a substrate for printing the Australian banknotes. The ultimate properties of polymer products are the result of a combination of factors, such as molecular structure of the resin and processing conditions. Understanding the influence of these factors on the final polymer properties would allow cost-effective development of more efficient technologies for manufacturing high quality products.

Rheology was found to be the most useful tool for assessing the interrelations between several aspects of molecular structure (more precisely, molecular weight and molecular weight distribution, MW and MWD) and the processability of polypropylene. As a science of flow and deformation, rheology studies the various aspects of deformation that occur during the BOPP processing. Shear flow dominates during the extrusion of the PP melt, while the extensional deformation dominates when it’s being blown into a bubble and stretched.

In the work presented here, several PP grades, including homo-polymers, co-polymers and blends, were characterised in terms of MW, MWD, shear and extensional rheology. Additionally, differential scanning calorimetry was used to determine the thermal properties of the grades and to provide information on the morphology of the materials at different temperatures. Gel-permeation chromatography was a method of choice to study the polymers’ MWD; moreover, by coupling the viscometer to the refractive index detector, it was possible to study the long-chain branching (LCB). None of the PP grades showed presence of LCB.

The shear rheological characterisation was performed in both steady and dynamic mode. The steady shear measurements provided the most relevant data for prediction of the polymer melt behaviour under processing conditions. However, dynamic or oscillatory shear measurements produced a large set of data useful for estimation of the linear visco-
elastic properties that can be related to their MWDs. Extensional rheology of PP was also carefully studied by measuring the transient extensional viscosity, also known as the stress growth coefficient, $\eta^*_{E}(t)$.

All measurements were conducted in such a way that would provide the most possible precision and accuracy. The error analysis was performed for all the rheological measurements. All tests were repeated several times in order to verify the repeatability. Wherever possible, the reproducibility of measurements was determined as well, by comparing the data obtained from different instruments. This was especially important in case of GPC analysis, which is a calibration-based technique and also for extensional rheometry, which is not a well-established method yet.

Furthermore, it was attempted to estimate the MWD of several PP homo-polymer grades from their steady shear viscosity curves, by inversion of blending laws. The resulting curves were much narrower than the GPC curves and did not retain the information on the broadness of distribution. The dynamic shear data were also utilised to estimate the MWD. First, the relaxation time spectra for polymer grades were calculated from their dynamic moduli, $G'$ and $G''$. A recently developed analytical relationship between relaxation spectrum and MWD was then applied to the commercial PP grades for the first time. The obtained distribution curves were narrower than the GPC ones, but they preserved their relative position and breadth, i.e. they could be used for comparison between grades. This provides a basis for the future work in utilisation of rheological measurement for MWD determinations.

Many correlations between rheological parameters and MW averages and polydispersities have been formerly known. Most common of them were tested and discussed for their reliability and practicality for polymer grades used in BOPP processing. The use of such correlations, e.g. between Mw and zero shear viscosity or between the degree of shear thinning and polydispersity, can provide an assistance for engineers involved in polymer processing.

Blending PP with an amorphous hydrocarbon resin – hydrogenated oligo-cyclopentadiene (HOCP), has been recently shown to improve final BOPP properties, such as gas
permeability. The use of a commercial modifier, EP1 that consists of 50wt% PP and 50wt% HOCP, for blending with different PP grades, was studied here for the first time. Rheological and morphological characterisation of the blends was performed and the correlation between miscibility and the rheological behaviour was drawn. It was found that two factors were highly significant: -the concentration of the oligomeric resin, HOCP, which lowered the viscosity and dictated the onset of phase separation and -the MWD compatibility of the PP grade with the polypropylene pre-blended in EP1.

Extensional rheological measurements were conducted with PP grades in different morphological states, controlled by temperature. Strain hardening was found for PP stretched from the semi-molten state, which exists at temperatures slightly lower than its melting point, Tm. The extensional viscosity index, EVI was introduced in this study as a measure of strain hardening for polypropylene and a practical tool for relating the results of extensional rheological measurements to processability of PP grades at different conditions. The results were supported by shear rheological, GPC, DSC and optical microscopy testings, where any of the listed methods by itself was not sufficient to predict the behaviour of semi-molten PP under extensional deformation.

It was shown that the factors that dominate the processability of polymers in industrial processing and their interrelationships are very complex. By identifying the key parameters of interest for a specific process (e.g. extensional viscosity, strain, strain rates, temperature, shear viscosity etc. in case of film blowing) it may become possible to develop models that predict the processing behaviour of the polymer grades. This work provides a basis for developing such models.
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NOMENCLATURE

A – area (m²)
a_T – shift factor
BOPP – biaxially oriented polypropylene
b_T – vertical shift factor
Cp – heat capacity
DSC – differential scanning calorimetry
Ea – activation energy (kJ)
EPR – ethylene-propylene rubber
EVI – extensional viscosity index
F – force (N)
\( G^0_N \) - plateau modulus
G(t) – stress relaxation modulus
G' - storage modulus
G” – loss modulus -
g_r – relaxation strength
GPC – Gel permeation chromatography
h(τ) – relaxation time spectrum
ΔH* - enthalpy (heat) of melting (kJ)
HOCP – Hydrogenated oligo(cyclopentadiene)
HS-OM – hot-stage optical microscopy
iPP – isotactic polypropylene
K – constant of proportionality
L – length (m)
LCB – long-chain branching
M – molar mass
m – parameter
\( M_c \) – critical molecular weight
MDSC – (Temperature) Modulated DSC
Me –molecular weight between entanglements
Mn – number- average molecular weight
Mv - viscosity- average molecular weight
MW – molecular weight
Mw - weight- average molecular weight
MWD – molecular weight distribution
Mz – z- average molecular weight
Mz+l – z+l- average molecular weight
N – number (of molecules)
n – power law parameter
Δp – pressure drop
PE – polyethylene
PI – polydispersity index (Mw/Mn)
PP – polypropylene
R – universal gas constant (8.314 J mol⁻¹K⁻¹)
RPI – rheological polydispersity index
SEC – Size-exclusion chromatography
T – temperature (K)
t – time (s)
Tc – crystallisation temperature
Tg – glass transition temperature
Tm – melting temperature
W – weight
w – weight fraction
xC - % crystallinity

GREEK SYMBOLS

α – Mark-Houwink parameter
β – mixing rule parameter
$\varepsilon_\text{H}$ – Hencky strain
$
\dot{\varepsilon}$ – extensional strain rate (s⁻¹)
γ – strain (%)
$
\dot{\gamma}$ – strain rate (s⁻¹)
\( \eta \) – viscosity (Pas)

\( \eta_0 \) – zero shear viscosity

\( \eta^* \) – complex viscosity (Pas)

\( \eta_\infty \) – infinite shear viscosity

[\( \eta \)] – intrinsic viscosity (dL/g)

\( \lambda \) – branching frequency

\( \rho \) – density (gc\( m^{-3} \), kgm\(^{-3} \))

\( \sigma \) – stress (Pa)

\( \tau \) – relaxation time (s)

\( \omega \) – angular frequency (rad/s)
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1. INTRODUCTION

1.1. BACKGROUND

Polypropylene (PP) is transformed into a diverse range of products by a variety of processes. This has been a major contributing factor in the commercial success of polypropylene. Figure 1.1 shows an increasing demand for PP in the last 15 years.

[Copyrighted material omitted. Please consult the original thesis.]

Figure 1.1 Increasing demand for PP resins (adopted from [Killeen, 1999])

A unique aspect of the PP processes compared to the other major plastics is the use of orientation to develop enhanced properties. The advantage of PP in mechanical properties, compared to polyethylene (PE) is shown in Figure 1.2:

[Copyrighted material omitted. Please consult the original thesis.]

Figure 1.2 Flexural modulus of polypropylene (PP) and polyethylene (PE)
A combination of ultimate properties (including thermal, mechanical, optical etc.) and the low price of the resin have established polypropylene as a major commodity plastic nowadays. The versatility of its processing led to a further development of new technologies, such as orientation processes in film production.

The biaxially oriented PP (BOPP) processes are the most popular methods for manufacturing PP films. BOPP film is a thermoplastic polymer film of polypropylene with an orderly molecular structure formed by biaxial orientation process. The processes improve the optical and gas barrier properties of the film. BOPP film is known for its excellent clarity, high tensile and impact strength, good dimensional stability and flatness, low electrostatic charge, corona treatment on one or both sides, waterproof and moisture repellent, excellent transparency, lower density, gas and moisture barrier properties, etc. Thus, it can be used as a substitute for cellophane, PVC, PE and other plastic films for enhancing product functions and high cost-efficiency. After the original use as a substitute for other plastic films, BOPP film became an irreplaceable material in packaging of snacks, confectionary, potato chips and tobacco products. One of the most prominent uses of BOPP is replacing paper for banknote printing in Australia.

The manufacturing of the BOPP film is usually achieved by so-called “double-bubble process”, schematically represented in Figure 1.3:

[Copyrighted material omitted. Please consult the original thesis.]
PP is extruded through an annular die into a tube, which is quenched with cold water. The tube (‘first bubble’) is then reheated and blown into a bubble (Figure 1.4). Simultaneous action of bubble pressure and drawing in the machine direction allows equal biaxial orientation in the film structure, which is responsible for its ultimate properties.

[Copyrighted material omitted. Please consult the original thesis.]

Figure 1.4 Polypropylene bubble in BOPP manufacturing
(adapted from http://www.films.ucb-group.com, 2001)

Different levels of structure can influence the final properties of the film:

1) *Molecular structure* (chemical composition, chain architecture and molecular weights of polymer chains) is both responsible for the flow behaviour of the melts and final mechanical properties.

2) During cooling and stretching, different *morphologies* can be developed and that is a predominant factor that governs mechanical and optical properties of the product.

3) Physical changes in polymer melts occur while they are subjected to different forms of deformation. These changes influence the *processing* behaviour, but the applied strain also influences the morphology, which affects the final properties.

The complexity of this relationship can be seen from the schematic diagram (Fig. 1.5):
PP is a product of polymerisation of propene, \( \text{CH}_3\text{CH}=	ext{CH}_2 \) (Figure 1.6):

The manufacturing conditions and structure of catalysts will govern the size and structure of the polymer chains. Most of the commercial PP grades consist of linear molecules (no long chain branching, LCB) of different length, i.e. they are polydisperse. The process is stereo-regular and the methyl groups (-CH\(_3\)) are oriented in the same fashion. The resulting polymer is isotactic, hence the polymer can crystallise.
Since the length (size) of polymer chains can be different, polymers are characterised by their molecular weight distributions (MWD) rather than single values of molecular weight. Small variations in MWD can have a great influence on polymers processability and final properties (Figure 1.8).

[Copyrighted material omitted. Please consult the original thesis.]

Fig. 1.8  MWD curves for two polymer grades with different rheological and physical properties (adopted from http://www.waters.com, 2000)

The link between molecular structure, processing behaviour and final properties is provided by rheology, the science of deformation and flow. Various complex flows occur during the BOPP processing: polymer pellets are transformed into a visco-elastic melt by action of thermal and mechanical energy in the extruder. It is then sheared through a die over a mandrel and quenched, allowing the PP chains to organise into very small crystals. After reheating, the soft tube is blown by air, providing a strong extensional deformation or strain, which is responsible for the orientation in film structure. Understanding of such flow behaviour and its dependence on polymer structure can lead to improvement and cost-effectiveness of the polymer film production.
1.2 OBJECTIVES

The overall aim of this work is to gain understanding of complex relationships between polymer structure, rheology and processability. The major objectives are:

- To find the most suitable correlations between MW, MWD and other structural parameters to the rheology of PP
- To identify the influence of rheological properties on the important parameters of blown film process
- To evaluate the influence of blending and blend composition on rheological and morphological properties of PP

Ultimately, the goal of this project would be to predict rheological behaviour of polymer grades from their molecular characteristics and utilise the rheology as an analytical tool for obtaining information on molecular structure.
2. LITERATURE REVIEW

2.1 INTRODUCTION

The properties of polypropylene (PP) are related to both the fabrication history of the material and its intrinsic polymer structure. Polymer structure is related to the catalyst, polymerisation and compounding technologies [Moore, (1996)]. The wide range of end-use applications for which PP is currently produced indicates the variety of properties that can be achieved. An understanding of the factors leading to the attractive end-use properties is essential to achieve unusual combinations of PP characteristics. Success in achieving this goal in the manufacturing process would provide a particularly attractive cost-performance profile for PP. Typical advantages of PP over the other commodity plastics are excellent mechanical properties, thermal stability and chemical resistance [Himont, (1993)]. The factors influencing the end-use properties of polymer grades are primarily their structure and morphology. Processing conditions and additives play important roles, as well. For example, cooling rate and nucleation can influence the crystallinity substantially.

The principal structural factors affecting end-use properties of PP are isotacticity, molecular weight and molecular weight distribution (MWD). In addition to these factors, chemical composition can be varied by co-polymerisation with polyolefins such as ethylene or butylene. However, oriented PP is usually manufactured from homopolymer and properties depend more on the orientation process than the polymer. Biaxially oriented PP (BOPP) films provide excellent levels of strength and stiffness, as well as an outstanding moisture barrier for the packaging industry. Modifications of polymers in these processes are most often aimed at improvements in processability. Therefore, the superior method of study for such complex systems is rheology, science of flow and deformation, with its constantly growing knowledge on interactions between components of polymer processing systems.
2.2 MOLECULAR STRUCTURE OF POLYPROPYLENE

2.2.1 Polypropylene chemistry

Strictly defined, PP would be whatever was obtained by polymerising propylene (propene, CH₃CH=CH₂) (Figs. 1.6 and 2.1):

\[
\begin{array}{c}
\text{CH₂} - \text{CH}_{\text{n}} - \\
\text{CH₃}
\end{array}
\]

Figure 2.1  Chemical structure of polypropylene

Prior to 1950, propylene polymer was a low molecular weight oil, of no interest then, or now. PP materials and related businesses grew out of the Ziegler-Natta discovery of catalysts capable of producing stereoregular [Ziegler, (1955); Natta and Corradini, (1960); Seymour and Cheng, (1986)]. Three factors control the stereo arrangement of the polymer:

1. **The degree of branching**: PP molecules are predominantly linear, i.e. the next monomer unit always adds at the chain end, rather than onto the backbone;

2. **Regiospecific methyl sequence**: monomer unit is always added head-to-tail, rather than head-to-head or tail-to-tail;

3. **Stereospecific addition**: monomer units always add in the same stereo arrangement, either d or l, but not in the alternating configuration.

If all the conditions given above are fulfilled, the product is isotactic PP, shown in Figure 2.2:

\[
\begin{array}{c}
\text{CH₂} - \text{CH} - \text{CH₂} - \text{CH} - \text{CH₂} - \text{CH} - \text{CH₂} - \text{CH} - \\
\text{CH₃} & \text{CH₃} & \text{CH₃} & \text{CH₃} & \text{CH₃}
\end{array}
\]

Figure 2.2  Chain structure of isotactic polypropylene

If the orientation of CH₃ groups was alternating, the product would be syndiotactic PP, yet with limited commercial application. Finally, irregular configuration leads to a usually undesired product, atactic PP. Tacticity is the most important factor that governs the
crystallinity of PP. Commercial PP grades are usually 80 to almost 100% isotactic [Simonazzi and Haylock, (1995)]. Degree of tacticity can be accurately determined by $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, but common practice is the use of an ‘isotacticity index’ defined as a PP fraction insoluble in boiling solvent, such as xylene [Butler, (1973)]. With highly isotactic PP, crystallinity of 40-70% can be achieved. Only the stereoregular blocks can pack closely to form crystals (Figure 2.3):

![Isotactic and atactic blocks](image)

**Figure 2.3** Packing of isotactic blocks of polymer chains

The size (length) of the chains can also influence crystallinity. Smaller molecules can move easily and arrange into crystalline regions. Governed by an increase of entropy, they can also move more easily into amorphous regions. That explains why crystallinity of PP increases with its molecular weight.

For some applications high crystallinity is not desirable. It can be reduced by introducing a small amount of another olefin as a co-monomer during production. The resulting propylene copolymers are usually random- or block- copolymers (Figure 2.4):

---A---A---B---B---B---A---B---A---B---B---A---

**random copolymer**

---A---A---A---A---A---A---B---B---B---B---B---

**block copolymer**

**Figure 2.4** Most common types of propylene co-polymers

(A- propylene, B- other olefin, eg. ethylene or butylene)

Another class of propylene copolymers was recently introduced – heterophaseic or impact-copolymers, where an elastomeric phase (ethylene-propylene rubber, EPR) is dispersed
uniformly within the PP homopolymer matrix. The reason for development of heterophase copolymers is the improvement in the low-temperature impact strength, while the random copolymers are mostly useful for improving optical properties (less crystallinity – better clarity) [Van der Ven, (1990)].

2.2.2 Polypropylene morphology

Meaning of morphology is the study of form and structure. When applied to polymers, it represents the study of order, and it mostly refers to polymer crystallinity [Coleman and Painter, (1997)]. Some polymers that are incapable of crystallising can also form ordered structure (block copolymers). Nevertheless, morphology is always involved with the study of blends, where immiscibility occurs.

All solids can exist as either amorphous or crystalline materials. Polypropylene is one of many polymers with semi-crystalline nature. The packing of PP chains starts with folding and stacking into lamellae (Fig. 2.5). As mentioned in Section 2.2.1, the process is thermodynamically driven towards higher crystallinity if the stereo-regularity is high. Still, some chains or parts of the chains cannot be incorporated into the lamellae, due to the entropy factor.

![Figure 2.5 Lamellar structure of PP chains](image)

The next level of morphological hierarchy is forming the crystals visible under the microscope, called spherulites (Figure 2.6).
a polymer crystalline spherulite

Figure 2.6  Forming the spherulitic structure of PP

The most important factors that are influencing PP crystallinity are tacticity, molecular weight and polydispersity, composition (of blends and copolymers) and intra-chain architecture (co-monomer distribution in copolymers). Additionally, processing conditions, such as shearing, orientation, thermal history and use of additives, can significantly modify the original PP morphology. Understanding the effects of structural and processing variables on PP morphology is essential for achieving the desired final properties.

In the crystalline state, iPP shows polymorphism, i.e. it can exist in several crystalline forms. The dominant form is designated as $\alpha$- or monoclinic form [Natta and Corradini, (1960)]. It can be recognised by spherulitic structure of type I and II, that both show Maltese cross pattern in polarised light (Figure 2.7) [Norton and Keller, (1985)].
The other crystalline forms of iPP are known as β- and γ-; their existence can be determined by wide-angle X-ray diffraction (WAXD) [Meille et al., (1994)]. It was found that β- form could be present in samples rapidly cooled from superheated melts, as well as under shearing conditions [Lovingier et al., (1977)]. The third, γ- form occurs rarely, eg. during crystallisation under high pressure, and it has not been regarded important yet. It is obvious that crystallisation kinetics play important role during cooling, allowing formation of structure thermodynamically less stable than α-form. Thus, under fast cooling (quenching) a mesomorphic form develops, especially when cooling rate exceeds 80°C/s [Piccarolo et al., (1992)]. It is relevant for the product final properties, since the unstable forms tend to change into more stable α-form, a behaviour known as ageing.

A technique typically used to study melting and crystallisation behaviour of polymers, and consequently their morphology, is differential scanning calorimetry (DSC). A DSC device looks generally like the one shown in Figure 2.8: during a run, both sample and reference pans are heated or cooled at the same rate and a difference between heat flows is recorded. A plot of heat flow or calculated specific heat versus time or temperature is called a thermogram.
Phase transformations, such as melting or crystallisation, are recorded as peaks (endothermic melting peak and exothermic crystallisation peak, as shown in Figure 2.9):

The heat capacity or specific heat, $C_p$, is calculated as a ratio of supplied heat and resulting temperature change. As shown in Figure 2.9, a rather small change in heat flow or $C_p$ can be noticed at low temperatures. It corresponds to a glass-transition temperature, $T_g$, and it is characteristic for amorphous materials. Below $T_g$, molecules have little mobility and the material is brittle. Above $T_g$, molecules can transform absorbed heat into kinetic energy and the material becomes soft or rubbery. If a polymer melt is quenched to temperatures below its $T_g$, crystallisation cannot occur due to low mobility of polymer chains. In case of polypropylene, the metastable form will be produced. During heating, above $T_g$, PP
chains will re-organise into crystals (exo-thermic peak in Fig. 2.9) that will melt at higher temperature (Tm, endo-thermic peak in Fig. 2.9). The heating and cooling rate will influence the values of Tm, Tc and Tg [Coleman and Painter, (1997)]. Therefore, the choice of conditions is important when performing a DSC scan. A sample is usually heated up to temperature well above melting point, to avoid previous thermal history effects. The cooling run is then performed, usually at 10°C/min, in order to record the crystallisation temperature (Tc). The melting temperature Tm will be taken from the next heating run at the same heating rate [Benzler and Nitschke, (1996)]. With semi-crystalline polymers, such as PP, it is not easy to detect the glass-transition; the use of modulated DSC technique can improve sensitivity [TA-Instruments, (1996)], but its use was not reported beneficial in the determination of other thermal properties [Haake, (1999)].

The equilibrium melting temperature (Tm⁰) of ideally (100%) crystalline iPP is not easy to determine experimentally; the usual technique is extrapolation, according to Flory equation (Eq. 2.1) [Flory, (1953)]:

\[
\left[\frac{1}{T_m} - \frac{1}{T_m^0}\right] \propto (\Phi_S - \Phi_S^2 \chi) \quad \ldots \quad (2.1)
\]

where \(\Phi_S\) is a volume fraction of diluent (amorphous component) and \(\chi\) is an interaction parameter. The value for Tm⁰ is quoted in a wide range of 180-220°C [Moore, (1996)]. The melting temperature (Tm) of commercial, Ziegler-Natta products is usually around 165°C.

DSC can be used for determination of another important characteristic of a semi-crystalline polymer: percentage of crystallinity. When the polymer crystals melt, they absorb heat; since melting is a first order transition, when the melting temperature is reached, the polymer's temperature won't rise until all the crystals have melted. This means that the heater under the sample pan is going to have to put a lot of heat into the polymer in order to both melt the crystals and keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up as a peak on a DSC plot, like the one in Figure 2.9. The area of this peak is proportional to the heat of melting characteristic for that polymer and its mass. The crystalline fraction of a polymer sample is calculated from the Equation 2.2:
\[ x_d(\text{PP sample}) = 100\% \cdot \frac{\Delta H^* (\text{PP sample})}{\Delta H_0(\text{iPP})} \quad \ldots \quad (2.2) \]

where \( \Delta H^* \) is experimentally determined heat of melting and \( \Delta H_0(\text{iPP}) \) is a reference value, usually quoted to be equal to 209 J/g [Fatou, (1971)].

### 2.2.3 Molecular Weight Distribution of Polymers

A key factor in determining polymer properties is polymer chain length, or molecular weight and its distribution. It is governed by the *degree of polymerisation* obtained by the process of polymer manufacturing and its impact on the commercial value of a polymer grade is simplified in Figure 2.10:

![Figure 2.10 Influence of the degree of polymerisation on the commercial value of polymer resins](image)

Polymers are often comprised of hundreds to thousands of chains of different length or molecular weight (MW), each with a finite concentration. This characteristic, known as a molecular weight distribution (MWD), plays an as important role as a chemical composition in shaping the polymer properties. Such polymers are known as *polydisperse*; most synthetic polymers belong to that group, as well as some natural macromolecules, such as polysaccharides and natural rubber. However, the most important bio-molecules, proteins and nucleic acids are predominantly *monodisperse*. Commercial PP grades produced by Ziegler-Natta catalytic polymerisation are quite polydisperse, i.e. they have a *broad* MWD. A typical distribution of molecular weights is represented in Figure 2.11:
Figure 2.11  A representation of molecular weight distribution of a polymer

To quantify the broadness of the MWD, several MW averages, or moments, can be calculated [Barth and Boyes, (1992)]: \( M_n \)- number-average and \( M_w \)- weight-average are the most important parameters, calculated as follows (Eqs. 2.3 and 2.4):

\[
M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum W_i}{\sum W_i} \quad \ldots \quad (2.3)
\]

\[
M_w = \frac{\sum W_i M_i}{\sum W_i} \quad \ldots \quad (2.4)
\]

where \( N_i, M_i \) and \( W_i \) are number, molecular weight and weight of the \( i \)-th species, respectively. The ratio of \( M_w \) and \( M_n \) is known as a polydispersity index, PI (Eq. 2.5):

\[
\text{PI} = \frac{M_w}{M_n} \quad \ldots \quad (2.5)
\]

To emphasise the importance of higher molecular weights, the other two averages, namely \( z \)- and \( z+1 \) averages, are in use (Eqs. 2.6 and 2.7):

\[
M_z = \frac{\sum W_i M_i^2}{\sum W_i M_i} \quad \ldots \quad (2.6)
\]

\[
M_{z+1} = \frac{\sum W_i M_i^3}{\sum W_i M_i^2} \quad \ldots \quad (2.7)
\]
The ratios of $M_z/M_n$, $M_z/M_w$ and $M_{z+1}/M_w$ are also used to describe the MWD. Polymers with $M_w/M_n < 1.05$ may be considered as monodisperse and they are usually produced by anionic polymerisation. Polydispersity of polymers made from free radical polymerisation is always greater than 2 [Cooper, (1987)].

### 2.2.4 Methods for Determination of Molecular Weight Distributions

Since polymers do not consist of only one molecular species, the classic methods used for determination of molecular weights of small molecules must be applied with much caution. The obtained result will be an average, and different methods will yield with different averages [Coleman and Painter, (1997)]. The most common techniques that can be applied to polymers are listed in Table 2.1:

<table>
<thead>
<tr>
<th>MW AVERAGE</th>
<th>SYMBOL</th>
<th>TECHNIQUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number average</td>
<td>$M_n$</td>
<td>End-group analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cryoscopy, Ebuliometry,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Osmometry</td>
</tr>
<tr>
<td>Weight average</td>
<td>$M_w$</td>
<td>Light Scattering,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Neutron Scattering</td>
</tr>
<tr>
<td>$z$-average</td>
<td>$M_z$</td>
<td>Ultracentrifugation</td>
</tr>
</tbody>
</table>

$M_n$ and $M_w$ of many polymers were determined by using the above methods before the techniques for fractionation were developed. **Osmometry** is still much employed in determination of polymers $M_n$; **light scattering** is a regular technique in polymer characterisation, providing not just $M_w$, but also a radius of gyration of polymer molecules. In addition to the above methods, measurements of solution viscosity can provide very useful information. This technique is based on determining the *intrinsic viscosity* or *limiting viscosity number* (IUPAC), $[\eta]$, as follows:
\[ [\eta] = \left( \frac{\eta_{sp}}{c} \right)_{c \to 0} = \left( \frac{\ln \eta_{rel}}{c} \right)_{c \to 0} \quad \ldots \quad (2.8) \]

where \( c \) = concentration (w/v), \( \eta_{sp} \) and \( \eta_{rel} \) are specific and relative viscosities, respectively, and \( \eta_{sp} = \eta_{rel}^{-1} \). Intrinsic viscosity depends on molecular weight, following the Mark-Houwink-Sakurada equation, usually nominated simply as Mark-Houwink equation (2.9):

\[ [\eta] = K M^\alpha \quad \ldots \quad (2.9) \]

Since the values of \( \eta_{sp} \) and \( \eta_{rel} \) are dimensionless, the dimension of intrinsic viscosity is reciprocal concentration, \( \text{dm}^3 \text{g}^{-1} \); for historical reasons, the unit of \( \text{dl/g} \) is still in use. The values of constants \( K \) and \( \alpha \) depend on polymer nature, the solvent and the temperature. Because viscosity measurements are related to molecular weight by a semi-empirical relationship, a new, viscosity-average MW must be considered for polydisperse polymers. Its calculation is shown in Equation 2.10:

\[ M_v = \left[ \frac{\sum N_i M_i^{(\alpha+1)}}{\sum N_i M_i} \right]^{\frac{1}{\alpha}} \quad \ldots \quad (2.10) \]

For the most probable distribution (see Figs. 2.11 and 2.12) it can be shown that: \( \text{Mn} : \text{Mv} : \text{Mw} = 1 : 1.67 : 2 \). The MWD curve in Figure 2.12 has a different shape from the one in Figure 2.11, although representing the same matter. The reason being MW-axis is logarithmic in Fig. 2.12, which is not always clearly marked in literature. The same happens with its direction, which is reverse, i.e. MW increases from right to left. The representation presented in Figure 2.12 is a consequence of processing the experimental data obtained from size-exclusion chromatography (SEC), which will be discussed later.
The methods described above can give valuable information about molecular weights, as well as on the breadth of distribution. However, not all the polymers have ideal log-normal distribution as shown in Figure 2.12. Many commercial polymers are manufactured with asymmetric or even bimodal distributions (Figure 2.13):

Obviously, knowledge of the MW averages is not sufficient and the development of methods for assessment of the whole MWD was crucial for polymer science. Gel permeation chromatography (GPC) established itself as a method of choice for MWD determination over the last three decades [Knapman, (1978)]. It is based on the principles of size exclusion chromatography (SEC) and both names and abbreviations are in use. Usually, term SEC is in use for proteins and other water-soluble compounds, while GPC indicates a technique for use with polymers soluble in organic solvents [Barth et al.,
(1994)]. Although the mechanism of GPC is constantly a subject of research, the basis of the method is readily understood. A column is packed with a porous material that does not interact with the sample, dissolved in an appropriate solvent. The solvent flows through the column, carrying the polymer molecules. They get separated in the column on the basis of their size, rather than molecular weight. Large molecules are effectively excluded from the solvent present in the pores, so they are soon eluted from the column. Smaller molecules fit better in the pores, so they spend more time in the pores and are eluted later (Figure 2.14).

[Copyrighted material omitted. Please consult the original thesis.]

Figure 2.14   Mechanism of GPC-SEC (adopted from http://www.waters.com)

A suitable detector inserted in the effluent stream from the column will give a response which is proportional to the amount of polymer present in the eluate at that time. The most widely used detector today for GPC analysis is the differential refractometer (DR). It is a concentration sensitive detector that simply measures the difference in refractive index (dRI) between the eluent in the reference side, and the sample + eluent in the sample side. It is a "universal" detector in that it will give a response for any polymer that has a significant difference in refractive index as compared to the eluent. In addition to DR, other detectors can be applied, such as viscometer and light-scattering detector, both sensitive to molecular weight, or a spectrometer (UV, IR, NMR) sensitive to both concentration and chemical composition. The instrumentation is schematically shown in Figure 2.15:
A plot of the detector's response is called a chromatogram, which shows the distribution of the intensity of the signal versus the retention time (Figure 2.16).

Chromatograms can be transformed into a MWD curve by using a calibration curve. There are three main calibration methods [Barth et al., (1994)]:

1) Relative calibration, with narrow polymer standards;
2) Broad standard calibration and
3) Universal calibration.

1). Relative calibration is based on the relationship between molecular weight and retention time (RT) [Yau et al., (1979)]. Retention times are determined for a series of narrow standards (nearly monodisperse polymers with known MW) and the calibration of MW as a function of RT is plotted. MWD of a broad polymer sample can be determined
by slicing its chromatogram and assigning to each slice the molecular weight that corresponds to given retention time. The area of the slice will be proportional to the amount or weight of molecules with that MW. Because a MWD represents a change in the amount or weight of polymer relative to a change in molecular weight, \( \frac{dW}{d\log M} \) is used as the ordinate, rather than the weight fraction, \( w \). To determine the weight fraction or a percentage of a sample at given MW, a cumulative distribution is used, which represents an integrated form of the differential MWD (Figure 2.17). This method is straightforward and accurate when the standards of the same type as the analysed sample are available.

![Differential and cumulative distributions](image)

**Figure 2.17** Differential and cumulative distributions

It is not always the case and polystyrene (PS) standards are major calibrants at the market, due to the fact that they can be produced by anionic polymerisation under ultra pure conditions [Polymer Labs, (1995)]. Since the relationship between MW and RT depends on polymer nature, the polystyrene calibration will produce inaccurate results when applied to eg. polyolefin samples. The obtained results would be called *apparent* molecular weights and could be used for comparative purposes only [Waters, (1999)].

2). The *broad standard calibration* can be applied when narrow standards of the same polymer type are not available [Balke *et al.*, (1969)]. One or two broad standards with known \( M_n \) and \( M_w \) are required and an iterative procedure is involved to generate a calibration curve by varying its slopes and intercepts until the specified MW averages are
obtained. Compared to relative calibration, this method has an advantage of obtaining absolute, rather than apparent molecular weights [Dobbin et al., (1982)]. However, its accuracy is limited to quality control and routine analysis.

3). **Universal calibration** is obtained by plotting $\log (M [\eta])$, rather than $\log M$, versus elution volume, EV, where $[\eta]$ is the intrinsic viscosity (Eq. 2.8) of the polymer measured for the same temperature/solvent system as for the mobile phase [Grubisic and Benoit, (1968); Grubisic et al., (1996)]. In this manner, all polymers, regardless of their chemical composition or conformation, will fall on the same calibration curve when chromatographed under identical conditions. This is a consequence of proportionality of the term $M[\eta]$ to the hydrodynamic volume (HV) of a polymer in solution. Because SEC separates on the basis of hydrodynamic volume or size, and not necessarily molecular weight, all polymer molecules of the same HV, irrespective of their composition, will elute at the same EV. To use this approach, a universal calibration curve is first constructed using narrow standards, similar to relative calibration. Additionally, intrinsic viscosities should be measured in order to build the plot of $\log (M [\eta])$ vs. EV. Alternatively, Mark-Houwink coefficients $K$ and $\alpha$ (Eq. 2.9.), if known, can be used. Consequently, the chromatograms of the broad polymer samples should contain the viscosity data, so the universal calibration curve can be applied. That can be achieved by using a viscosity detector, or by using Mark-Houwink parameters from the literature [Brandrup and Immergut, (1989)].

The use of an on-line viscometer allows obtaining additional information on polymer molecular architecture – branching. It is known that macromolecules that contain long-chain branches (LCB) occupy less space in dilute solutions than linear molecules of the same molecular weight [Scholte, (1982)].
Figure 2.18 Viscosity fit as a tool for LCB characterisation (LDPE)

The size of a polymer molecule in dilute solution is usually represented by mean-square radius of gyration, \( <S^2> \). Factor \( g \) was introduced to characterise the ‘shrinkage’ of a molecule due to branching:

\[
g = \frac{\langle S^2 \rangle_{br}}{\langle S^2 \rangle_{lin}} \quad \cdots \quad (2.11)
\]

Intrinsic viscosity depends on the effective hydrodynamic radius, \( R \), and another factor of LCB can be introduced:

\[
g' = \frac{[\eta]_{br}}{[\eta]_{lin}} = \frac{R^3_{br}}{R^3_{lin}} = g^{3/2} \quad \cdots \quad (2.12)
\]

For practical reasons, \( g' \) is usually called a branching index. It can be calculated as a ratio of experimentally determined \([\eta]\) and a theoretical (linear) fit (dashed line in Fig. 2.18). To smooth the noisy data at low and high MW ends of the plot, experimental \([\eta]\) can be fitted to a polynomial before taking the ratio. The resulting \( g' \) curve in Figure 2.18 shows that amount of LCB increases (\( g' \) decreases) with increasing molecular weight. For the comparison between grades, an average value of the \( g' \) can be taken.
Another useful parameter can be calculated from the intrinsic viscosity data, usually represented as branching frequency, \( \lambda \), which is the number of branches per unit of MW. As it is a small number, it can be multiplied by \( 1,000 \times M_{\text{monomer}} \) to obtain the branching frequency per thousand C-atoms. Value of \( \lambda \) is obtained from GPC- \([\eta]\) chromatograms by fitting the experimental data to the Zimm-Stockmayer equation [Zimm and Stockmayer, (1949)]:

\[
\log[\eta] = \log K + \alpha \log M_i - \frac{\varepsilon}{2} \log \left[ \frac{\lambda M_i}{c_1} \right] + \sqrt{1 + \frac{\lambda M_i}{c_2}} \quad \ldots \quad (2.13)
\]

where \( \varepsilon \) is a shape factor (0.9 for LDPE) and \( c_1 = 9\pi/4 \) and \( c_2 = 7 \) for the three-branch point. The described procedure is not only useful for obtaining the information on branching, but also as a correction tool for obtaining the accurate MW results for branched polymer samples [Waters, (1999)]. The validity of the procedure was tested in a study of MW and gyration index of an LDPE standard SRM 1476 [NBS, (1969)] and a satisfactory accuracy was found [Beer et al., (1999)].

Another method that utilises separation based on hydrodynamic volume is field flow fractionation (FFF) assisted with multi-angle light scattering (MALS) detection [White, (1997)]. The technique relies on a combination of field-driven and diffusive transport mechanisms, and it allows separation of macromolecules with MW in the range \( 10^3 - 10^{15} \) g/mol and particles of 5nm – 100 \( \mu \)m. This is an advantage compared to SEC, where selective permeation in a column is limited to approx. \( 10^7 \) g/mol, and for many polymers it is not possible to find an appropriate solvent. The instrumentation is still under development and many problems with resolution and accuracy are to be solved.

The only method that allows determination of MWD of a polymer without prior fractionation is Matrix-Assisted Laser Desorption/Ionisation - Time of Flight Mass Spectroscopy (MALDI-TOF MS) [Creel, (1993)]. The apparatus is shown in Figure 2.19:
A small amount of polymer sample is loaded on a matrix of a UV-absorbing compound irradiated by a UV laser. Excited by irradiation, polymer molecules are ionised and desorbed from the matrix. Polymer ions then travel driven by electric field towards a detector. Smaller ions reach the detector sooner than the larger ones. The result is a discontinuous plot of the MWD of the sample. The advantage of the method compared to SEC is that it does not require calibration with polymer standards, since the molecular weights are determined by mass spectrometry. The major problem in application is degradation of macromolecules of MW > 3\times 10^5 \text{ gmol}^{-1} \text{ [Guttman et al., (1997)].}

\subsection*{2.2.5 Polypropylene Blends}

The concept of combining two or more different polymers to obtain a new material system with desirable features of its components is not new. In Section 2.2.1 we could see that various olefins, such as ethylene, could be added to propylene during polymerisation; the resulting co-polymers showed qualitatively new behaviour compared to either polypropylene (PP) or polyethylene (PE). The other approach of mixing two distinguished polymers (in this example PP and PE) would lead to a physical blend, with properties of both components, as well as new properties characteristic for that blend [Paul and Barlow, (1980)]. The main difficulty of creating useful polymer blends was immiscibility or phase separation, which usually leads to poor mechanical properties. Therefore, much effort was done in research and development (R&D) for processing industry, in order to obtain compatibilisation of the components.
Basic key to understanding of polymer-polymer miscibility is thermodynamics; to obtain mixing of two components, the free energy of mixing, $\Delta G_{\text{mix}}$ must be negative (Eq. 2.14):

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0 \quad \ldots \quad (2.14)$$

The enthalpy of mixing, $\Delta H_{\text{mix}}$ is usually positive (endothermic), even for the systems of similar polymers (such as polyolefin blends). It means that the factor of entropy ($\Delta S_{\text{mix}}$) plays an important role, and since the level of disorder does not increase by much while mixing the macromolecules, it is expected for most blends to undergo phase separation [Coleman and Painter, (1997)]. At a given temperature, it is often possible to obtain a concentration range in which two polymers are miscible. In Figure 2.20, polymers A and B are miscible up to concentrations of 30% A in B, as well as 30% B in A. It is a case of partial miscibility and the boundaries are given by minima of the free energy curve vs. concentration (usually volume fraction, $\phi$).

Figure 2.20  Concentration range of miscibility for the blends of polymers A and B

Mathematically, this can be expressed by Equation 2.15 [Paul and Barlow, (1980)]:

$$\left[ \frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi_2^2} \right]_{T, p} > 0 \quad \ldots \quad (2.15)$$

where $\phi$ stands for volume fraction.

The composition range over which the two polymers phase-separate is not constant. It can change with temperature. For some polymer pairs that range gets smaller as temperature increases. Eventually, if such a pair is heated high enough, that range of immiscibility will disappear. The temperature at which this happens is called the upper critical solution temperature (UCST). The Figure 2.21a shows this. The inverse parabola is the boundary
between those temperatures and compositions at which there is one phase, and those at which there is phase separation. For some polymer pairs the range of immiscibility decreases with decreasing temperature. Consequently, the temperature at which the range of immiscibility disappears is called the lower critical solution temperature or LCST (Fig. 2.21b).

![Phase diagrams](image)

**Figure 2.21** Phase diagrams with upper (a) and lower (b) critical solution temperatures

The final morphology of a blend depends not only on thermodynamics, but also on the way of its preparation, i.e. on rheology [Utracki, (1991)]. During mixing, one component gets dispersed into another. Which component will be a dispersed phase and which one will be the matrix depends on their concentrations (\(\phi\)) and viscosities (\(\eta\)) [Dumoulin et al., (1991)]. The region of phase inversion is given by Eq. 2.16 [Jordhamo et al., (1986)]:

\[
\frac{\phi_1}{\phi_2} = \frac{\eta_1}{\eta_2}
\]

It is also possible to obtain a co-continuous morphology or inter-penetrating network (IPN), where both components form continuous phases (matrices) simultaneously. Even if miscibility cannot be achieved, a blend can exhibit good final and processing properties. Such systems are usually called *compatible blends* and they may contain additional agents – compatibilisers, which lower the interfacial forces and allow inter-penetration. In case of PP/PE system, such agents could be ethylene-propylene co-polymers [Simonazzi and Haylock, (1995)]. Such blends, produced in reactor by Catalloy® process (Montell Inc.) are usually designated as polymer alloys, due to their excellent dispersion and compatibility [Killeen (1999)]. These new materials advance the applicability of PP,
especially in blown film manufacturing, by improving its processability without sacrifices in final properties [Paulik and Neifil, (1998)].

Another class of PP blends gained much popularity in BOPP processing, namely blends with 'hard resins' [Muke et al., (1999)]. The term comprises different low-molecular weight polymers and oligomers, also known as 'hydrocarbon resins', most important of them being hydrogenated poly-dicyclopentadiene and oligo-cyclopentadiene [Ivanov et al., (1999)]. They are both amorphous materials and, when added to PP, improve its mechanical and optical properties [Di Liello et al., (1989)], as well as lower the permeability to moisture and gases [Cimmino et al., (1994)], which is especially of interest in food packaging. Hydrogenated oligo-cyclopentadiene (HOCP) is a mixture of cis- and trans- isomers of the following structures A and B (Fig. 2.22), that have been hydrogenated after the oligomerisation [Silvestre et al., (1996)]:

\[ \text{A} \]
\[ \text{B} \]

(1,4- structure) \hspace{2cm} (1,2- structure)

Figure 2.22 Structure of oligo-cyclopentadiene

First studies of the PP/HOCP systems, performed by DSC, led to a conclusion that the components were completely miscible [Martuscelli et al., (1989)]. The single glass-transition temperature was observed, and it followed theoretical relation that describe miscible blends [Fox, (1956)] (Eq. 2.17):

\[
\frac{1}{T_g} = \frac{w(\text{iPP})}{T_g(\text{iPP})} + \frac{w(\text{HOCP})}{T_g(\text{HOCP})} \quad \ldots \quad (2.17)
\]

More detailed study by using hot-stage optical microscopy (HSOM) and wide angle X-ray scattering (WAXS) [Cimmino et al., (1993)] revealed that the blends were partially miscible. The proposed phase diagram (Fig. 2.23) showed presence of both LCST and UCST, suggesting the existence of a closed-phase loop. In other words, the iPP and HOCP are miscible at temperatures higher than 240°C and lower than 90°C, whereas phase
separation takes place in the range between these two temperatures. According to the above reference, miscibility at low temperatures (<90°C) referred to the amorphous phase.

[Copyrighted material omitted. Please consult the original thesis.]

Figure 2.23  Phase diagram, Tg and Tm for PP/HOCP blends
(Adapted from [Cimmino et al., (1993)])

Additionally, adding HOCP to PP causes:

1) a narrowing of the crystallisation window, measured by Tc – Tg;
2) a depression in the rate of crystallisation, at given Tc, and
3) a shift of the crystallisation peak to lower temperatures.

All these phenomena were assumed to inhibit the crystallisation of PP and permit the necessary conditions for the formation of smectic form of polypropylene [Cimmino, S., et al., (1991)]. A study of [Bartczak and Martuscelli, (1997)] showed further that the above phenomena influenced not only the system in quiescent state, but also during drawing and orientation, which gave the explanation for the advanced properties of resin-modified films, compared to plain PP films.
2.3 RHEOLOGY OF POLYPROPYLENE

2.3.1 Introduction to Rheology

Rheology is the science of deformation and flow of matter. It is the study of the manner in which materials respond to applied stress or strain. To control rheological properties of polymer resins means to rule the ease of their processing and mastering the quality and appearance of the plastic products, as illustrated in Fig. 2.24. This control represents the balance between final properties and ease of processing: along the line is the region of common experience. Above the line is the target of a successful product, and below the line, the ‘disaster region’. Movement towards the target may be achieved by manipulation of the polymer structure, which may itself be modified by processing history. It is thus appropriate to study rheology-structure interrelations as a mean of enhancing product quality and reducing processing costs.

[Copyrighted material omitted. Please consult the original thesis.]

Figure 2.24 Relationship between end properties and ease of processing
(Adapted from [Cogswell, (1981)])
2.3.2 Types of Deformation

Generally, three different kinds of deformation can be applied: shear, extension and compression. First two are presented by following figures that show the deformation of rectangular bars (Figures 2.25 and 2.26):

![Shear deformation of a rectangular bar](image)

Figure 2.25 Shear deformation of a rectangular bar

In simple shear, the lower surface is stationary and the upper plate is linearly displaced by an amount equal to $\delta L$. The angle of displacement, or shear, $\gamma$, can be expressed as:

$$\tan (\gamma) = \delta L / h$$

(2.18)

With small deformations, the angle of shear (in radians) is equal to the magnitude of shear strain, $\gamma$: $\tan (\gamma) = \gamma$.

Extensional deformation can be represented by simple elongation of a rectangular bar (Figure 2.26):

![Extensional deformation of a rectangular bar](image)

Figure 2.26 Extensional deformation of a rectangular bar
The initial length of a bar is \( L_0 \) and the elongated length is \( L \), where \( L = L_0 + \partial L \), with \( \partial L \) representing the increase in length. This deformation may be expressed in terms of Cauchy strain (also known as engineering strain), \( \varepsilon_c \):

\[
\varepsilon_c = \frac{\partial L}{L_0} = \frac{(L - L_0)}{L_0} = \frac{L}{L_0} - 1
\]

or Hencky strain (also called true strain), \( \varepsilon_h \) or simply \( \varepsilon \), which is determined by evaluating an integral from \( L_0 \) to \( L \):

\[
\varepsilon = \int_{L_0}^{L} \frac{dL}{L} = \ln \frac{L}{L_0}
\]

Cauchy and Hencky strains are both zero when the material is unstrained and approximately equal at small strains. At higher strains, the use of Hencky strain is more convenient to use, and it is related to \( \varepsilon_c \) (Eq. 2.23):

\[
\varepsilon = \ln \left( 1 + \varepsilon_c \right)
\]

### 2.3.3 Polymer melts in steady shear flow

Fluids can be studied by subjecting them to continuous shearing at a constant rate. Ideally, this can be accomplished using two parallel plates with a fluid in the gap between them (Fig. 2.27). The lower plate is fixed and the top plate moves at a constant velocity \( v \), which is an incremental change in position obtained in a small time, divided by that time: \( v = \partial L/\partial t \).

Force acting per unit area on the upper plate is resulting in a shear stress, \( \sigma \). The rate of strain, or shear rate, is defined as:

\[
\dot{\gamma} = \frac{d\gamma}{dt} = \frac{d}{dt} \left( \frac{\partial L}{h} \right) = \frac{v}{h}
\]

33
From the Eq. 2.22 one can see that the unit for shear rate is s\(^{-1}\). Simple shear flow is also called viscometric flow. Viscosity, as a viscometric function is defined as:

\[
\eta(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}} \quad \ldots \quad (2.23)
\]

If \(\eta(\dot{\gamma})\) is constant, the fluid is regarded as Newtonian. Polymer melts are shear thinning or pseudo-plastic fluids, which means that they show negative deviation from the Newtonian behaviour, i.e. the apparent viscosity decreases with increasing shear rate. Typical shear thinning behaviour is presented in a plot of viscosity versus shear rate (Figure 2.28):

The plot in Figure 2.28 is usually called a flow curve. A typical flow curve of a polymer melt is represented by a full line, which tends to a plateau at low shear rates:

\[
\lim_{\dot{\gamma} \to 0} \left( \eta(\dot{\gamma}) \right) = \eta_0 \quad \ldots \quad (2.24)
\]
Parameter $\eta_0$ is known as zero shear viscosity. In special cases, usually in polymer solutions, viscosity function may tend to another plateau at high shear rates, described by a value of infinite shear viscosity, $\eta_\infty$. The infinite shear region of the flow curve in Fig. 2.28 is given by a broken line and it is rarely observed in polymer melts, probably due to problems associated with measurements of melt viscosity at high shear rates [Nielsen, (1997)].

2.3.4 Viscoelastic behaviour of polymer melts

Polymer melts, as well as other non-Newtonian fluids, respond to deformation in a way that cannot be described by viscosity function only. If normal stresses are different from zero, a material exhibits elasticity. Such fluids are called viscoelastic, and their behaviour is somewhere between elastic, or solid-like, and viscous, or liquid-like. A difference between viscous, elastic and viscoelastic response to deformation can be observed in a step strain experiment [Steffe, (1996)]. The sample is given an instantaneous strain and the stress required to maintain the deformation is observed as a function of time. This experiment is commonly referred to as ‘stress relaxation’ test and it may be conducted in
shear, uniaxial extension and uniaxial compression. A wide range of behaviour may be observed (Figure 2.29):

![Diagram showing types of rheological behaviour in step strain experiment](image)

**Figure 2.29** Types of rheological behaviour in step strain experiment

No relaxation would be observed in a purely elastic material, while a purely viscous fluid would relax instantaneously. Viscoelastic materials relax gradually, with the end point that depends on the material tested: in viscoelastic solids, stress would decay to an equilibrium value ($\sigma_0$). In viscoelastic liquids, the stress will eventually decay to zero, i.e. until there are no residual stresses.

The relaxation data are usually presented in terms of relaxation modulus, $G(t)$ (Eq. 2.25):

$$G(t) = \frac{\sigma}{\gamma_{\text{const}}} \quad \ldots \quad (2.25)$$

Eq. 2.26 describes gradual decay of stress from initial stress $\sigma_0$ to zero. It defines $\lambda$ as the time it takes for the stress to decay to $1/e$ (approx. 36.8%) of its initial value:

$$\sigma = f(t) = \sigma_0 e^{-\frac{t}{\lambda}} \quad \ldots \quad (2.26)$$
For a real system, the continuous relaxation function, $G(t)$ can be expressed through a spectrum of relaxation times (symbol $\tau$ is accepted, rather than $\lambda$):

$$
G(t) = \int_{0}^{\infty} \frac{h(\tau)}{\tau} e^{-\frac{t}{\tau}} d\tau \quad \ldots \quad (2.27)
$$

### 2.3.5 Temperature Dependence of Melt Rheology

Temperature has a significant effect on the rheological properties of polymer melts [Mavridis and Shroff, (1992)]. Quantitative knowledge on this dependence is important for several reasons. First, it allows estimating the viscosity at different temperatures, rather than conducting the actual measurements. Second, it provides a tool for polymer characterisation [Harrell and Nakajima, (1984)]. The temperature effects need also to be modelled appropriately for all computer simulation work. Finally, it is of great importance to fundamental studies on the mechanism of flow.

The influence of temperature on viscosity was studied on Newtonian fluids first. Thus, when applying the Arrhenius-type equation to polymer melts, the Newtonian or zero shear viscosity can be used [Rheometrics, (1992)]:

$$
\eta_0(T) = Ke^{\frac{-E_a}{RT}} \quad \ldots \quad (2.28)
$$

The flow activation energy, $E_a$, can be determined from a logarithmic plot of $\eta_0$ vs. $1/T$, where the slope is equal to $-E_a/R$ and $R$ is the universal gas constant. It is a measure of the sensitivity of the zero shear viscosity of a material to its temperature. It was found for most polymer melts that the same relationship applies in the whole range of viscosity/shear rate data. For that reason, they can be referred to as ‘thermorheologically simple’ materials [Markovitz, (1975)]. Since the influence of temperature is in the same direction as the effect of shear rate or frequency on viscosity, the rheological data determined at one temperature can be shifted horizontally and superimposed with data collected at another temperature. This allows constructing the *master-curves*, usually with dynamic shear data (Figure 2.30).
In Figure 2.30 dynamic shear data ($\eta^*/\alpha_T, G'$) are plotted against $\alpha_T \omega$, where $\alpha_T$ is the shift factor. The complex viscosity data collected at temperature higher than the reference temperature are shifted to the right and the corresponding moduli are shifted to the left. In that manner, building a master-curve, or time-temperature superposition (TTS), allows extending the frequency range [Haugh, (1959); Kao, (1995)].

The Arrhenius equation (2.28) can be re-written to describe the temperature dependence of shift factors (Eq. 2.29):

$$a_T = Ke^{-\frac{E_a}{R(T-T_{ref})}}$$

In the temperature range from $T_g$ to $T_g+100^\circ C$, where $T_g$ is the glass-transition temperature, the Williams-Landel-Ferry (WLF) equation provides a better fit [Ferry, (1980)]:

$$\log a_T = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}}$$
The principle of time-temperature superposition can be applied to other linear viscoelastic properties, as well, since it is based on the temperature dependence of relaxation times:

\[ \tau(T) = a_T \tau(T_{ref}) \]  

\[ G_N^0(T) = G_N^0(T_{ref}) / b_T \]

If the horizontal shifting doesn’t yield satisfactory results, the vertical shift factor, \( b_T \) (Eq. 2.32) has to be applied. This is the case with branched polymers, such as LDPE [Verser and Maxwell, (1970)] and immiscible blends [Dumoulin, et al., (1991)], so these systems are not regarded as ‘thermorheologically simple’.

### 2.3.6 Extensional Viscosity of Polymer Melts

Molten polymers undergo extensional flow in many important industrial processes, such as thermoforming [Lau, (1999)], blow moulding [Pagelhof, et al., (1994)] and film blowing [Bhattacharya, (1999)]. The nature of the simple extensional (tensile) deformation was shown in Figure 2.26 and the strain (true or Hencky strain) was defined by Eq. 2.20. In extensional flow, time-dependent or transient rheological behaviour is usually measured, because the sample often breaks before reaching the steady state [Meissner, (1985)]. The most important parameter in transient or start-up flow, transient extensional viscosity, is defined as tensile stress growth coefficient [Dealy, (1995)]:

\[ \eta_E^+(t, \dot{\varepsilon}) = \sigma_E / \dot{\varepsilon} \]  

The steady state extensional or tensile viscosity is defined as:

\[ \eta_E(\dot{\varepsilon}) = \lim_{t \to \infty} \left[ \eta_E^+(t, \dot{\varepsilon}) \right] \]

If the material of interest tends toward linear viscoelastic behaviour at small strain rates, the following relationships are valid:
\[
\lim_{\dot{\varepsilon} \to 0} \eta^+_{\varepsilon}(t, \dot{\varepsilon}) = \eta^+_{\varepsilon}(t) = 3\eta^+(t) \quad \ldots \quad (2.35)
\]

\[
\lim_{\varepsilon \to 0} \eta^+_{\varepsilon}(\varepsilon) = 3\eta_0 \quad \ldots \quad (2.36)
\]

Relationships between shear and extensional viscosities (Eqs. 2.35 – 2.36) were of great importance in developing the methods for extensional measurements, providing a reference for testing their accuracy. The three-fold zero shear viscosity is usually referred to as Trouton viscosity [Trouton, (1906)].

When a material is subjected to a biaxial strain, \( \varepsilon_B \), similar equations can be developed [Dealy, (1995)]. In the linear viscoelastic regions (at very low strain rates, \( \varepsilon_B \)), biaxial extensional viscosity is defined as:

\[
\lim_{\dot{\varepsilon}_B \to 0} \eta^+_{\varepsilon_B}(\dot{\varepsilon}_B) = 6\eta_0 \quad \ldots \quad (2.37)
\]
2.3.7 Measurements of Melt Extensional Viscosity

Several techniques were employed in extensional viscosity measurements:

1) *Melt spinning* technique was utilised by Meissner to develop the Rheotens melt strength tester [Meissner, (1971)], commercialised by Goettfert. The experimental set-up and the typical results are shown in Figure 2.31:

![Figure 2.31 Rheotens melt strength measurements: experimental set-up (left) and typical results (right)](image)

A polymer strand is continuously extruded through a die. It is stretched by a pair of counter-rotating nip-rollers placed on a balance beam (force measurement). The Rheotens curves are usually plotted as force vs. time, linear velocity or draw ratio. The force tends to a plateau at high draw ratios and it is taken as a value of melt strength (in centinewtons, cN). There are many difficulties in obtaining the true extensional viscosity from the Rheotens test, due to the non-uniform drawing and non-isothermal conditions [Muke, *et al.*, (2001)]. However, the melt strength data were proved to be very useful as a qualitative measure of relevant extensional properties (melt strength, drawability, onset of draw resonance) in polymer processing [Bennat and Wagner, (1998)].

2) *Converging flow* in a capillary die is a combination of shear and extensional deformation. As a consequence of materials elasticity, a pressure drop greater than zero can be measured during the extrusion through an orifice (zero-length) die [Bagley, (1957)]. Cogswell pioneered the use of the capillary data to extract the extensional properties, by using the following equations [Cogswell, (1978)]:

41
\[
\eta_E = \frac{9}{32} \frac{(n+1)^2}{\eta} \left( \frac{\Delta P_0}{\gamma} \right)^2 \quad \cdots \quad (2.38)
\]

\[
\sigma_E = \frac{3}{8} (n+1) \Delta P_0 \quad \cdots \quad (2.39)
\]

\[
\dot{\varepsilon} = \frac{\sigma_E}{\eta_E} \quad \cdots \quad (2.40)
\]

The above equations were rigorously tested and proved to be satisfactory for practical determination of steady state extensional viscosity [Padmanabhan and Macosko, (1997); Binding (1998)] improved the equations assuming the power-law dependence of extensional stress on strain rate. The huge interest of polymer engineers in utilising capillary flow for both shear and extensional viscosity measurement led to the development of Advanced Capillary Extrusion Rheometer (ACER™, Rheometrics), which allows lubricated skin-core converging co-extrusion [Pendse and Collier, (1995)]. Equipped with specially designed hyperbolic dies, the instrument can operate at strain rates in the range of 0.1 – 500 s\(^{-1}\) [Rheometrics, (2000-2001)].

3) **Lubricated squeeze flow** is a phenomenon that provides an indirect measurement of biaxial extensional viscosity [Kompani and Venerus, (2000)]. Equibiaxial extension is generated by applying downward force on a molten sample held between two parallel plates. The plates are lubricated in order to avoid shearing. The technique is easy to use and it can provide useful experimental data. However, the maximum available strains and strain rates are limited (\(\dot{\varepsilon} < 1\text{s}^{-1}\)), which prevents the use of the method in evaluating polymer behaviour in processes where strong deformations and strain rates are employed.

4) **Direct measurements** of extensional viscosity have been the ultimate goal of many rheologists in the last few decades [Bhattacharya, (1997)]. The basic idea behind construction of rheometers that can measure transient extensional viscosity was to provide an effective clamping of the sample and its uniform stretching. That can be achieved by two different techniques: 1) translating clamps, used in the Muenstedt- type rheometer
and 2) counter-rotating clamps, applied in the Meissner-type rheometer [Meissner, (1972)].

In the Munstedt-type rheometer, the polymer sample is suspended vertically in an oil bath as shown in Figure 2.32. One sample end is fixed to a load cell, where the force measurements are taken. The other end is fixed to a thin metal tape, which is rolled upwards by a servomotor, providing extension to the sample. Samples for this instrument are small and easy to produce. A commercial version of this rheometer appeared in 1981 as the Rheometrics Extensional Rheometer – RER [Sammut, P. and Gendron, R., (2001)].

[Copyrighted material omitted. Please consult the original thesis.]

Figure 2.32  Schematic drawing of the Munstedt-type extensional rheometer
(Adapted from [Muenstedt, H., (1979)])

The main disadvantage of this type of rheometer is the maximum strain (< 4) that is limited by the height of the oil bath. Furthermore, there are zero flow conditions at both ends of the sample. This leads to necking, which is the reason for non-uniform drawing and early failure of the sample [Meissner, (1985)].

Meissner-type rheometer is based on the constant length of the sample that is extended between two pairs of rotary clamps (Figure 2.33 left). Further developments made use of conveyor belts (Fig. 2.33 right), which are applied in the commercial Rheometrics Melt Extensional rheometer, RME [Meissner and Hostettler, (1994)].
Figure 2.33 Stretching devices in Meissner-type rheometers: rotary clamps (left) and conveyor belts (right)

There are also disadvantages of Meissner-type rheometers; major of them is the slippage at the clamps, which causes the error in strain rates [Schulze, et al., (2001)]. The design can be simplified by removing one pair of rotary clamps and attaching a Linear Voltage Displacement Transducer (LVDT) to that sample end [Laun and Muenstedt, (1978)]. Based on this concept, the first extensional rheometer in Australia was designed and built at RMIT University [Field and Bhattacharya, 1996], schematically shown in Figure 2.34.

Figure 2.34 Laun-Munstedt modified Meissner type RMIT Extensional Rheometer

A great deal of melt extensional viscosity measurements was achieved since the RME was introduced. In the RME a molten polymer sample is uniaxially elongated by two pairs of
rotating belts. The corresponding tensile force acting on the sample is measured by a force transducer. During the measurement, the sample is supported by a cushion of nitrogen or air, which are also used for heating. Tests are performed at constant strain rates, \( \dot{\varepsilon}_0 \), given by the velocity, \( v \) of the conveyor belts and the effective distance between the clamps, \( L_0 \):

\[
\dot{\varepsilon}_0 = 2 \frac{v}{L_0} \quad \ldots \quad (2.41)
\]

The extensional viscosity is calculated from the tensile force \( F(t) \), the initial sample cross-section area \( A_0 \) and the nominal strain rate \( \varepsilon \), as:

\[
\eta_E(t) = \frac{F(t)}{A_0} \frac{e^{\dot{\varepsilon}_0 t}}{\dot{\varepsilon}_0} \quad \ldots \quad (2.42)
\]

The maximum Hencky strain accessible is 7, which corresponds to a stretch ratio of about 1100. The major drawback of the RME is the deviation from the nominal strain rate during the measurement [Wassner, (1998)]. The phenomenon was well documented by Schweitzer, who proposed the possible explanations [Schweizer, (2000)]: experimental set-up errors, flow within the clamps, inhomogeneous samples and non-uniform cross-sectional area along the sample. If the appropriate corrections are applied for the above observations, RME data are reproducible with the results obtained by Munstedt-type rheometer (RER) [Sammut and Gendron, (2001)], as shown in Figure 2.35.

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2.4 RELATIONSHIPS BETWEEN STRUCTURE AND RHEOLOGY OF POLYPROPYLENE

2.4.1 Significance of rheology ↔ structure relationships

The application of rheological methods to gain information about molecular characteristics of polymers is widely accepted in both academic and industrial research today [Gahleitner, (1999)]. There are two major reasons for the constantly increasing interest in that area: 1) direct methods for MWD determination (GPC-SEC, Section 2.2.4) are considered time consuming, limited by polymer solubility and not suitable for on-line monitoring in industrial processes and 2) sensitivity of GPC-SEC to high molecular weights is usually considered as unsatisfactory [Wood-Adams and Dealy, (1996)].
A multitude of research work has been published dealing with the problem of interconversion between rheological data and MWD of polymers. These papers can be split into two categories:

1) Development of empirical or semi-theoretical correlations between singular rheological parameters (such as zero-shear viscosity, cross-over modulus etc.) and MW averages (such as Mw) or polydispersity (Mw/Mn).

2) Full-scale interconversions between rheological functions [such as relaxation modulus, G(t)] and molecular weight distribution.

In regards to what rheological techniques were utilised, the publications comprise research in the following areas:

- Correlations between the steady shear data (viscosity function) and MWD;
- Interconversions between viscoelastic functions (such as dynamic moduli, relaxation modulus, relaxation spectra) and MWD and
- Effect of molecular weight distribution on extensional properties of polymer melts.

In addition to the above topics, the effect of long-chain branching on polymer rheology was thoroughly studied (Section 2.4.4).

2.4.2 Viscosity function related to molecular weight distribution

Viscosity of polymer melts is a function of shear rate that tends to a plateau at low shear rates (Eq. 2.24). Zero shear viscosity, \( \eta_0 \), being a fundamental property of polymer melts, has been the subject of intensive studies aimed at elucidating its relationship with the polymeric structure [Ferry, (1980)]. A double regime of \( \eta_0 \) was found, depending on the molecular weight. At low molecular weights the relationship of viscosity with MW is substantially linear [Nielsen, (1997)]. At MW higher than a critical value, \( M_c \), the relationship was found to follow the power law:

\[
\eta_0 \propto M^{3.4}
\]  \hspace{1cm} \text{(2.43)}

The 3.4 power law was first proposed in 1951 by Fox and Flory [Fox and Flory, (1951)] on the basis on measurements on narrow distribution fractions of polystyrene and
polyisobutylene (PIB). The transition between two regimes occurs at $M = M_e$, which was found to be equal to about $2M_c$, where $M_c$ is the average MW between entanglements (Figure 2.36). The nature of the entanglements has often been discussed and criticised; it is convenient to consider them as being time-fluctuating and de-localised [Locati et al., (1999)].

![Figure 2.36  MW dependence of zero shear viscosity](image)

The number of entanglements per molecule, $n_e$ can be calculated as:

$$n_e = \left( \frac{M}{M_e} - 1 \right)^{\frac{1}{t}}$$

(2.44)

The above relationships are valid for monodisperse systems. In case of polydisperse polymers, a weight average molecular weight, $M_w$, usually substitutes $M$ in Eq. 2.43 [Gahleitner, et al., (2000)]. Values of power-law index in Eq. 2.43 different from 3.4 can be found in literature, such as 5.7 for commercial PS grades [Montfort, et al., (1986)]. For most linear polyolefins, values in the range of 3.2 to 3.6 are acceptable [Steeman, (1998)]. The relationship similar to Eq. 2.43 was found to be applicable for viscosity-average molecular weight, $M_v$ [Minoshima, et al., (1980)]. For a series of commercial PP grades, Steeman also found that the zero shear viscosity depends, besides on the weight average molecular weight, also on both polydispersity indices, $M_w/M_n$ and $M_z/M_w$:
\[ \eta_0 = KM_w^\alpha \left( \frac{M_w}{M_n} \right)^b \left( \frac{M_\ell}{M_w} \right)^c \]  \hspace{1cm} \ldots \quad (2.45)

It is generally accepted that polydispersity is the major factor that influences the shape of the viscosity flow curve [Tzoganakis, et al., (1989)]. That can be represented by plotting the reduced viscosity, \( \eta/\eta_0 \), as a function of \( \eta_0 \gamma \) [Vinogradov and Malkin, , (1966)].

On such plots, \( \eta/\eta_0 \) falls of more rapidly with \( \eta_0 \gamma \) for the samples with broader MWD [Minoshima, (1980)]. For polypropylene, Dumoulin found that index \( n \) in the power-law model for viscosity [(Bhattacharya, (1997)], follows quite well the polydispersity, \( M_w/M_n \) [Dumoulin, et al., (1993)]. It was found by Goettfert [Goettfert, et al., (1995)] that sensitivity of power-law index \( n \) on polydispersity is rather low. The common experience that polymer grades with broader distribution are more shear thinning is a consequence of reducing the shear rate when shear thinning starts with increasing polydispersity. Goettfert derived the power-law in order to derive a shape factor, \( sf \) that correlates better to \( M_w/M_n \) than the other parameters from steady shear measurements [Goettfert, (1995)]:

\[ sf = \frac{\left[ 1 + \left( \frac{n-1}{n} \right)^{\frac{n-2}{2}} \right]^{\frac{3}{2}}}{k(n^2 - 3n + 2)^\gamma} \]  \hspace{1cm} \ldots \quad (2.46)

Numerical procedures developed for viscosity function – MWD transform are based on the inversion of blending law [Bersted and Slees, (1977); Malkin and Teishev, (1991)], given by Eq. 2.47:

\[ \eta^{1/\alpha} = \sum w_i \eta_i^{1/\alpha} \]  \hspace{1cm} \ldots \quad (2.47)

where \( \alpha \) is the exponent associated with the dependence of viscosity on molecular weight (generally taken to be equal to 3.4, as in Eq. 2.43). In Eq. 2.47 \( w_i \) is the weight fraction of the \( i^{\text{th}} \) component and \( \eta_i \) is its viscosity. The basic assumptions of this approach are: 1) The viscosity is constant until the shear rate approaches a critical value (\( \dot{\gamma}_c \)) above which the fluid undergoes non-Newtonian flow; 2) The mixing rule (Eq. 2.47) is independent of
composition, $M_w$ and $\gamma_c$. The procedure involves definition of dimensionless forms of the viscosity $[Y = (\eta / \eta_0)^{1/\alpha}]$, rate of deformation $[X = (\gamma / \gamma^c)^{\mu/\alpha}]$ and molecular weight $(m = M / M_w)$, related by the Eq. 2.48 [Tuminello, et al., (1993)]:

$$Y(X) = \int_{0}^{1/X} mf(m)dm + \frac{1}{X} \int_{1/X}^{\infty} f(m)dm \quad \ldots \quad (2.48)$$

The MWD function can be extracted from Eq. 2.48 as:

$$f(m) = -\frac{1}{\nu^2m} \left(\frac{\eta}{\eta_0}\right)^{1/\alpha} \left(\frac{\gamma}{\gamma^c}\right)^{1/\alpha} \left[\alpha^2 \frac{d^2 \ln \eta}{\ln \gamma^2} + \nu \frac{d \ln \eta}{\ln \gamma} + \left(\frac{d \ln \eta}{\ln \gamma}\right)^2\right] \quad \ldots \quad (2.49)$$

where $\nu$ is the slope of the viscosity function in the power law region. Frequency, $\omega$ can replace shear rate in Eq. 2.49 to allow use of dynamic data $\{\eta^*(\omega)\}$ [Wood-Adams and Dealy, (1996)]. Although numerical analysis shows the validity of the transformation procedure [Liu, et al., (1998)], the nature of the experimental data (level of noise in steady shear or limited frequency in dynamic shear measurements) was a limiting factor for its wider application.

### 2.4.3 MWD related to viscoelastic properties

There have been numerous attempts to determine the MWD of polymers from the measured rheological data, which were based on either phenomenological or theoretical concepts. The most popular theoretical concept is the mixing rule, proposed independently by Des Cloizeaux [Des Cloizeaux, (1988)] and Tsenoglou [Tsenoglou, (1987), (1991)]. From a molecular point of view, polydisperse polymers are characterised by their MWD, represented as a function $W(M)$. The characteristic material function of linear viscoelasticity is the relaxation modulus, $G(t)$. Following the concept of ‘double reptation’ [Des Cloizeaux, (1988)], the above authors developed an equation that represents the quadratic mixing rule (Eq. 2.50):
\[ G(t) = G_N^0 \left[ \int_0^\infty F^2 (M,t) W(M) dM \right]^2 \]  

(2.50)

where \( G_N^0 \) is the plateau modulus and \( F(M, t) \) is a stress relaxation function, usually denoted as a kernel function. The key assumptions leading to Eq. 2.50 are that the polymer chains move by reptation, that chain entanglements support the stress and that the stress at any time \( t \) following a step strain is proportional to the fraction of the entanglements at \( t=0 \) that have not yet been lost by reptation of involved chains [Wasserman and Graessley, (1996)]. The plateau modulus, \( G_N^0 \), is related to the molecular weight between entanglements, \( M_e \): 

\[ G_N^0 = \rho RT / M_e \]  

(2.51)

In Eq. 2.51 \( \rho \) is the melt density at the temperature of measurement, \( T \) (K) and \( R \) is the universal gas constant, \( R = 8.314 \text{ J mol}^{-1}\text{K}^{-1} \). The Eq. 2.50 was initially derived for a case of monodisperse polymers and many authors have evaluated the use of the model for polydisperse polymer melts [Leonardi, et al., (2000)]. The choice of the kernel function, \( F(M, t) \) is very important for the accuracy of the results. The most important kernel functions are known as: -Tuminello kernel (step function); -the single exponential kernel; -the Doi kernel; -the BSW kernel and -Des Cloizeaux kernel. The above functions are listed and elaborated in many references, eg. [Thimm, et al., (2000)]. It was shown [Maier, et al., (1998)] that the single exponential kernel (Eq. 2.52) fits the experimental data best, in spite of its simplicity. It was also employed in the software package commercialised by Rheometrics [Franck, A.J.P., et al., (1998)].

\[ F(t,M) = e^{\frac{t}{\tau(M)}} \]  

(2.52)

In Eq. 2.52, \( \tau \) (relaxation time) is related to \( M \) as:

\[ \tau = k M^\alpha \]  

(2.53)

The Eq. 2.53 represents the scaling of the relaxation time spectra to molecular weights. Constants \( k \) and \( \alpha \) can be determined experimentally [Maier, D., (1998)]. Rather than
quadratic mixing rule (Eq. 2.50), a generalised mixing rule (Eq. 2.54) can be employed [Anderssen and Mead, (1998)]:

\[
G(t) = G_N 0 \left[ \int_{m_i}^{\infty} \frac{1}{m} \frac{w(m)}{m} dm' \right]^\beta \]

With the generalised mixing parameter, \( \beta = 2 \), Eq. 2.54 reduces to the quadratic mixing rule, Eq. 2.50. For different polymers, values greater than 2 were found, for instance \( \beta \approx 3.84 \) for PS, 3.2 for PP and 3.3 for polymethyl-methacrylate (PMMA) [Thimm, et al., (1999)].

The most common approach to the calculation of MWD from the viscoelastic data is extracting the relaxation functions from the dynamic moduli, \( G' \) and \( G'' \), which are related to the relaxation time spectra by Eqs. 2.55 a and b, based on the generalised Maxwell model:

\[
G'(\omega) = \int_0^\infty h(\tau) \frac{(\omega \tau)^2}{\tau + (\omega \tau)^2} d\tau \quad \ldots \quad (2.55a)
\]

\[
G''(\omega) = \int_0^\infty h(\tau) \frac{\omega \tau}{\tau + (\omega \tau)^2} d\tau \quad \ldots \quad (2.55b)
\]

The estimation of the relaxation time spectra, \( h(\tau) \) from the dynamic moduli is an ill-posed inverse problem, which can be solved by using Tikhonov regularisation technique [Honerkamp and Weese, , (1993)]. The stress relaxation modulus, \( G(t) \) can be easily calculated from \( h(\tau) \) by using Eq. 2.27. To estimate the MWD from the relaxation modulus, another ill-posed problem should be solved, i.e. inversion of Eq. 2.50. To avoid the second ill-posed problem, Thimm et al. developed an analytical relationship between relaxation time spectra and molecular weight distribution [Thimm, et al., (1999)]:

\[
w(m) = \frac{1}{\beta} \frac{\alpha^{1/\beta}}{G_N^{\alpha^{1/\beta}}} \left[ \int_{m}^{\infty} \frac{h(m')}{m'} dm' \right]^{\frac{1}{\beta - 1}} \quad \ldots \quad (2.56)
\]
To utilise the Eq. 2.56, the relaxation time spectra, $h(\tau)$ must be estimated from the dynamic moduli by inversion of Eqs. 2.55 a and b and then transformed into molecular weight relaxation function, $\tilde{h}(m)$ using the scaling relation, Eq. 2.53. In addition, the distribution and relaxation functions were normalised, such that:

$$\int_{m_0}^{\infty} \frac{w(m)}{m} \, dm = 1$$

$$\cdots \quad (2.57)$$

and

$$\int_{\tau_s}^{\infty} \frac{h(\tau)}{\tau} \, d\tau = G_N^{0}$$

$$\cdots \quad (2.58)$$

In the above equations, $\alpha$ is the MW scaling index $\approx 3.4$, $\beta$ is the generalized mixing parameter and $m = M / M_0$, where $M_0$ is the monomer molecular weight. The determination of plateau modulus, $G_N^{0}$ limits the accuracy of the above transformations when applied to semi-crystalline polymers, such as PP, because the dynamic moduli cannot be measured in the plateau frequency region [Eckstein, et al., (1998)].

Although theoretically established, the methods for MWD calculations from the viscoelastic data are still imperfect due to the complex mathematical transformations and experimental limitations. Therefore, many authors attempted to develop empirical procedures that can utilise the available data. Eggen and Bryntesen made use of the multivariate analysis to transform rheological shear data into MWD [Eggen, S. and Bryntesen, H., (2000)]. Giudici et al. developed a neural network system that can ‘learn’ how to transform dynamic moduli into MWD, on the basis of the previous experimental inputs [Giudici, R., et al., (2000)].

For many practical purposes, especially in the industrial rheology and quality control (QC), obtaining the complete MWD curve of a polymer is not always a goal. Finding more or less simple correlations between rheological properties and structural parameters (such as $\eta_0$ dependence on Mw, Eq. 2.43) was especially welcomed by polymer processors in the
past two decades. The milestone for that work was grounded by Zeichner and Patel, who defined the rheological polydispersity index, \( RPI \) [Zeichner and Patel, (1981)]:

\[
RPI = 10^5 \text{ [Pa]} / G_C
\]  \( \ldots \)  \( (2.59) \)

Where \( G_C \) is the value of modulus at the cross-over frequency, \( G_C = G' (\omega_c) = G'' (\omega_c) \). They found an excellent correlation between RPI and Mw/Mn for peroxo-degraded PP grades. Shang optimised the experimental conditions for standard determination of RPI for commercial PP samples [Shang, S.W., (1993)]. Although criticised [Chambon, F., (1995)], the technique sustained popularity and it’s being constantly adjusted [Bafna, S., (1997)]. Another useful parameter, called the ‘modulus separation index’, was proposed more recently by Yoo [Yoo, H.J., (1993)]. From a frequency sweep data, the distance between \( G' \) and \( G'' \) curves is measured at a constant modulus value, namely 1000 or 500 Pa:

\[
Modsep = \omega' / \omega''
\]  \( \ldots \)  \( (2.60) \)

where \( \omega' \) is the frequency at which \( G' = 1000 \) or 500 Pa and \( \omega'' = \omega \) (\( G'' = 1000 \) or 500 Pa). The modulus separation method has the great advantage over RPI when the cross-over frequency cannot be reached experimentally. Tzoganakis analysed the correlation between \( Modsep \) index and Mw/Mn and suggested that it was based on the distribution of relaxation times [Tzoganakis, (1994)].

Steeman analysed the most commonly used rheological indices both experimentally and theoretically [Steeman, P.A.M., (1998)] and concluded that none of them was a function of only one molecular parameter. He found that zero shear viscosity depended not only on weight-average molecular weight, but also on polydispersity (Eq. 2.45) and that both \( RPI \) and \( Modsep \) indices were strongly influenced by Mz/Mw. The presence of additives in commercial polymer grades is also a factor that can effect the above correlations [Tollefson (1996)].
2.4.4 Long chain branching and rheology of polypropylene

For a linear polymer, such as PP manufactured by Ziegler-Natta catalysis, the MWD function is sufficient to describe its molecular structure. Recently, long chain branching (LCB) was introduced to PP molecules by means of electron beam irradiation [Scheve, et al., (1990); Sugimoto, et al., (1999)], in order to increase the melt strength. The presence of LCB in PP had a strong influence on both shear and extensional rheology of the samples [Hingman and Marczinke, (1994)]: \( \eta_0 \) was higher than expected from the Mw calibration (Eq. 2.43) and the onset of shear thinning was shifted to lower shear rates. The same effect was found earlier from the studies on LDPE, where the high zero shear viscosity is explained by the contribution of branches to the number of entanglements [Jacovic, et al., (1979)]. At high stresses or shear rates, this contribution is reduced and the inherently smaller coil dimensions become responsible for the lower viscosity, similar to the effect of hydrodynamic volume on solution viscosities (Section 2.2.4). The effect of LCB on \( \eta_0 \) can be expressed by the following multivariable power function [Dobkowski, (1998)]:

\[
\eta_0 = KM_x^{a_1} q^{a_2} g'^{a_3} \quad \ldots \quad (2.61)
\]

where \( M_x \) is a MW average Mw or \( M_z \), \( q \) is a polydispersity, \( M_w/M_n \) or \( M_z/M_w \) and \( g' \) is the gyration index (Eq. 2.12). A parameter derived from the shape of the viscosity curve was found to be useful as a rheological measure of LCB in polyethylenes [Lai, et al., (1994)]. It is known as Dow Rheology Index (DRI), Eq. 2.62:

\[
DRI = \frac{3.56 \times 10^4 [Pa] \cdot \tau_0}{\eta_0} - 0.1 \quad \ldots \quad (2.62)
\]

\( \tau_0 \) in Eq. 2.62 is a characteristic time constant, obtained from fitting the shear data to the Cross model, equal to \( K^{1/m} \) in Eq 2.63.

\[
\eta = \frac{\eta_0}{1 + K \gamma^m} \quad \ldots \quad (2.63)
\]

DRI is also sensitive to polydispersity [Steeman, (1998)], that limits its use to relatively narrow LDPEs produced by metallocene catalysts.
2.4.5 Extensional viscosity of polypropylene in relation to its structure

Extensional properties of polypropylene were studied to a lesser extent than its shear properties, due to the problems associated with measurement techniques (Section 2.3.7). The study of extensional flows was mainly done as a continuum mechanics approach, the main goal being to test constitutive equations. An integral constitutive equation by Lodge [Lodge, (1968)] was based on the rubber elasticity theory, with considerations specific to the topology of molten polymers. It describes melt extensional behaviour in both linear and non-linear viscoelastic region. As shown by Laun [Laun, (1978) and (1986)], the transient flow in the linear region can be predicted from the polymer relaxation properties:

\[ \eta^E_E(t) = \sigma^+_E(t) / \dot{\varepsilon} = 3 \sum_i g_i \tau_i (1 - e^{-t/\tau_i}) \]  \hspace{1cm} (2.64)

where \( g_i \) stands for relaxation strength, \( g_i = h(\tau_i) \). Using Wagner’s time-integral constitutive equation [Wagner, 1976], the extensional viscosity of commercial PP samples was successfully predicted [Fulchiron et al., (1993)]. Based on the scaling relationship for linear viscoelasticity (Eq. 2.53), Lanfray and Marin proposed a principle of time-molecular weight equivalence [Lanfray and Marin, (1990)] (Eq. 2.65) and verified its validity for several commercial PP samples:

\[ \sigma_r(t, \dot{\varepsilon}, M_b) = \sigma_r \left( \frac{L}{a_M}, \dot{\varepsilon} a_M, M \right) \]  \hspace{1cm} (2.65)

where \( \sigma_r \) is the reduced stress and \( a_M \) is the shift factor that scales as \( M_w^{3.4} \).

As a linear polymer, PP is not expected to show strain hardening (positive deviation from the \( \eta^E_E(t) \) calculated by Eq. 2.64), which is a characteristic behaviour for LDPEs with high degree of branching [Meissner, (1969)]. In order to enhance the extensional properties, i.e. processability for thermoforming and blow-moulding applications, LCB was introduced to polypropylene [Kurzbeck, et al., (1999)]. Such a PP grade showed a pronounced strain hardening, in the greater extent than expected from the degree of branching, which is similar to the results obtained earlier by [Hingman and Marczinke, (1994)]. Kurzbeck explained this observation by the combination of two structural factors: presence of LCB and a broad MWD with a high MW shoulder. In the same reference, a heterophasic PP co-
polymer grade was also studied at the same conditions and it showed no strain hardening and a small influence of phase separation on the extensional behaviour.

The effect of strain hardening was also produced in linear polymers that were drawn in the partially molten state [Hingman (1995)]. This behaviour was carefully studied by Rauschenberger, who explained the strain hardening on the basis of remained crystallinity [Rauschenberger, (1998)]:

[Copyrighted material omitted. Please consult the original thesis.]

Figure 2.37  Extensional viscosity of PP in molten and rubbery state
(adopted from [Rauschenberger, V., (1998)])

- With reducing the test temperature in Fig. 2.37, extensional viscosity increases due to the shift in relaxation times; the shape of the $\eta^*_e(t)$ curve does not change, as long as the melt is homogeneous.

- If temperature is further reduced (below Tm), small crystals can occur and act as filler particles; the filler effect causes the viscosity to rise steadily with time, without reaching the steady state. The particles (crystallites) are not cross-linked and are not deformed; the stress around them can locally exceed the critical melt strength. The result is melt rupture at rather low elongation.

- The strain hardening effect can be seen at slightly lower temperatures, where permanent network points (cross-links) are present in the melt. Such a network doesn’t exist in the purely molten state, but in semicrystalline state polymer chains may be incorporated into two or more crystals thus linking them together. At high strain the chain segments

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between the cross-links become completely stretched, giving rise to a high draw force and a high extensional viscosity. The strain hardening behaviour of PP in semi-molten state allows blowing a bubble in the BOPP processing, which would not be possible in the completely molten state of a linear polymer with such a low melt strength as that of polypropylene.
3. MATERIALS AND EQUIPMENT

3.1 MATERIALS

3.1.1 Polypropylene grades

All polypropylene grades characterised in this work (PP homopolymers, propylene copolymers and a PP modifier) were supplied by UCB Films Ltd., Wigton, UK. Their codes, description, densities and melt flow indices (MFI, according to the manufacturers) are listed in Table 3.1:

Table 3.1 Polypropylene grades for potential use in BOPP processing

<table>
<thead>
<tr>
<th>Grade (Code name)</th>
<th>Polymer type</th>
<th>$\rho$ (solid)$^a$</th>
<th>MFI$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA3</td>
<td>Homopolymer</td>
<td>0.90</td>
<td>3.5</td>
</tr>
<tr>
<td>MA4</td>
<td>Homopolymer</td>
<td>0.90</td>
<td>7.0</td>
</tr>
<tr>
<td>MM1</td>
<td>Homopolymer</td>
<td>0.90</td>
<td>9.0</td>
</tr>
<tr>
<td>TN1</td>
<td>Homopolymer</td>
<td>0.90</td>
<td>6 - 9</td>
</tr>
<tr>
<td>TN2</td>
<td>Homopolymer (nucleated TN1)</td>
<td>0.90</td>
<td>6 - 9</td>
</tr>
<tr>
<td>EP1</td>
<td>PP modifier (master-batch)</td>
<td>0.975</td>
<td>11.0$^c$</td>
</tr>
<tr>
<td>MA1</td>
<td>Heterophase copolymer</td>
<td>0.89</td>
<td>6.0</td>
</tr>
<tr>
<td>MA5</td>
<td>Heterophase copolymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA2</td>
<td>Ethylene-propylene copolymer</td>
<td>0.89</td>
<td>9.5</td>
</tr>
<tr>
<td>SEP</td>
<td>Ethylene-propylene copolymer</td>
<td>N/A</td>
<td>8.0 - 10.0</td>
</tr>
<tr>
<td>DPE</td>
<td>Butylene-propylene copolymer</td>
<td>N/A</td>
<td>7.5 - 9.5</td>
</tr>
<tr>
<td>TEPB</td>
<td>Ethylene-propylene-butylen copolymer</td>
<td>N/A</td>
<td>7.0 - 9.5</td>
</tr>
</tbody>
</table>

$^a$ gc m$^{-3}$; $^b$ Melt Flow Index, g / 10 min at 230°C, 2.16 kg load (ASTM 1238); $^c$ at 190°C, other conditions same as $^b$.

The choice of materials was governed by two main reasons: 1) from practical point of view, it was reasonable to study the grades either used before or recommended for use in BOPP processing and 2) scientifically, it was desirable to investigate a larger population of samples with differences in parameters that would be studied, e.g. chain structure (homo- and co-polymer), morphology (blends), molecular weight (homopolymer grades). Polymer grades MA3, MA4, MM1, TN1 and TN2 are described by manufacturers as
isotactic polypropylene homopolymers for use in film blowing processes. They all have
the same density at room temperature and different MFI, which is a measure of melt
fluidity (Section 3.2.5). Grade TN2 is a nucleated version of TN1, i.e. a nucleating agent
was added in order to modify the rate of crystallisation and size of the crystals. Grade
named EP1 is described as a PP modifier for use as a master-batch. It is a 50wt% / 50wt%
blend of iPP with hydrogenated oligo-cyclopentadiene (HOCP) (Fig. 2.22). Grades
designated as MA1 and MA5 are heterophasic copolymers (Section 2.2.1), designed by
manufacturer to improve PP's flexibility. Grades MA2, SEP, DPB and TEPB are all
propylene co-polymers with ethylene or butylene. They have a low content of a co-
monomer (3-7%) and are intended for use as inner or outer coats for the BOPP films.

3.1.2 Polypropylene blends

The blends studied in this work were prepared by blending two of the homopolymer
grades, namely MA3 and MM1 with EP1 master-batch, in a Brabender twin-screw
extruder at a temperature of 220°C and an extrusion rate of 18-20kg/hr. After extrusion the
blends were cooled with air and pelletised. The composition of the blends (wt/wt) were as
follows:
MA3/EP1: 100/0, 90/10, 85/15, 70/30, 50/50, 30/70 and 0/100;
MM1/EP1: 100/0, 90/10, 80/20, 70/30, 50/50, 30/70 and 0/100.

3.1.3 Polymer standards for GPC analysis

A range of polymer standards (polymeric materials with defined MW and distribution) is
in use for GPC analysis, whether to calibrate the system or to verify the accuracy of the
measurements and performance of the instrument. The narrow standards used in this work
were supplied by Polymer Laboratories: the S-H2-10 polystyrene calibration kit consisted
of ten nearly monodisperse polystyrenes (Mw/Mn between 1.03 and 1.13), prepared by
anionic polymerisation. In addition, three other narrow PS standards were purchased from
the same supplier, in order to improve accuracy and definition of the calibration curve.
Every PS standard came with a Certificate of Analysis, where the molecular weights,
determined by three methods: SEC, Light Scattering and Viscometry, were presented. The
peak molecular weights (Mp) of the standards in the calibration kit were in the range of

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925 – 13,200,000, evenly spaced on the logarithmic scale. The additional standards were with $M_p$ values of 50,400; 126,700 and 275,200; their molecular weights were chosen to be in the region where $M_w$ values of most polyolefin samples were detected.

Broad polyethylene standards, supplied by National Institute of Standards & Technology (NIST), USA, were regularly used to verify the validity of the GPC analysis. Their characteristics are listed in Table 3.2:

Table 3.2 Polyethylene standards for GPC analysis

<table>
<thead>
<tr>
<th>Standard</th>
<th>Type</th>
<th>$M_w^a$</th>
<th>$M_n^b$</th>
<th>$M_w^b$</th>
<th>$M_z^b$</th>
<th>$M_w/M_n$</th>
<th>$[\eta]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM 1475a</td>
<td>HDPE</td>
<td>52,000</td>
<td>18,310</td>
<td>53,070</td>
<td>138,000</td>
<td>2.90</td>
<td>1.010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 2,000</td>
<td>± 360</td>
<td>± 620</td>
<td>± 3,700</td>
<td></td>
<td>± 0.86</td>
</tr>
<tr>
<td>SRM 1476</td>
<td>LDPE</td>
<td>89,300</td>
<td></td>
<td></td>
<td>3.6</td>
<td></td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 7,000</td>
<td></td>
<td></td>
<td>± 0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a^)$ - by light-scattering; $b^)$ - by SEC; $c^)$ - at $130^\circ$C in TCB

Data for the Standard Reference Material (SRM) 1475a in Table 3.2 are taken from the appropriate Certificate (NISTIR 5199, 1993). The SRM 1476 does not have certified values for molecular weights; data in Table 3.2 are the averages of the results obtained by GPC in eight laboratories, listed in [Beer, et al., (1999)].

### 3.2 EQUIPMENT

Instruments utilised for molecular, morphological and rheological characterisation of polymer grades will be described in details in this section. The actual measurement techniques will be discussed in Chapter 4. Equipment used for sample preparation will be briefly described in Chapter 4, as well.

#### 3.2.1 Gel-permeation chromatography

Gel-permeation or size exclusion chromatography (GPC - SEC) was performed on a Waters Alliance GPCV2000 chromatographer, equipped with both differential refractometer and viscometer detector. The principles of polymer MWD determination are
described in Section 2.2.4 and the instrumentation is schematically shown in Fig. 2.15. The actual look of the instrument is presented in Figure 3.1. The reason for a robust appearance of the instrument is the need for maintaining the constant high temperature (up to 180°C) throughout the system. Except for the solvent management compartment (1), where the solvent is pre-heated to max. 50°C, and the data acquisition system (5), all other compartments (2-4) are kept at high temperature, usually 130-150°C for polyolefin analysis.

![Image of Waters Alliance GPCV2000 chromatographer](image)

**Figure 3.1 Waters Alliance GPCV2000 chromatographer:**
1) solvent management compartment; 2) sample compartment; 3) syringe compartment; 4) analysis compartment and 5) PC data acquisition system

Solvent used as an eluent was an HPLC-grade of 1,2,4-trichlorobenzene (TCB) (M = 181.45 g mol⁻¹, ρ<sub>room</sub> = 1.45 g cm⁻³, T<sub>b</sub> = 212°C), supplied by Merck Inc. The constant flow of the solvent is provided by the software controlled pulse-free pumps situated in the solvent management compartment (1), with the precision of 0.075 %RSD (relative standard deviation) [Fotheringham and Murphy, (1998)]. Instrument is equipped with a carousel, located in the sample compartment (2), which allows automatic loading of up to 24 samples, placed in standard 10 mL vials. The temperature control system in the carousel compartment allows programming the temperature zones: the samples can be kept at lower temperature to avoid degradation and transferred to a hot zone prior to injection. Polymer dissolution is further assisted by a programmable mixing device. Automated sample injection is performed via a custom designed Rheodyne® L.P. valve fitted with a fixed-volume sample loop. The syringe compartment (3) can be open and the syringe can be used for dispensing the desired volume of solvent at elevated temperature into the vials.

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A set off two Waters Styrage HT 6E columns was equilibrated with TCB at 140°C with a flow rate of 1.0 mL min\(^{-1}\) in order to perform the analysis. The maximum number of six conventional 7.8 mm i.d. × 300 mm columns can be fitted into the analysis compartment (4). Both detectors, connected in series are also placed in the analysis compartment.

Instrument is controlled by Waters Alliance GPC 2000 Software, which allows precise definition of running conditions, instrument diagnostics and troubleshooting, programming and automatic execution of analytical tasks. The acquired data are processed by Waters Millenium\(^{32}\) Software, which incorporates data storage and viewing, calibrating the system, calculating the MWD, MW averages and LCB indices and reporting and exporting the results. Both program packages operate on Windows \textsuperscript{TM} NT 4.0 operating system.

### 3.2.2 Differential Scanning Calorimetry (DSC)

All DSC tests were performed using Modulated DSC 2920, manufactured by TA Instruments (Figure 3.2). It allows both standard mode of operation (without modulation) and modulated scans [TA Instruments, (1997)]. The operating temperatures available are in the range from \(-70\) to \(400^\circ\)C with the scan rates from \(0.01 - 10^\circ\)C/min (with modulation) or \(0.01 - 20^\circ\)C/min (no modulation). The heating and cooling curves were analysed by TA Universal Analysis Software, running on an IBM OS/2 platform. Either helium or nitrogen can be used as purging gases. The thermal response of the calorimeter was calibrated from the heat of fusion of ultra pure indium, \(\Delta H = 28.4\) J g\(^{-1}\).

![Figure 3.2 MDSC 2920 modulated DSC by TA Instruments](image)
3.2.3 Hot-stage optical microscopy (HS-OM)

Optical micrographs of thin polymer films were taken by Nikon Labophot-2 optical microscope equipped with Mettler FP82HT hot stage. The system allows observing the changes in polymer morphology at temperatures from ambiental to 400°C, with a magnification in the range of 50 × - 400 ×. The microscope was equipped with a video camera and the whole runs were recorded on a VHS videocassette. The images presented in this work were captured by using the built-in media player on a Macintosh Power PC computer.

3.2.4 Rotational rheometers

3.2.4.1 Rheometrics Mechanical Spectrometer RMS 605

A strain rate controlled rheometer RMS 605 (Fig. 3.3 left) used in this study was equipped with D=25mm parallel plates. Sample heating was provided by blowing the hot air or nitrogen. Instrument control and data acquisition was provided by Rheometrics Orchestrator® Software.

![Figure 3.3 Rotational rheometers: RMS 605 (left) and SR-200 (right)](image)

3.2.4.2 Stress-controlled Rheometer SR-200

The stress-controlled rheometer used for steady and dynamic shear characterisation of PP grades was the Rheometrics SR-200 (figure 3.3 right). Polymer samples were heated by electrically heated lower plate. The top plate of 25 mm diameter was used; the set-up was
surrounded by an environmental chamber through which the nitrogen was purged. Rheometrics Rhios® Software was in use for controlling the instrument and collecting the data.

3.2.5 Capillary rheometers

3.2.5.1 Melt Flow Indexers

The weight of a polymer melt extruded through a capillary die of standard dimensions, under a constant load and at constant temperature, is a relative measure of its fluidity, called Melt Flow Index (MFI). Two instruments were used to determine the melt flow index of the polymer grades: Ceast Modular Flow Indexer and Davenport Flow Indexer. Tests on both machines were conducted under the same experimental conditions, according to the standards procedure (ASTM 1238), described in section 4.4.3.1. Compared to the Davenport device, the Ceast MFI allows automated cutting of the extrudate and measuring the volumetric flow index.

3.2.5.2 Davenport capillary rheometer (Ram Extruder)

Davenport Ram Extruder (Figure 3.4) is an instrument capable of measuring viscosity of polymer melts at shear rates from approx. 1 to above 10,000 s⁻¹.

Figure 3.4  Capillary rheometer (Davenport RAM Extruder)
A hydraulically driven piston (1) pushes the molten polymer from the barrel (2) to a capillary die (not visible, at position 4) at constant speed, that can be inspected on the scale (7) and controlled via regulator (6). The resulting pressure is measured by a transducer (3) mounted just above the die. The actual temperature measured by thermocouples (5) can be seen at the display (8). Two Dynisco® pressure transducers were in use, depending on the melts’ viscosity: 1) 0-500 and 2) 0-10,000 psi. A set of dies in use was with following L/D (mm/mm): 32/8, 32/2 and 20/1. Other dies, including zero-length dies were also available. The pressure data for the set piston speeds were collected manually, using either a chart recorder or a digital voltmeter. The relevant corrections were applied using a Microsoft™ Excel spreadsheet.

3.2.6 Extensional rheometers

3.2.6.1 RMIT Extensional Rheometer

A schematic of the RMIT University rheometer is given in Figure 2.34. It is a custom-built, Meissner type rheometer, based on the recommendations by [Laun and Munstedt, (1978)]. The test is commenced with the floating sample being drawn down between the two counter-rotating rollers at a constant strain rate and the other end is attached to a linear variable differential transducer (LVDT) (Schaevitz, model FTA-G-50) force-measuring device. The polymer melt is stretched until the sample ruptures with the force being continuously recorded during the stretching. The instrument performs under a precise constant strain rate so that only the stress imposed by the wheels is acting on the sample. Temperature control is generally within +/-0.5°C. The tests were carried out at a temperature of 180°C and strain rate of 0.1s⁻¹.

3.2.6.2 Rheometrics Melt Extensional rheometer (RME)

Operating principles of the RME are described in Section 2.3.7. Figure 3.5 shows the stretching device within the rheometer housing. Two sets of counter-rotating belts are used to stretch the sample once it has reached the equilibrium test temperature. Each of the belts is equipped with a special welded metal tongue that bridges the gap between the edge
of the clamp and the sample supporting table to eliminate sagging and flow of the melt in the gap.

![The RME stretching device](image)

Figure 3.5 The RME stretching device

The strain rates in the range of 0.0001 - 1.0 s⁻¹ are available, with the maximum Hencky strain of 7. Tensile force in the range of 0.001 to 2 N can be measured, with the resolution of 0.001 N. Maximum oven temperature is 350°C and the sample temperature can be controlled down to ± 0.2°C. The stream of purging gas provides both support of the molten sample and better temperature control. The use of nitrogen is recommended, in order to avoid the oxidative degradation of the polymer.
4. EXPERIMENTAL TECHNIQUES AND DATA ANALYSIS

4.1 GEL-PERMEATION CHROMATOGRAPHY

Gel-permeation or size-exclusion chromatography (GPC-SEC) was performed by using the Waters Alliance GPCV 2000 chromatographer, in order to obtain the molecular weight distributions of polymer grades studied in this project. The procedure included calibrating the system, verifying the method, running the polymer samples (GPC analysis) and analysing and interpreting the results.

4.1.1 Calibrating the system

Universal calibration method, described in Section 2.2.4, has been applied to calibrate the GPC system. Experimental procedure that leads to a useful calibration curve consists of the following steps:

- Preparation for running narrow polystyrene (PS) standards;
- Running the narrow PS standards and
- Processing the results

4.1.1.1 Preparation for running narrow polystyrene (PS) standards

Narrow PS standards with molecular weights in the range of 925 to 13,200,000 were chosen for calibration, in order to cover the whole range of MW expected to be found in Ziegler-Natta catalysed polypropylenes. Also, the range complies with the exclusion limits of the columns in use (Waters Styrage Column – Care and Use Manual). The standards are weighed on a precise balance (5 decimal places, ± 0.01 mg) and dissolved in 1,2,4-trichlorobenzene (TCB). The solvent for use in GPC analysis has to be filtered through a 0.45 mm filter prior to circulation through the system, in order to remove the particles that can block the solvent pathways or damage the columns. It is recommended to mix the solvent with activated silica gel before filtration to remove the moisture. Used solvent can be recycled by vacuum-distillation.

Since it is required to know the weight/volume concentration of polymer standards, the volume of the solution can be determined by two different ways: 1) by dispensing the exact
volume of solvent using the device in the syringe compartment (Section 3.2.1) or 2) by
determining the weight of the solution and calculating its volume using the density at the
relevant temperature. The second method was applied, because mass measurements
provide better accuracy than volume measurements [Hynes, (1999)]. The whole procedure
includes the following measurements: - mass of the empty vial with a cap is \( m_i \); - using the
vial as a tare, a PS standard is weight to obtain its mass \( m \); - the vial is filled with approx. 9
mL of TCB, sealed and weighed again – this mass is \( m_2 \). The solution will expand when
heated to 140°C to approx. 10 mL; the exact concentration of the solution is calculated
using Eq. 4.1:

\[
\frac{m}{(m_2 - m_1) / \rho_{TCB}^{140^oC}}
\]

The density of TCB at 140°C was determined as \( \rho_{TCB}^{140^oC} = 1.311 \text{ gcm}^{-3} \). The suitable
concentrations of PS standards depend on their molecular weights. Since the intrinsic
viscosity depends on MW according to Mark-Houwink equation (Eq. 2.9), it is
recommended to adjust the concentration of each standard to yield the detector response
that falls in the limits of viscometer’s best accuracy, which is achieved with using the Eq.
4.2 [Hynes, F., (1999)]:

\[
c_{rec} = 0.25 / KM^\alpha
\]

with \( K = 1.5 \times 10^4 \) and \( \alpha = 0.7 \). It was calculated that the recommended concentrations,
\( c_{rec} \) are in the range from 0.0173 mg/mL for PS with MW of 13,200,000 to 13.98 mg/mL
for the PS standard with MW of 925. It is allowed to prepare the PS standard solutions
with concentrations in the range of ±50% of \( c_{rec} \).

The instrument has to be configured properly before each run. That includes parameters
such as temperature and flow rate, which can be controlled using Alliance GPC 2000
Software. It is important to mention the difference between nominal and experimental
flow rate. This is due to the difference between densities of the solvent at room
temperature and analysis temperature. The flow rate at working temperature (140°C) can
be determined as:
Flow Rate = Mass Flow Rate / \rho_{TCB} \quad \ldots \quad (4.3)

The mass flow rate is easy to measure accurately, as it is the weight of solvent collected per unit time. It was found that measured flow rate was 8-9% higher than the nominal one. For that reason, the nominal flow rate of 0.92 mL/min was set for the experiments in order to achieve the ‘true’ flow rate of 1.00 mL/min.

4.1.1.2 Running the narrow PS standards

The polystyrene standard solutions, as prepared in 4.1.1.1, are placed in the carousel in the sample compartment of the instrument (#2 in Fig. 3.1). The instrument is then programmed to run the samples, using the Alliance™ GPC 2000 Software, as shown in Fig. 4.1. The sequence, called Sample Set Method, contains information relevant both for running the samples (vial position, instrument parameters, No. of injections) and for calculations that will be performed by Millenium™ Software (sample name and type, components and their molecular weights and concentrations). After starting the Sample Set Method, the instrument performs the instructions and saves the acquired data as a named Sample Set.

Figure 4.1 Creating the Sample Set Method in Waters Alliance™ GPC 2000 Software
4.1.1.3 Processing the results for narrow standards

A Sample Set acquired as shown in the above Section is accessible to the Millenium\textsuperscript{32} Software, where it can be processed by applying a Method Set. The Method Set combines the instructions on what kind of data (different detectors) will be treated and how (Processing Method), what kind of results will be obtained and how they will be presented (Reporting Methods). The Processing Method is the crucial part of the Method Set. It defines the parameters for integration of raw chromatograms, so the molecular weights can be properly assigned to the dRI peaks, and the intrinsic viscosity can be calculated from the area of the viscometer peaks and given concentration.

![Image](image.png)

Figure 4.2 Processing the results for narrow PS standards with Millenium\textsuperscript{32} Software

An important parameter that has to be determined experimentally for every GPCV instrument is the *inter-detector time*. Since two detectors are connected in series, a molecular species that was detected by dRI will reach the viscometer after some time, $\Delta t$, that can be determined as an average of differences between retention times for viscometer and refractometer peaks for all narrow standards [Waters, (1997)]. For the GPC instrument at RMIT, this value taken as an average of more than 100 narrow PS runs over a period of 18 months, was determined as equal to -0.054 minutes. Once established in the Method Set, this parameter allows deriving the viscosity channel (relative viscosity data), so it can match with the concentration channel (dRI data). After setting all the parameters,
the Method Set can be applied to all narrow standards, which will result in the calibration curve, as shown in Figure 4.3. Once calibrated, the curve becomes a part of the Processing Method that can be applied to both narrow and broad unknown samples, in order to obtain their molecular weight distributions.

![Calibration curve and viscosity plot reviewed by Millenium software](image)

**Figure 4.3** Calibration curve and viscosity plot reviewed by Millenium Software

The calibration curve achieved in this work (top plot in Fig. 4.3) was characterised by the following parameters: -elution volume range: \( V_0 = 11 \, \text{mL} - V_T = 23 \, \text{mL} \); - 3rd order polynomial fit \( \log M[\eta] = f(EV) \), \( R^2 = 0.9996 \); - standard error = 4.82 %. The Mark-Houwink parameters for polystyrene obtained from the viscosity plot (bottom plot, Fig. 4.3) were \( K = 1.8 \pm 10^{-4} \) and \( \alpha = 0.67 \), which was in an excellent agreement with the values published elsewhere [Rudin, et al., (1984)].

### 4.1.2 Verification of the accuracy of GPC analysis with broad PE standards

Before applying the Processing Method as developed in Section 4.1.1 to PP samples, its’ validity was tested on the broad MWD polyethylene standards (Table 3.2). The tests included categories such as repeatability, reproducibility and accuracy of the obtained
results. Due to the nature of GPC analysis (separation of molecules according to their size, not MW; a relative method, since it depends on calibration; theoretical assumption that the universal calibration is valid) and incomplete understanding of the influence of many experimental parameters, it is only possible to verify the validity of the analysis by comparing the results with certified or literature values for the appropriate standards.

4.1.2.1 Repeatability

PE standards (Table 3.2) were run several times over a period of time before and during the analysis of PP samples. The results are listed in Table 4.1:

Table 4.1 GPC Analyses of Polyethylene Standards

<table>
<thead>
<tr>
<th></th>
<th>1475a&lt;sup&gt;a&lt;/sup&gt;</th>
<th></th>
<th>1476&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>M&lt;sub&gt;W&lt;/sub&gt;</td>
</tr>
<tr>
<td>Mean</td>
<td>18,880</td>
<td>55,740</td>
<td>2.96</td>
</tr>
<tr>
<td>RSD%&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.6</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Δ% Certificate&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Δ% Reference&lt;sup&gt;e&lt;/sup&gt;</td>
<td>5</td>
<td>-4</td>
<td>-10</td>
</tr>
</tbody>
</table>

<sup>a</sup> - 5 runs; <sup>b</sup> - 3 runs; <sup>c</sup> - Relative standard deviation; <sup>d</sup> - % difference from certified values (NISTIR 5199); <sup>e</sup> - % diff. from reference values ([Brun, (1999)] for 1475a and [Beer, et al., (1999)] for 1476)

It can be seen from Table 4.1 that a high level of repeatability was achieved, with the relative standard deviation of MW averages being below 5%.

4.1.2.2 Reproducibility and accuracy

It was shown above that a good repeatability of MW averages from GPC analysis could be achieved. The accuracy of the results can be verified only by comparing them to the absolute values. Unfortunately, such values are not available for polyolefins. Instead, either certificate or reference values can be found (Table 3.2). Comparison with such values, achieved under most carefully controlled conditions, allows verification of the reproducibility of the measurements. In addition, the values of MW averages can be compared to results of analysis different than SEC (Table 2.1). Comparison of the weight-average MW (M<sub>W</sub>) of PE standard SRM 1475a from GPC and Light-Scattering
determinations (Table 3.2) shows a good agreement and provides a high confidence in GPC applicability.

Compared to certificate values, the results obtained at RMIT show high level of reproducibility (less than 5% difference). In all measurements, the $M_w$ of SRM 1475a was higher than the certificate value, what was also observed by many authors using the same GPCV configuration [Morrison, (2000)]. It is not clear whether it is due to the hardware or software configuration of Waters GPCV2000 or problems with the technique itself. The results compiled by Dr Yefim Brun, Waters [Brun, (1999)], from 32 measurements of SRM 1475a MW averages, show the $M_w$ value of 58,300±1,100, which is 4% higher than the RMIT value. Generally, the results obtained in the RMIT GPC Lab can be considered reproducible within the ±5% limits of relative standard deviation.

### 4.1.3 GPC analysis of PP grades

Polypropylene homo- and co-polymers were characterised in terms of their molecular weight distributions using the Processing Method and calibration curve, developed as described in Section 4.1.1. The general guidelines for determination of MWD of polydisperse polymers are given in the ASTM standard D 3536 – 91. The most valuable recommendations for running the PP samples can be found in [IUPAC Technical Report, (1997)].

#### 4.1.3.1 Sample preparation for GPC analysis of polypropylene

The issue of sample preparation is of great importance in case of polyolefins, such as PE, PP and their co-polymers. They can be dissolved in only a few solvents and only at elevated temperatures. The conditions for PP dissolution recommended by IUPAC are: solvent 1,2,4-trichlorobenzene (TCB), polymer concentration 0.1-1 mg/mL, addition of anti-oxidant (0.5 mg/mL), dissolution time 4 h at 150°C under nitrogen with occasional stirring. After a substantial number of tests and in collaboration with Waters representatives, the following procedure was established for use in the RMIT GPC Lab: 10-12 mg of polymer are cut (shaved) from at list 5 pellets and weighed on an analytical balance (4-5 decimal places) using a vial as a tare; approx. 9 ml of TCB with 0.2 mg/mL of Santanox® is added and the vials are sealed. The concentrations are calculated as
described in Section 4.1.1.1. Sealed vials are placed in an oven heated to 160°C and the
dissolution is enhanced by occasional shaking. After 2 hours the vials are quickly
transferred to the instrument carousel and the Sample Set is started.

4.1.3.2 GPC analysis of PP samples and data analysis

The program sequence (Sample Set Method) for running broad polyolefin samples is
prepared in a similar fashion to the one described in Section 4.1.1.2. The most important
difference is that the dRI channel must be inverted in the Instrument Method, since the
polyolefin solutions have lower refractive index than pure solvent. The inversion allows
obtaining positive dRI peaks for polyolefins. The syringe draw rate must be lowered, due
to higher viscosity of polyolefin solutions compared to PS. Also, the spinning speed and
duration of vial mixing should be increased to prevent any precipitation or gel formation.
Generally, two injections per vial were performed for all tested samples and the tests were
repeated at least twice.

When the Sample Set is completed, the data are accessible in the Millenium\textsuperscript{32} Software; a
typical chromatogram obtained for a broad sample is shown in Fig. 2.16. The
chromatograms are processed by applying the Method Set, which generates the MWD
curve using the principles of universal calibration, elaborated in Section 2.2.4. When
processing the PP chromatograms, one should take care of two phenomena: 1) the area
under the dRI peaks is proportional to the sample concentration; it means that the ratio
Area / c is constant for a given polymer type. If this is not the case, the concentration can
be calculated from the peak area and replace the nominal value. 2) The presence of long-
chain branching in polymer can effect the calculations and alter the MW averages and
polydispersity indices. The viscosity plot (Figure 2.18) should be checked for each result
and the appropriate viscosity fit should be applied. As expected for linear polymers, the
intrinsic viscosity of PP samples followed the Mark-Houwink equation. Most care was
taken when analysing the co-polymers, but no evidence of LCB could be extracted from
their viscosity plots.
4.1.3.3 Evaluation of PP GPC analysis results

The complete MWD obtained for the PP grades will be discussed in details in Chapter 5. In this section, the results will be evaluated in terms of their repeatability and reproducibility. The most excessive study on reproducibility of PP MWD measurements [IUPAC Technical Report, (1997)] conducted as a round-robin test in 14 laboratories (38 runs), showed that high degree of discrepancy can occur. After neglecting the extremely low results (probably due to thermo-oxidative degradation), the data analysis produced relative standard deviation of $M_w$- averages equal to 6.0% for PP grade-1 and 13.6% for PP grade-2. With polydispersity, $M_w/M_n$, the RSD was as high as 10.1% for grade-1 and 17.3% for grade-2. The 'more reproducible grade' (PP-1) was a low MFI grade designed for blow moulding and thermoforming, while the other one was a controlled-rheology high-MFI grade. The higher RSD of polydispersity is expected, since it involves two MW averages with their standard deviations. Compared to $M_w$ values obtained from light-scattering measurements, the GPC weight-averages were off by less than 5%. The above study intended to show that accurate determination of $M_w$ could be performed by means of GPC.

As shown in Section 4.1.2, the GPC instrument at RMIT performs with high degree of repeatability, which is of great importance in obtaining consistent and reliable results. As tested for standard polyethylene, the results are reproducible as well, which is crucial for a relative analytical method that depends on calibration. Similar procedure was employed to test the validity of the results for PP samples. All the samples were run at least 3 times with 2 injections from each sample, which gives a minimum number of six runs per sample. The results presented further in this work are the averages of these runs. The relative standard deviations of the results were calculated and shown in Table 4.2; the RSD was in the range of 0.3 – 3.9 % for $M_w$ and 1.0 – 13.0 % for polydispersity, $M_w/M_n$. That shows a very good repeatability of $M_w$; the repeatability of $M_w/M_n$ was less satisfactory, but still acceptable, compared to the IUPAC results.
Table 4.2 Repeatability and reproducibility of PP GPC results

<table>
<thead>
<tr>
<th>Grade</th>
<th>%RSD (Mw) (6 runs - RMIT)</th>
<th>Δ% (Mw) (RMIT-Waters)</th>
<th>%RSD (Mw/Mn) (6 runs - RMIT)</th>
<th>Δ% (Mw/Mn) (RMIT-Waters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM1</td>
<td>2.3</td>
<td>15.1</td>
<td>1.1</td>
<td>-7.2</td>
</tr>
<tr>
<td>TN1</td>
<td>2.5</td>
<td>7.8</td>
<td>6.9</td>
<td>-4.0</td>
</tr>
<tr>
<td>MA4</td>
<td>1.4</td>
<td>2.3</td>
<td>11.2</td>
<td>-18.0</td>
</tr>
<tr>
<td>MA3</td>
<td>1.5</td>
<td>3.7</td>
<td>8.7</td>
<td>-13.2</td>
</tr>
<tr>
<td>EP1</td>
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<td>-3.9</td>
<td>8.9</td>
<td>-12.2</td>
</tr>
<tr>
<td>MA5</td>
<td>2.7</td>
<td>0.5</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>MA1</td>
<td>3.0</td>
<td>1.6</td>
<td>2.0</td>
<td>-9.5</td>
</tr>
<tr>
<td>DPB</td>
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<td>1.9</td>
<td>7.0</td>
<td>0.4</td>
</tr>
<tr>
<td>SEP</td>
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</tr>
<tr>
<td>MA2</td>
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</tr>
<tr>
<td>TEPB</td>
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<td>8.8</td>
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</tr>
</tbody>
</table>

All PP grades were also run in the Waters Inc. laboratories, Milford, MA by Dr Y. Brun. In that way, it was possible to verify the reproducibility of MWD results. The test conditions (flow-rate, temperature) were identical for two instruments. The only difference between instrument configurations was in terms of number of columns, that was three for the Waters USA GPC. The relative difference between two sets of results is also shown in Table 4.2. One can see that Mw obtained at RMIT were slightly higher than USA Mw (less than 10%, except for MM1 and MA2). This can also be noticed from the plot of Waters USA results versus RMIT results (Fig. 4.4); the slope of the regression line is close to 1, but the intercept is greater than zero.

In case of polydispersities, the RMIT results for Mw/Mn were generally lower than USA ones. Except for two extremes, the relative difference was less than 15%, which is a degree of reproducibility similar to that shown in the IUPAC study. More deviations in Mw/Mn were observed as a result of higher level of uncertainty of Mn. This can be explained by a small drift of the baseline at higher retention times and the inevitable interference with low-MW peaks (antioxidants), which makes the peak integration less accurate.
4.2 DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetry (DSC) was performed using the Modulated DSC 2920, manufactured by TA Instruments, in order to characterise the thermal behaviour of polypropylene grades. The obtained parameters (Tg, Tm, Tc, %crystallinity) are of great importance for assessing the processability of polymers. Also, important information can be extracted from the shape of the curve and number of the peaks, in regards to composition of the co-polymers. Even more significant is the use of DSC in morphological study of the blends.

4.2.1 DSC analysis of PP homo-polymer grades

Thermal behaviour of PP is generally tested using the standard method, ASTM D3417-83. Since there is a broad distribution of lamellar thickness of PP crystals, the melting peaks are broad and their positions depend on the heating rates and crystallisation conditions [Hingman, et al., (1995)]. When the purpose of the study is not only measuring the thermal parameters (Tg, Tm and Tc), but also the thorough assessment of polymer’s behaviour under different thermal regimes, the conditions of the test can be specified in a
different fashion. In this work, most care was taken to compare the behaviour of different PP grades only if their DSC data were collected under the same conditions. For that reason, homo-polymers were analysed by using the conditions in accordance to the standard: heating and cooling rates were 10°C/min, sample was heated to well above melting temperature before crystallisation (to prevent the effects of previous thermal history) and the values of $T_m$ and $\Delta H$ were collected from the second heating run.

Due to the very long testing times, it was inconvenient to repeat the tests for all the samples for statistical analysis of repeatability. However, one of the grades (MA3) was tested 3 times and it was found that both $T_m$ and $T_c$ can be determined within the range of ±0.2°C with 95% confidence. The difference between melting points determined from the first and second heating runs was found to be small, generally less than 0.3°C. This observation suggests that if a quick thermal analysis of PP were needed, the result would be still acceptable for comparison. The melting temperatures of PP homo-polymer grades, collected as described above, were found to be in a narrow range of 163.5°C (MM1) – 166.1°C (MA3), which is in agreement with literature values for iPP [Moore, (1996)]. More scatter was found in determination of crystallisation temperature. The observed range of $T_c$ was 117.6°C (TN1) – 127.6°C (MA4). The glass transition temperature ($T_g$) of PP is not easy to detect, due to its semi-crystalline nature. For that reason, the first heating curves were carefully examined, since they were obtained directly from a fast-cooled, less crystalline sample. The parallel use of heat flow and heat capacity, available in modulated DSC, was beneficial. The $T_g$, determined as an inflection point of the heating curves was in the range of −9°C to −14°C for the PP grades.

The percentage crystallinity was calculated from the area of the melting peaks, using Eq. 2.2. The accuracy of such determination is rather low, since the area under the peak depends on the quality of the baseline and boundaries of integration. The values of $\Delta H^*$ found for PP samples were in the range of 80 Jg$^{-1}$ (MM1) – 110 Jg$^{-1}$ (MA4), which corresponds to crystallinity of 38% – 53%. The most emphasis on crystallinity determination was put on the PP blends with an HOCP-based modifier, EP1 (Section 4.2.3). The crystallinity of the EP1 was determined to be 21%, which is approx. half of the pure PP. As expected, the crystallinity of co-polymers was found to be much lower than of the pure PP grades (Section 4.2.2).
DSC was also used to investigate the influence of sample preparation conditions on polymer's thermal properties. Two TN1 samples were prepared in a different manner: sample 1 was compression moulded and sample 2 was extruded. They were both scanned by DSC under the same conditions (10°C/min) and the first heating curves were shown in Figure 4.5a. It can be seen that the melting peak of a compression-moulded sample is narrower. The melting temperatures were determined as 165.6°C (sample 1) and 164.0°C (sample 2). The calculated crystallinity was 46% for sample 1 and 42% for sample 2. The purpose of this test was to investigate the difference in extensional viscosity measurements in regards to sample preparation. Similar tests can be arranged for investigation of polymer behaviour under conditions that simulate those in the particular process.

![Figure 4.5 Influence of thermal history on TN1 melting peaks in DSC](image)

Figure 4.5 Influence of thermal history on TN1 melting peaks in DSC
a) Sample 1- compression moulded, 2- extruded; b) 1- first heating run, 2- remelting

In Fig. 4.5b, the second heating run was presented for the compression-moulded sample (curve 2), compared to the first run (curve 1). Curve 2 in Fig. 4.5b shows the re-melting of the PP that was crystallised under the cooling-rate of 10°C/min, while the curve 1 is valid for the same polymer but crystallised under different thermo-mechanical conditions (low and non-uniform cooling-rate, high pressure). It can be concluded that the previous thermal history affects both the shape of the curve and the numerical value of $T_m$, as discussed above for the standardisation of test parameters in DSC analysis.
4.2.2 DSC analysis of propylene co-polymer grades

Co-polymer grades described in Section 3.1.1 were also characterised by DSC, using the scan-rate of 10°C/min. The determined values of $T_m$ and $T_c$ were more diverse than it was case with homo-polymer grades. For that reason, they can be used for a qualitative comparison between grades, along with the actual curves that show different shapes and number of peaks. The difference between endotherms for the first and second heating runs was apparent and more pronounced than for the homo-polymers. Most co-polymers showed only one, very broad peak in the first run and multiple, more or less resolved peaks in the second run. The highest temperature peaks from the second runs were considered as the melting temperatures of co-polymers. The values of $T_m$ for random co-polymers were in the range of 142.2°C (TEPB) – 150.3°C (DPB). All random co-polymers (MA2, SEP, DPB and TEPB) showed only one sharp crystallisation peak at lower temperature than for the pure PP. The $T_c$ values were in the range of 89.6°C (TEPB) – 99.9°C (DPB). The percentage of crystallised PP was calculated from the area under the crystallisation peaks (exotherms), since they were much sharper and the baseline was more stable. The $\Delta H^*$ was found to be in the range of 46 Jg$^{-1}$ (MA2) – 75 Jg$^{-1}$ (DPB), which corresponds to crystallinity range of 22% - 36%. The glass-transition temperatures of co-polymers were hard to detect on the heating curves. The inflections on the cooling curves were assigned to glass-transitions and they were in the range of –23°C to –26°C.

The presence of a second crystallisation peak on the exotherms (cooling curves) for the grades MA1 and MA5 was significant to distinguish them from the random co-polymers. This behaviour can be assigned to the presence of long blocks of ethylene units in the polymer chains, which gives rise to polyethylene crystallisation and phase separation [Feng, et al., (1998)]. The melting behaviour of the two heterophasic co-polymers was found to be very distinct: MA1 behaved more like a random co-polymer, while MA5 showed two completely resolved peaks, corresponding to separate PE and PP phases.
4.2.3 Analysis of PP modifier EP1 and its’ blends

The master-batch grade EP1 was known to contain approximately 50wt% HOCP (Fig. 2.22). This was verified by solvent extraction and both virgin EP1 and its components underwent detailed DSC study. The blends of EP1 with two PP homo-polymer grades were prepared (Section 3.1.2) and characterised.

4.2.3.1 Composition analysis of EP1

The nature of EP1 was examined by extracting 10g of material with 100mL of boiling n-heptane, which is a good solvent for amorphous compounds like HOCP, but not for iPP. The extraction was carried out for 8h, the extract was decanted from the precipitate and evaporated in vacuum. The weights of dried extract (HOCP) and precipitate (PP) were 4.49g and 4.56g, respectively, or 49.6% HOCP and 50.4% PP with 9.5% losses. That proved the nominal composition of the master-batch, i.e. 50/50 wt/wt. Figures 4.6 a and b show the DSC traces of the extract and precipitate, respectively. The amorphous component showed the glass transition in a broad temperature range (40-90°C), while the precipitate showed a melting curve characteristic for PP ($T_m \approx 160°C$).

Figures 4.6 a (left) and b (right): a) DSC trace of n-heptane extract from EP1  
b) DSC melting curves of PP component of EP1: 1-first run; 2-second run
4.2.3.2 Thermal analysis of EP1

A low scan rate of 4°C/min was chosen for the DSC study of EP1 and its’ blends, as a compromise between resolution and convenience. The following tests were performed on an EP1 sample:

1) The influence of quenching the EP1 melt at different conditions was studied by extruding the polymer strand at temperatures 200°C or 250°C into icy water or liquid nitrogen. Four samples were obtained: 250°C to W(ater), 250°C to N₂, 200°C to W and 200°C to N₂. The samples were kept on ice before DSC scanning. The melt temperatures of 200°C and 250°C were chosen, as the former should correspond to a phase separated melt, and at the later the melt should be homogeneous, according to [Cimmino, et al., (1993)]. The quenching temperatures were chosen in order to verify the influence of target temperature and the quenching rate on thermal properties of the system, so the appropriate technique could be employed for further study. The results of these tests will be discussed in details in Chapter 5.

![Graph showing heat flow vs. temperature](image)

**Figure 4.7 Influence of crystallisation conditions on EP1 melting curves**

2) The effect of maximum melt temperature to which the samples would be scanned on the DSC curves was evaluated using the following test: quenched EP1 sample was heated up to 180°C, which is in the region of immiscibility and then cooled down to 30°C with the scan rate of 4°C/min. After equilibrating for 5 minutes, the sample was reheated to 250°C, i.e. to the region of miscibility. After cooling under the same conditions as for the
previous run, the sample was heated again. The following conclusions can be made from the obtained melting curves, presented in Figure 4.7: quenched or fast-cooled sample of EP1 shows only one melting peak, while the presence of multiple peaks can be observed on slowly crystallised samples. The melt temperature at the start of slow crystallisation did not affect the shape and position of the curves, since the melt had to pass slowly through the immiscibility region even when cooled from 250°C.

4.2.3.3 Blending MA3 and MM1 with EP1 and DSC analysis of the blends

The materials were blended using a Brabender twin-screw extruder, at temperature of 220°C with the extrusion rate of 18-20 kg/h. The extruder’s hopper was fed with manually pre-mixed pellets of polymer grades. After extrusion the blends were cooled with air and pelletised. The samples for DSC analysis were cut directly from the pellets (10-15 mg). The DSC runs were performed using the following procedure: The first heating runs were from -30°C to 200°C in which the $T_g$ and $T_m$ were determined. The next step was cooling from 200° to 30° when $T_c$ were collected. The second heating run was then performed and the multiple peaks occurred for the samples with higher concentration of EP1. This phenomenon was attributed to phase separation. All scan rates were 4°C/min. Since the HOCP is an amorphous component, the area under the melting peak is proportional only to PP crystallinity. Hence, the percentage of crystallinity was determined using the same equation (Eq. 2.2) as for pure PP. The thermal parameters were studied qualitatively and with reference to blend compositions (Chapter 5). Generally, adding EP1 to PP grades caused decrease in %crystallinity, $T_m$ and $T_c$, and increase in $T_g$. Samples of pure PP grades and blends with low EP1 content (≤ 30%) showed single melting peaks in the second heating run, while multiple peaks occurred for the blends with the concentration of EP1 of 50% and above.

4.3 HOT-STAGE OPTICAL MICROSCOPY

Optical microscopy was employed to observe the morphological changes in the blends’ melts during heating and cooling. For that purpose, the microscope was equipped with a hot stage (Section 3.2.3) that was programmed to reproduce the heating and cooling rates used previously for DSC. The samples for the HS-OM were made by pressing a pellet
between flat steel moulds in the Wabash compression press (Section 4.4.1) into a 15-20 \( \mu m \) thin film. A 10×10 mm piece of film was cut and placed on a microscope slide and sealed with a glass cover using the silicone glue. The slide was clamped into the hot stage, which was placed onto the microscope. The film was examined under the transmitted light using 100× magnification. The melts were studied using no polarisation; otherwise the phase separation would not be noticed (Fig. 4.8 left). Polarised light was used at temperatures below the onset of crystallisation; the characteristic Maltese-cross patterns appeared for the PP spherulites, while the amorphous regions remained dark (Fig. 4.8 right):

![Optical micrographs of EP1 at 114°C (left) and MA3/EP1 90/10 at 100°C (right)]

The whole hot-stage runs were recorded on a VHS cassette and the desired images were captured using the media player on a Macintosh Power PC computer. The scale can be added to an image using the IP Lab image processing software.

4.4 SHEAR RHEOLOGICAL MEASUREMENTS

Steady shear measurements were performed by combining the results of two rotational rheometers (Section 3.2.4) and a capillary rheometer (Section 3.2.5.2). Dynamic shear tests were carried out using the stress-controlled rheometer, SR200. For both rotational rheometers, flat circular samples (discs) were required, while the capillary rheometer operated with pellets.
4.4.1 Sample preparation for rotational rheometers

Polymer samples for use in the rotational rheometers were prepared by compression moulding, using the Wabash compression press. This technique allows preparing the sheets that can be cut into 25 mm discs using the sample cutter provided by Rheometrics. The general principles of the procedure were minimising the time that polymer melt spends in the press and providing the even distribution of the melt without boundaries between pellets. Since these requirements were in collision, the optimisation of the process was performed by trial and error. With the available moulds it was possible to produce sheets of the following dimensions: 160×160×2 mm, which corresponds to the polymer weight of approx. 46 g. The mould was filled with the amount of polymer pellets slightly higher than the calculated value (eg. 50-55 g), in order to provide an overflow, which will enhance the mixing and guarantee a flat upper surface. The produced sheets were inspected visually for non-uniformity and voids. The following technique was accepted for PP homopolymer grades: - mould filled with PP pellets is placed in the press pre-heated to 220°C; - after 5 minutes the pressure (25 tons per 5" diameter) is applied and maintained for another 5 minutes; - after removing the mould from the press, it is cooled slowly by air for 15 minutes and then by water to allow removing the sheet from the mould. Similar conditions were applied for the co-polymer grades, with a decrease in temperature to 200°C.

4.4.2 Steady shear measurements using rotational rheometers

Both RMS605 and SR200 were utilised for steady shear measurements. Settings of the test parameters depended on the instrument in use, as well as on the grade tested. As a strain-controlled instrument, RMS605 can perform a rate sweep, i.e. the desired range of shear rates can be specified in the Rheometrics Orchestrator® test set-up. The available shear rate range of approx. 0.01 – 5.0 s⁻¹ was limited by low torque resolution (at values below 2 gcm [2×10⁻⁴ Nm]) at low shear rates and irreversible melt rupture at high shear rates. The stress-controlled instrument SR200 is capable of performing the stress sweep tests, in which the shear stress is increased in the specified range. The SR200 measurements are mostly limited by the maximum stress values (approx. 6,400 Pa for the 25mm plate). In both cases, it is necessary to determine the time in which viscosity reaches the steady state
value. This can be achieved by performing a step test, in which viscosity is monitored during time for a given shear rate (RMS605) or stress (SR200). The results obtained by two instruments were corrected for parallel plate geometry and analysed in terms of repeatability, reproducibility and accuracy.

4.4.2.1 Step tests and transient shear behaviour

Characteristic step tests are presented in Fig. 4.9, showing a step-rate test for MA2 at 190°C (left) and step-stress tests for MA5 at 180°C.

![Figure 4.9 Step tests: MA2 at 190°C (RMS605, left); MA5 at 180°C (SR200, right)](image)

The shear rate of 0.01s⁻¹ was chosen for the step-rate experiment and it was shown that approx. 50-60 s is needed to reach the steady state viscosity at this shear rate. It was noticed that the viscosity started decreasing after approx. 100 s, which can be explained by reaching high values of total strain and also by lubricating effects of degradation products formed on the sample edges exposed to hot air. One can see that the step-rate tests can be utilised as a mean of transient flow characterisation, eg. for comparison with extensional viscosity.

The step-stress experiments were conducted using the SR200. In the test shown in Fig. 4.9 (right) three values of stress were evaluated: 50, 70 and 100 Pa (from left to right). The SR200 data were less noisy than the RMS605 ones, and the steady state was easier to detect. In case of MA5 at 180°C, the specified stress of 50 Pa generated the shear rate equal to 0.0045 s⁻¹ at the equilibrium time of around 200 s. Since the instrument allows testing in the inert atmosphere, the tests can be continued by specifying higher stresses,
using the same sample. It is important to note that the steady state was reached in much shorter time for the consecutive steps in comparison to the first one, which cannot be explained by higher corresponding shear rates only. This effect of pre-shearing was utilised to enhance the instrument performance. Another beneficial feature of SR200 was the automatic steady state sensing that shortens the testing times and increases accuracy.

4.4.2.2 Viscosity function measured by rotational rheometers

Viscosity of polymer grades as a function of shear rate was measured at temperatures of 190°, 210°, 230° and 250°C. The tests were repeated at least twice. It was found that the SR200 measurements could be repeated to within 2% relative difference, while the results for RMS605 were rather scattered. Comparison between two sets of results collected from two instruments showed that SR200 and RMS605 produced similar results at 190°C (less than 5% RD), while the RMS605 results were 10-15% lower at higher temperatures. This could be only explained by oxidative degradation of polymer samples, as a result of blown air heating system in RMS605. The results at 210°C were brought to agreement by using the nitrogen blowing at both machines. However, the consumption of nitrogen by RMS605 is too high for practical purposes (2-3 tests with one gas cylinder).

To assure the accuracy of the results, the testing geometry must be considered. Both rheometers applied calculate the shear stress from the torque, $T$ using the equation:

$$\sigma = \frac{2T}{\pi R^3} \quad \ldots \quad (4.4)$$

which is valid for the cone and plate geometry. However, in case of parallel plates, the Eq. 4.5 has to be used:

$$\sigma_R = f(R, \dot{\gamma}_R) = \frac{T}{2\pi R^3} \left[ 3 + \frac{d \ln T}{d \ln \dot{\gamma}_R} \right] \quad \ldots \quad (4.5)$$

It means that the torque dependence on shear rate has to be plotted, so $d \ln T / d \ln \dot{\gamma}$ can be determined. Then, the ‘true’ or corrected stress can be calculated (Eq. 4.5), and hence the corrected viscosity (Eq. 2.27). This procedure, known as Burgers correction, has a negligible effect at very low shear rates, where the slope $d \ln T / d \ln \dot{\gamma}$ is close to unity.

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With increasing shear rate, the corrected values become up to 5% lower than apparent viscosity (Fig. 4.10, - squares: uncorrected [apparent] viscosity, connected triangles: corrected viscosity):

Figure 4.10 Effect of the Burgers correction on viscosity results: SR200, MA4 at 230°C

4.2.2.3 Error analysis of steady shear measurements

It was shown above that the steady shear data obtained by using the SR200 were both repeatable and reproducible (+2% and ±5%, respectively). The applied corrections provide the accuracy required in flow characterisation. Nevertheless, there is still a degree of experimental uncertainty when measuring the steady shear viscosity of polymer melts that cannot be eliminated or corrected, which is a consequence of the uncertainty in measuring or controlling the instrument parameters listed in Table 4.3:

Table 4.3 Errors involved in the instrument parameters control for the steady shear measurements using SR200

<table>
<thead>
<tr>
<th>Errors</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp(°C)</strong></td>
<td>+/−0.1</td>
</tr>
<tr>
<td><strong>Torque(Nm)</strong></td>
<td>+/−0.0000001</td>
</tr>
<tr>
<td><strong>ω(rad/s)</strong></td>
<td>+/−0.10%</td>
</tr>
<tr>
<td><strong>Gap Height(mm)</strong></td>
<td>+/−0.10%</td>
</tr>
<tr>
<td><strong>Radius(mm)</strong></td>
<td>+/−0.50%</td>
</tr>
</tbody>
</table>
Knowing the parameters in Table 4.3 (obtained from the SR200 manual), one can calculate the contribution of each of them to the total error of measurement. The effect of temperature can be evaluated using the Eq. 2.28 and an average value of $E_a$ for PP ($\approx 40$ kJmol$^{-1}$). Torque, $T$ is taken in account for calculating the shear stress (Eq. 4.5); angular velocity, $\omega$ and gap height, $h$ are used to calculate shear rate (Eq. 4.6) and the plate radius, $R$ is involved in both equations.

$$\dot{\gamma}_R = \omega R / h \quad \text{...} \quad (4.6)$$

The total experimental error, $\bar{x}$ can be calculated from the partial errors, $\bar{x}_1, \bar{x}_2, \ldots$ using the equation:

$$\bar{x} = \sqrt{\sum_i \bar{x}_i^2} \quad \text{...} \quad (4.7)$$

Using the data from Table 4.3 it was calculated that the uncertainty of the SR200 measurements was not greater than 0.5%, which is a high level of precision. Since the repeatability of $\pm 2\%$ was achieved in the practical work, it can be stated that the contribution of sample preparation and other experimentation errors were also low.

### 4.4.3 Steady shear measurements using capillary rheometers

A single-point viscosity test, known as a melt flow rate or melt flow index (MFI), was performed on the PP grades using the melt flow indexers described in Section 3.2.5.1. The measurements of melt viscosity at temperatures $190^\circ, 210^\circ, 230^\circ$ and $250^\circ$C in the shear rate range of approx. $1 - 10,000$ s$^{-1}$ were conducted using the Davenport capillary rheometer (Section 3.2.5.2).

#### 4.4.3.1 Melt flow index (MFI) measurements

The MFI was determined using the following procedure: the barrel of the apparatus was filled with polymer pellets where they were allowed to melt for 6 minutes; polymer melt was then extruded under the 2.16 kg load. The polymer strand was cut at 60s intervals.
After cooling, the cut strands were weighed using a three decimal places balance (±0.001g). The MFI values were taken as the average mass of five sample cuts, multiplied by 10. The tests were performed twice using the Ceast Modular Flow Indexer and once with the Davenport Flow Indexer.

The tests performed with Ceast MFI showed good repeatability (0 – 5 % relative difference); compared to manufacturer’s values, both instruments gave lower results, but the Davenport results were closer (<10% RD). The most difference between experimental and manufacturer’s values was noticed for MA2. As stated by manufacturers, the MFI values are not to be considered as product specifications. They are only a qualitative indicator of melt’s flowability at typical extrusion conditions.

The Ceast MFI measurements were also utilised to determine the melt density at 230°C. It was facilitated by measuring the time for which the load travels between two labels. The corresponding volume was given in the manual, so the volumetric flow index (VFI) could be calculated. The melt density was then calculated using the equation:

\[ \rho [g/cm^3] = \frac{\text{MFI [g/10min]}}{\text{VFI [cm}^3/10\text{min]}} \]  \hspace{1cm} (4.8)

4.4.3.2 Capillary rheometry using Davenport Ram Extruder

Capillary measurements were conducted at temperatures 190°C, 210°C, 230°C and 250°C for the PP homo-polymers and some of the co-polymers (MA1 and MA2). Most co-polymers were characterised by capillary measurement at 230°C (SEP, DPB and TEPB), while the tests with EP1 blends were performed at 190°C, 230°C and 250°C. All experiments were carried out in accordance to the standard procedure (Davenport Ram Extruder Manual): the barrel was filled with polymer pellets that were pushed by the piston until the pressure reached 2% of the full-scale deflection (FSD). This was repeated twice in order to eliminate trapped air and to enhance the melt homogeneity. The tests were started 15 minutes after the instrument loading had begun by setting the lowest value of the piston speed. After taking the pressure reading, the piston speed was doubled, which allows collecting equidistant points on a logarithmic plot. The linear velocity of the melt, \( V \) was calculated from the piston speed using the calibration given in the manual and the pressure drop, \( \Delta P \) was calculated from the voltmeter readings using the calibration provided by
transducer manufacturer. The apparent shear rate ($8V/D$) and the apparent shear stress were calculated using the equations 4.9 and 4.10, respectively.

$$
\dot{\gamma}_w = \left( - \frac{d\nu}{dr} \right)_w = \frac{8V}{D} \left[ \frac{3n'+1}{4n'} \right] = \frac{4Q}{\pi R^3} \quad \ldots \quad (4.9)
$$

$$
\sigma_w = \frac{\Delta PD}{4L} = \frac{\Delta PR}{2L} \quad \ldots \quad (4.10)
$$

The correction for non-Newtonian behaviour, known as Rabinowitsch-Moony correction, was applied by calculating the slope of the $ln$(stress) vs. $ln$(shear rate) relationship, according to Eq. 4.11 [Berli and Deiber, 2001]:

$$
n' = \frac{d \ln(\Delta PD / 4L)}{d \ln(8V / D)} \quad \ldots \quad (4.11)
$$

The corrected shear rate was then re-calculated using the Eq. 4.9. Bagley correction for elastic (entrance) effects was applied by plotting the pressure drop vs. L/D at three apparent shear rates (usually 48, 96 and 192 s$^{-1}$). From the graph, known as the Bagley plot (Figure 4.11), the ‘extra length’ X was taken and the shear stress was recalculated by replacing the die length, L with (L+X) in the Eq. 4.10.

![Figure 4.11 Bagley plot, pressure drop vs. L/D ratio at apparent shear rates: 1) 48s$^{-1}$, 2) 96s$^{-1}$ and 3) 192s$^{-1}$](image)

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The effects of two corrections are shown in Figure 4.12; it can be seen that both effects were more pronounced at higher shear rates/stresses. For most of the grades, the corrections for non-Newtonian behaviour shifted the experimental data points to the higher shear rates by 10 - 30%. The extra length X was generally found to be in the range of 0.5 - 2 mm, which shifted the viscosity curve downwards by 10 - 40%.

![Figure 4.12 Effects of corrections on capillary measurements (SEP at 230°C, 2/32 die): squares- uncorrected data; diamonds- Rabinowitsch-Mooney; triangles- Bagley correction](image)

Other sources of error were also taken in account. To verify the effects of viscous heating, a hole was drilled in the die so the thermocouple tip can fit in. Temperature was monitored during extrusion at high shear rates and the increase was found to be less than 0.5°C, which is lower than the limits of possible temperature control (± 1°C). It is known that the wall-slip could occur in the capillary extrusion [Han, (1976)]; the effect was evaluated by plotting the shear stress against the apparent shear rates, using dies with same L/D ratios. The results for TN1 at 230°C, using four different dies with the L/D = 16, are presented in Fig. 4.13. It can be seen that all curves were superimposed on each other, which means that the correction for wall slip was not required [Hatzikiriakos, (1991)]. That was in agreement with results of other authors [Kazatchkov and Hatzikiriakos, (1994)], who found that wall slip effects were negligible for PP melts.
Figure 4.13 Evaluation of wall slip effect using *stress-apparent shear rate* plot

The maximum shear rate for accurate measurements by the apparatus was around 10,000 s\(^{-1}\). Above that value, the extrusion became unstable, which impeded the pressure readings in case of low-viscosity melts, or even caused the melt fracture of high viscosity melts.

### 4.4.4 Dynamic shear measurements

Testings of polymer grades in dynamic (oscillatory) shear mode were conducted by using the stress-controlled rheometer SR200. To assure the maximum accuracy of the results, tests were performed following the widely accepted recommendations of The National Physical Laboratory, UK [Rides and Allen, (1996)]. Due to the test duration, thermal stability of the samples had to be tested; the region of linear viscoelasticity was determined at several frequencies and temperatures. The dynamic frequency sweeps were then carried out for polymer grades at temperatures 190°, 210°C, 230°C and 250°C.

#### 4.4.4.1 Thermal stability of PP melts

Rheological measurements can be utilised to verify if the sample undergo thermal degradation during the tests at elevated temperatures. That was achieved by doing the *Time Sweeps*; in that kind of test, both temperature and frequency are kept constant and
any rheological property (usually $G''$) is monitored. If the tested variable remains constant within accepted limits (e.g. ±2%) during the test time, the effect of degradation on the results can be neglected. For PP grades it was found that the rheological properties ($G'$ and $G''$) were constant over the 60 minutes period, at 230°C and in the inert atmosphere (nitrogen).

### 4.4.4.2 Determination of the linear viscoelastic region

By definition, the linear viscoelastic properties are independent on strain; in dynamic testings, this is achieved by conducting the tests in the region of strains for which the dynamic moduli remain constant in the Stress Sweeps. The typical results of the stress sweeps are shown in Fig. 4.14. As the oscillatory stress (at chosen frequency) increases, the strain increases as well, while modulus remains constant until a sudden drop at higher strains (Fig. 4.14 left). For accurate determination of the viscoelastic region, it is beneficial to plot the $G'$ vs. strain (using linear y-axis, Fig. 4.14 right).

![Image of stress sweeps](image)

Figure 4.14 Determination of the linear viscoelastic region by doing stress-sweeps: $G'$ and strain vs. stress (left); $G'$ vs. strain (right)

The stress sweeps were conducted with typical polymer grades (MA3- homopolymer, MA2- copolymer and EP1- blend), at temperatures 190 - 230°C, using the frequencies 0.1, 1 and 10 rad/s. The linearity of measured viscoelastic properties was found for the strains in the range of 5 - 15% (both homo- and co-polymers). The blend EP1 was found to have a narrower viscoelastic region, i.e. 8 - 12%.
4.4.4.3 Dynamic frequency sweeps

The SR200 rheometer can perform dynamic shear measurements in the frequency region of $1 \times 10^5$ - 500 rad/s. The test set-up for PP grades specified the lower frequency limit of 0.01 rad/s, which allowed the tests to be completed in approx. 60 minutes. In that manner, the degradation effects were eliminated (Section 4.4.4.1). Analysis of the results showed that above frequencies of approx. 300 rad/s, the desired level of strain could not be achieved, due to the instrument inertia. Such data points were neglected. The tests were repeated at least twice to verify the repeatability of the measurement; the reproducibility of the results was checked by using the same instrument, but different geometries (cone and plate), over a long period of time and using the samples prepared with different moulds.

The repeatability of the measurement was found to be in the range of 2 - 5%, while the tests could be reproduced within the range of 3 - 7%. The partial errors approach was used to calculate the measurement uncertainty (as it was performed in Section 4.2.2.3), which was found to be less or equal to 1.0%. The level of precision and repeatability achieved was astonishing, compared to the results of the round robin study mentioned before [Rides and Allen, (1996)], where the repeatability of 4 – 8% and reproducibility of 21 – 32% were achieved.

4.4.5 Extensional Viscosity Measurements

The transient (start-up) viscosity measurements were carried out using the two extensional rheometers: the RMIT Extensional Rheometers at temperature of 180°C and strain rate of 0.1 s$^{-1}$ and the RME at temperatures 180°, 170° and 165°C using the strain rates of 0.01, 0.1 and 1.0 s$^{-1}$.

4.4.5.1 Sample preparation for the extensional viscosity measurements

To prepare the samples for the extensional rheometers, one has to ensure that they are uniform in terms of dimensions, homogeneous (void-free) and stress-free. For two extensional rheometers, different sample geometries were used:
The RMIT Rheometer required circular rods, usually prepared by extrusion in case of polyethylene. This technique was not useful for PP, due to its’ higher crystallinity and non-uniform cooling, which caused void-formation. For that reason, the double-stage compression moulding technique was optimised: polymer grades were first compression moulded into plaques at 200°C that were then cut into square rods. Finally, the circular rods were produced by compression moulding the square rods using a circular mould at approx. 165°C. The rod samples produced had a sufficient test length (≥245mm) and diameter of 7.3 - 7.5mm. This was a slow procedure, but the one that ensured a homogeneous sample.

Sample preparation for the RME was performed by compression moulding of the PP granules using smooth finished mild steel moulds. The procedure described in Section 4.4.1 for sheet compression moulding was modified as follows: moulding temperature 200°C, pressure 20 tons/5” diam. ram, slow cooling under pressure for min. 30 minutes. The process was optimised by trial and error approach and it assured production of flat, homogeneous and relatively stress-free plaques, 1 - 2 mm thick. The samples for the RME testings were cut using a sample cutter into rectangular bars (Fig. 4.15) of following dimensions: $L_0 = 58 - 68$ mm, $W_0 = 6 - 8$ mm and $H_0 = 1 - 2$ mm.

![Image of polymer sample](image)

Figure 4.15 Polymer sample for extensional viscosity measurements using the RME

The homogeneity of the samples for both rheometers was checked by using an optical microscope. If any voids or granule boundaries were found, the samples were rejected. The samples were also tested for presence of residual stresses. Randomly chosen samples were placed into a hot silicon oil bath (at approx. 200°C). Under such conditions, the stress relaxation causes changes in sample geometry. With the samples produced as above, the only significant change noticed was increasing the volume, due to the change in density.
The PP homo-polymer samples for testing at 165°C underwent a further treatment: they were re-melted in the oven at 180°C for 2-3 minutes and quenched in ice-cold water. The reason for that was to assure identical thermo-mechanical history of the samples that would be tested in the semi-molten state. So produced samples corresponded more closely to the conditions present in the BOPP processing (quenching the extruded tube).

4.4.5.2 Extensional viscosity measurements using the RMIT rheometer

The RMIT extensional rheometer was used for measuring the transient extensional viscosity of the polymer melts at 180°C and strain rate 0.1 s⁻¹. A schematic of the rheometer is given in Figure 2.34. The test sample is placed in a silicone oil bath and allowed to reach the equilibrium test temperature (15 minutes). The test is commenced with the floating sample being drawn down between the two counter rotating rollers at a constant strain rate with the other end attached to a linear variable differential transducer (LVDT). The polymer melt is stretched until the sample ruptures with the force being continuously recorded. Data were collected using the DTWin data acquisition program, which recorded force readings (mV) from the LVDT at 0.2-second intervals. The low viscosity nature of the PP melts yielded low force readings even with a very sensitive force-measuring device. Background noise for a typical force reading result shown in Figure 4.16 for TN1 was smoothed by applying the Fast Fourier Transform (FFT) using Table Curve TCWin Software. An 8mm video camera was used to record the sample extension and images were downloaded for analysis using GrabIT™ Pro software. The scatter of the data was due to the difficult determination of the sample diameter at any point during the deformation. The results seemed to be independent of the polymer tested. The fact that the error in deformation was quite similar for different grades (PP, copolymers, PE) suggested that the error is an instrument or technique error, associated with drawing the polymer melt from one end. The deviation at small strains (ε < 1) was quite low, but at higher strains the actual strain was significantly lower than the nominal value, for approx. 30%. A second order polynomial was used to fit the measured strains and to correct them (Fig. 4.17).
Figure 4.16 Tensile force measurements using RMIT Extensional Rheometer

Figure 4.17 Corrections for strain in extensional viscosity measurements

From the measured force and corrected strain rates, the extensional viscosity was calculated using the equation 2.42, where the initial area $A_0$ was calculated from the measured rod diameter $d$, $A_0 = \pi d^2 / 4$. 
4.4.5.2 Extensional viscosity measurements using the RME

Extensional viscosity of polymer grades at nominal strain rates 0.01, 0.1 and 1.0 s\(^{-1}\) was measured using the RME, at temperatures 180°, 170° and 165°C. A sample (Fig. 4.15) was fit into the RME stretching device (Fig. 3.5) in a way that provides a uniform stretching. It means that the belt tongues were properly placed to prevent sample from sticking to the table, through which the flow of hot nitrogen was maintained as a source of additional cushioning. When testing the low viscosity melts (PP at temperature 180°C), the spacers (pins), 0.5 mm thicker than the sample are placed on the clamps to prevent squashing the molten samples during clamping. The strain rate acting on the sample during testing is calculated from the Eq. 2.41, with \(L_0\) measured as equal to 54 mm. The cross-sectional area of a sample at experimental temperature can be estimated from the dimensions measured at room temperature (\(W_0\) and \(H_0\)) using the Eq. 4.12:

\[
A_0 = H_0 W_0 \left(\frac{\rho_0}{\rho_T}\right)^{\frac{2}{3}}
\]

\[\ldots\] (4.12)

The melt density at temperature \(T\) can be estimated from the following equation:

\[
\rho_T = \frac{1}{1.1402 + 0.00094 \times T(°C)}
\]

\[\ldots\] (4.13)

Corrections to strain rate were performed at several melt temperatures and nominal strain rates. Procedure employed to measure the actual strain rate was similar to the technique utilised with the RMIT Extensional Rheometer (Section 4.4.5.2). Stretching of the sample was monitored using a digital video system (Sony TRV 120; 450 digital zoom) controlled by the EZYDV\(^\circledR\) software. It was possible to determine the true strain rate from the width of the samples, according to the relationship (Eq. 4.14):

\[
W(t) = W_0 e^{-\epsilon t/2}
\]

\[\ldots\] (4.14)

Another purpose of the video footage was to determine whether the sample was drawn uniformly (Fig. 4.18). The technique has been widely accepted by many authors involved in extensional rheology [Meissner and Hostettler, (1994); Schweizer, (2000); Schulze, (1998)]. The correction for strain rate seemed to be a systematic instrument error,
independent of polymer type. When testing the low viscosity melts (PP homo-polymers at 180°C and co-polymers at any temperature), only the lower belts were employed for stretching and there was no need to make corrections for strain rate. That was found to be very beneficial when the maximum tensile force was less than 5cN in the experiments. In other cases, the top belts should be used to provide clamping and uniform stretching. The actual strain rate in case of using top belts was found to be 11 - 13% lower than the nominal strain rate, which was used to correct the experimental data.

![Image Description](image.png)

Figure 4.18. Typical extensional flow of a polymer melt (TEPB, 165°C, 1.0 s⁻¹)

### 4.4.5.3 Reliability of extensional viscosity measurements

The corrections described above were intended to provide the maximum level of accuracy in measuring extensional viscosity of PP melts. Nevertheless, there is a degree of uncertainty of measurements that cannot be avoided. The maximum precision in controlling the instrument parameters can be obtained from the RME Manual; the precision of measuring the sample dimensions can also be estimated (±0.2 mm) and used to calculate the partial errors. By using the Eq. 4.7, the total uncertainty of the RME measurements was found to be approx. 8%, which is much lower precision compared to rotational shear rheometers. The expected error is greater at the commencement of the test (low strain data), then decreases and remains constant until the strain of 4. At higher strains, the error can be above 15%, what suggests that the data at such strains should be neglected. The repeatability of the results was verified by repeating the tests at least twice and it was found to be in the range of 10 - 15%. This is higher than the estimated error from the
instrument and technique uncertainties, which can be attributed to the differences in the thermo-rheological history of the samples.

Since there is no standard material for which the extensional viscosity is known, the most suitable procedure for evaluating the accuracy of the measurements is reproducing the results obtained from shear rheometry, according to Eq. 2.36. The transient shear viscosity curves can be obtained by start-up flow experiments (step-rate tests, Section 4.4.2.1) or calculated from the relaxation spectra using the Eq. 2.64. The fair agreement of $\eta_e$ with $3\times \eta$ is an indicator of accuracy achieved by measurements. Figure 4.19 presents the typical situation in evaluating the experimental results:

![Graph showing viscosity over time](image)

**Figure 4.19** Repeatability and reproducibility of extensional viscosity, MA3 at 180°C

Transient extensional viscosity of MA3 was measured at nominal strain rate of 1.0 s$^{-1}$ and at temperature of 180°C. Two runs were performed and the raw data (open symbols) were corrected using the actual strain rate (0.87 s$^{-1}$). The corrected data (full symbols) were compared to three-fold transient shear viscosity, obtained from a step-rate test (line). A good repeatability of two runs could be noticed. At strains (equal to strain rate × time) between 0.3 and 1.1, the extensional measurements were also reproducible with shear results. Small disagreement at low strains was probably attributed to experimental errors in both modes, i.e. low torque in shear and inaccurate time in extension. The positive
deviation of extensional curves from the three-fold shear curves is a phenomenon referred to as strain hardening (Section 2.4.5). Strain hardening behaviour is not easy to quantitate; it is convenient to use a ratio of extensional viscosities at strains, eg. 3 and 1. Such an index can be used for comparative purposes. Additionally, the reproducibility of the measurements can be tested by participating in the round-robin tests with other laboratories, using the same or different instruments to measure the extensional viscosity of the same grade at same conditions. Such a test was achieved for a LLDPE grade Dow PL1880 at 150°C and it was found that both RMIT Extensional Rheometer and the RME at RMIT produce results reproducible within 10% with other laboratories. However, the former one showed the highest degree of ‘artificial’ strain hardening, so the more accurate and easier to use RME was accepted for characterisation of polymer grades in this study.
5. RESULTS AND DISCUSSION

5.1 GEL-PERMEATION CHROMATOGRAPHY

Polypropylene homo-polymer and co-polymer grades were analysed by GPC - SEC and their MWD curves were compared. Calculated MW averages allowed the quantitative meaning of comparisons. No branching (LCB) was found in any of the grades. The nature of the EP1 modifier was revealed and the MWD of its PP component was determined.

5.1.1 MWD of polypropylene homo-polymer grades

The MWD curves obtained for PP homo-polymer grades are shown in Figure 5.1:

![Figure 5.1 MWD curves of PP homo-polymer grades](image)

The GPC analysis of TN2 was performed and the obtained results matched completely with the TN1 results, which agreed with the manufacturers specifications. TN2 was a nucleated version of TN1; the nucleating agents are low-MW compounds, added in a low concentration, which cannot significantly influence the GPC results. For clarity, the GPC data for TN2 were omitted from Figure 5.1 and Tables 5.1 and A1. Complete list of numerical values of MW averages and polydispersities are given in Table A1. The most
important MW moments are comprised in Table 5.1, so a quantitative comparison became possible.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
<th>Mw/Mn</th>
<th>Mz/Mw</th>
<th>[η]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM1</td>
<td>52,130</td>
<td>279,330</td>
<td>801,990</td>
<td>5.36</td>
<td>2.87</td>
<td>1.36</td>
</tr>
<tr>
<td>TN1</td>
<td>54,990</td>
<td>282,270</td>
<td>844,130</td>
<td>5.15</td>
<td>2.99</td>
<td>1.38</td>
</tr>
<tr>
<td>MA4</td>
<td>49,960</td>
<td>313,030</td>
<td>1,063,620</td>
<td>6.33</td>
<td>3.40</td>
<td>1.50</td>
</tr>
<tr>
<td>MA3</td>
<td>48,050</td>
<td>385,300</td>
<td>1,420,340</td>
<td>8.06</td>
<td>3.69</td>
<td>1.75</td>
</tr>
</tbody>
</table>

From Table A1, one can conclude that determination of MW averages was performed with a high level of repeatability (1.5-2.5%). The polydispersity (Mw/Mn) results were less consistent, especially in case of MA3 (8.7%) and MA4 (11.2%); this was due to the broadness of their peaks that obstructed the accurate integration. Comparison of the results with the data obtained from the Waters Laboratories in Milford, USA (Table A2) showed relatively good reproducibility of the GPC tests at RMIT University. The relative difference between Mw averages was found to be in the range 0-10% (with 95% confidence), whilst for the polydispersity the range was 3-14% (95% confidence). Two extreme differences were found, i.e. for Mw of MM1 (15%) and complete results for MA2 (>20%). The results obtained in our laboratories were averages of min. 3 runs (×2 injections) obtained during a period of time when the instrument was under constant statistical control using the PE standards (Section 4.1.2), which gives confidence in their maximum possible accuracy.

It can be seen from Fig. 5.1 and Table 5.1 that two of the PP grades (MM1 and TN1) possessed very similar molecular weight distributions. They are both known as standard BOPP processing grades, obtained from different manufacturers. The other two PP grades showed slightly lower Mn, but higher Mw and consequently broader distribution. The most significant was the difference in z-average molecular weight (Mz): TN1 had slightly higher Mz than MM1 (5%); the value for MA4 was significantly higher (33% higher than MM1), while the Mz of MA3 was 77% higher than Mz of MM1.

These figures revealed the assumptions the manufacturers had when designing the polymer’s molecular structure (Section 2.4): increase in polydispersity would lead to more
pronounced shear thinning, i.e. easier extrusion; higher \( M_w \) (and especially \( M_z \) or high MW tail) would cause better extensional and final film properties. This will be discussed in details in later sections, after the rheology data would be presented. In reality, it is not easy to evaluate the influence of MWD on overall BOPP processability (source: UCB Films). There is an impression that TN1 gives better films than MM1 (which can be only explained by higher \( M_z \)); although promising for providing excellent film properties, MA3 is extremely difficult to process. No information was available for MA4, but according to its MWD, it could be the best choice for BOPP processing, after complete evaluation of its rheological properties.

### 5.1.2 MWD of propylene co-polymer grades

Six polypropylene co-polymer grades were analysed by GPC and the complete results are given in Table A1. Table 5.2 shows the most important \( M_W \) moments and polydispersity indices. The grades in Tables are sorted according to their \( M_w \) averages. First two of them (MA5 and MA1) were heterophasic co-polymers with unknown amount of ethylene-propylene rubber. The other four were known to be random co-polymers (ethylene-propylene – SEP and MA2, butylene-propylene – DPB and ethylene-butylene-propylene – TEPB), designed for use as coats for PP films, i.e. for co-extrusion.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mn</th>
<th>( M_w )</th>
<th>( M_z )</th>
<th>( M_w/M_n )</th>
<th>( M_z/M_w )</th>
<th>([\eta])</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA5</td>
<td>27,670</td>
<td>120,710</td>
<td>378,800</td>
<td>4.38</td>
<td>3.14</td>
<td>1.23</td>
</tr>
<tr>
<td>MA1</td>
<td>43,800</td>
<td>249,700</td>
<td>830,310</td>
<td>5.70</td>
<td>3.33</td>
<td>1.50</td>
</tr>
<tr>
<td>DPB</td>
<td>69,820</td>
<td>264,400</td>
<td>622,150</td>
<td>3.81</td>
<td>2.35</td>
<td>1.33</td>
</tr>
<tr>
<td>SEP</td>
<td>60,470</td>
<td>277,270</td>
<td>1,014,520</td>
<td>4.59</td>
<td>3.66</td>
<td>1.40</td>
</tr>
<tr>
<td>MA2</td>
<td>71,460</td>
<td>285,250</td>
<td>711,590</td>
<td>4.05</td>
<td>2.50</td>
<td>1.42</td>
</tr>
<tr>
<td>TEPB</td>
<td>71,640</td>
<td>288,550</td>
<td>691,250</td>
<td>4.03</td>
<td>2.40</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Special care was taken in detecting the possible presence of long-chain branching (LCB) in ‘flexible co-polymers’ (MA1 and MA5). No LCB was found, probably due to the small amount and limited length of the cross-linking chains, that could not be detected by deviation of intrinsic viscosity from the Mark-Houwink fit. The repeatability of the GPC results was very good for \( M_w \) (0.3 – 3.9%) and satisfactory for \( M_w/M_n \) (1.0 – 7.0 %, excluding MA2 with standard deviation of 13%). The results were also reproducible with
data from Waters, USA, except for MA2 (> 20% relative difference). The MWD curves are shown in Figures 5.2 (MA1 and MA2) and 5.3 (random co-polymers):

Figure 5.2 MWD curves of MA1 and MA5

Figure 5.3 MWD curves for random co-polymer grades

MA5 was the grade with the lowest MW averages; its peak was smooth and symmetrical, not showing any influence of chemical composition distribution (CCD) on the MWD. MA1 was with the second lowest Mw, but closer to the other grades. Its MWD was the
broadest amongst co-polymers. No evidence could be found in GPC analysis that would suggest a different structure of these grades compared to the other ones. The random co-polymers were all very similar in terms of their MWDs, except SEP that was slightly broader. Most Mn values were higher than for the PP homo-polymers, which led to lower polydispersity (Mw/Mn in the range 3.8 – 4.6). DPB possessed the highest Mn, but low Mw and especially Mz. That made it the grade with the narrowest MWD out of all analysed polymers.

5.1.3 MWD of EP1 blends

The chromatogram shown in Fig. 2.16 was obtained for the EP1 grade. The broad, intensive peaks at low retention times belonged to PP component of the master-batch. The other component, HOCP was evident as a negative dRI peak and a weak viscometer peak at high retention times. The peaks of two components were resolved well, which allowed the separate analysis of the components. The MWD of the PP component is shown in Figure 5.4; the MWD curves of MM1 and MA3 were also added to the graph, to allow analysis in relation to their blends with EP1.

![Figure 5.4 MWD curves of EP1 (PP component), MM1 and MA3](image_url)

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The MW averages and polydispersities of PP component of EP1 are listed in Table 5.3. The MWD of HOCP could not be determined, since its peaks were in the region close to total permeation. Still, it could be estimated that the M\text{Peak} of HOCP was less than 1,000.

Table 5.3 MW moments of the PP component of EP1

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
<th>Mw/Mn</th>
<th>Mz/Mw</th>
<th>[η]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP1</td>
<td>82,450</td>
<td>386,570</td>
<td>1,361,920</td>
<td>4.71</td>
<td>3.52</td>
<td>1.80</td>
</tr>
</tbody>
</table>

It can be seen that the PP component of EP1 possessed high Mw and Mz values that were very similar to MA3. However, it was much narrower; its shape looked more like the MWD of MM1, but shifted to higher MW end. From these data, it can be predicted that the blends of EP1 with MA3 will have very similar Mw and Mz, but the decreasing polydispersity with increasing %EP1. The blends of MM1 with EP1 are expected to show the increase in Mw and Mz with increasing %EP1, without much difference in polydispersity. The MWDs of the blends can be calculated, using the equation:

\[
f(d \log M_i) = w_1 f_1(d \log M_i) + w_2 f_2(d \log M_i)
\]  

(5.1)

where \( w_1 \) and \( w_2 \) are the weight fractions of the blended polypropylenes and \( f_1 \) and \( f_2 \) the corresponding distributions (dW/dlogM of the \( i^{th} \) slice). The calculated curves are presented in Figures A1 (MA3/EP1 blends) and A2 (MM1/EP1 blends). In both cases, the GPC analysis of 50wt%/50wt% blends was carried out. A very good agreement between experimental and calculated curve was found. The molecular characteristics of the blends are providing the basis for understanding of their rheological behaviour, discussed later in this chapter.

5.2 DSC ANALYSIS OF POLYMER GRADES AND BLENDS

Using the MDSC (Section 4.2), thermal analysis of the grades was conducted. The obtained results were utilised for the prediction of the measurement window in extensional rheology, for a structural study of the co-polymers and as an analytical tool for the morphological study on blends.
5.2.1 Thermal analysis of PP homo-polymer grades

PP grades (MA3, MA4, MM1 and TN1) were analysed as described in Section 4.2.1. The results are listed in Table 5.4:

<table>
<thead>
<tr>
<th>Grade</th>
<th>Tg</th>
<th>Tm</th>
<th>Tc</th>
<th>ΔH</th>
<th>% Cryst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM1</td>
<td>-10</td>
<td>163.5</td>
<td>122.4</td>
<td>80.3</td>
<td>38</td>
</tr>
<tr>
<td>MA4</td>
<td>-14</td>
<td>165.6</td>
<td>127.6</td>
<td>111.2</td>
<td>53</td>
</tr>
<tr>
<td>MA3</td>
<td>-11</td>
<td>165.9</td>
<td>122.7</td>
<td>85.0</td>
<td>41</td>
</tr>
<tr>
<td>TN1</td>
<td>-9</td>
<td>166.0</td>
<td>117.6</td>
<td>87.1</td>
<td>42</td>
</tr>
</tbody>
</table>

The results in Table 5.4 are sorted by their Tm: it appears that the melting temperature of MM1 was the lowest and of TN1 the highest. Except MM1, all PP grades had Tm very close to each other (165.6°C - 166.0°C). There was more scatter in the crystallisation temperatures (117.6°C for TN1 - 127.6°C for MA4). The glass-transition temperatures were found to be in the range of -9°C to -14°C. All the results agreed with expected values for iPP. The enthalpy of melting (ΔH) was determined to be in the range of 80 - 111 Jg⁻¹, which corresponds to percentage crystallinity of 38% (MM1) – 53% (MA4). Typical behaviour of PP during heating is presented in Fig. 5.5:

![Figure 5.5 DSC heating curve of a polypropylene grade (MA4)](image)

Figure 5.5 DSC heating curve of a polypropylene grade (MA4)
The glass transition temperature of PP can be observed when the sample is heated from (or cooled to) low temperatures, such as -40°C. During heating, the mobility of polymer chains increases, which is reflected by a change in heat flow. The transition is weak and not sharp; that complicates the detection of Tg. In Fig. 5.5 the glass-transition region has been zoomed in for better viewing. The significance of Tg determination is in the estimation of products properties at low temperature: below their Tg, materials are brittle, which limits their use at low ambient temperatures. The heating curve becomes uneven again in the temperature range of 40 – 90°C. This is the result of reorganisation of PP chains from an unstable, mesomorphic state into a stable crystalline, α- form. This observation suggests that the fast cooled PP will undergo slow morphological changes, known as ageing, if it was not allowed to anneal. Another implication of the transformations in this region is that the melting peak observed at higher temperature represents the melting of the most stable α- form, regardless the previous thermal history of the sample. In that way, the DSC provides information of a material’s inherent crystallinity, but not the crystallinity of a sample itself.

Another characteristic of the melting behaviour of polypropylene can be observed from Fig. 5.5: unlike monomeric compounds, polymers don’t melt at an exact temperature, but in a broad temperature range. In the calorigram shown, one can see that the melting starts at around 120°C and finishes at around 170°C. The shape and broadness of the peak depends on the heating rate, but the area under the peak (that is proportional to the enthalpy of melting, ΔH*) remains more or less constant. This can be explained by recrystallisation: thinner crystals melt at lower temperature, but the polymer chains are easily incorporated into thicker crystals, which are thermodynamically more stable. With increasing temperature during the scan, the crystals can actually grow until they receive enough heat to melt. Such behaviour plays an important role in BOPP processing, where the quenched PP tube is reheated to below its melting point. The polymer at such conditions is in a semi-molten or rubbery state, which provides good extensional properties. When it’s been blown and stretched, the remaining crystallites get oriented that provides desired optical and mechanical properties of the product.

In spite of the limitations, DSC analysis can provide additional information on the samples with different thermo-mechanical history. As presented in Section 4.2.1, two TN1 samples
prepared for extensional viscosity measurements were analysed by mean of DSC and their endotherms are shown in Fig. 4.5. The numerical data are given in Table 5.5:

<table>
<thead>
<tr>
<th>TN1 Sample</th>
<th>Tm (°C)</th>
<th>Onset of Tm</th>
<th>% Cryst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Molded (1)</td>
<td>165.6</td>
<td>152°</td>
<td>46.0</td>
</tr>
<tr>
<td>Extruded (2)</td>
<td>164.0</td>
<td>134°</td>
<td>42.0</td>
</tr>
</tbody>
</table>

It was apparent that the fast-cooled, extruded sample (2) melted at lower temperature, which was not only observed from its Tm, but even more significantly from the onset of the peak (134°C). Sample 1, which was cooled slowly (and under pressure), started melting at much higher temperature (152°C), for its crystals had enough time to grow and pack more uniformly. The practical implication of the differences between two samples for extensional rheometry is that sample 2 could melt more easily in the rheometer and being stretched, while sample 1 was not stretchable at all.

5.2.2 Thermal analysis of co-polymer grades

5.2.2.1 DSC study on random co-polymer grades

A common melting behaviour of random co-polymers is shown in Fig. 5.6 (MA2). It shows the difference between PP homo- and co-polymers melting behaviour: - homo-polymer's melting peaks are usually single and occur at higher temperature (Fig. 5.5); - a co-polymer's melting peak is weaker, multiple and shifted to lower temperatures. The total enthalpy of melting (sometimes known as heat of fusion), ΔH*(MA2) was determined as equal to 46 Jg⁻¹, which corresponded to PP crystallinity of 22%. This was approx. equal to half of the PP crystallinity in homo-polymers. Low crystallinity of co-polymers can be explained by their structure (Sections 2.2.1 and 2.2.2); the presence of ethylene co-monomer disturbs the isotacticity of PP chains required for their packing into crystals. The crystals formed are thinner than in a homo-polymer, thus melting at lower temperature; apparently, the percentage of crystallinity is also lowered. The nature of multiplicity of the melting peaks is not completely understood [Feng, et al., (1998)], but it could be connected to the thermodynamics of recrystallisation processes during heating. The bimodality of
lamellar thickness distribution was probably not a case, since only a sharp, single crystallisation peak was detected (Fig. A4).

![Graph](image)

**Figure 5.6 Melting curve of a co-polymer grade (MA2)**

The other random co-polymers used in this study (SEP, DPB and TEPB) showed similar melting and crystallisation behaviour as MA2. In the first heating run (Fig. A5), only the single, broad peaks could be noticed. After crystallisation (traced by DSC as shown in Fig. A6), the multiple peaks occurred (Fig. A7). The results are summarised in Table 5.6:

<table>
<thead>
<tr>
<th>DSC 10°C/min</th>
<th>Melting Peaks</th>
<th>Crystallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>MA2</td>
<td>71.7</td>
<td>115.7</td>
</tr>
<tr>
<td>SEP</td>
<td>134.8</td>
<td>142.5</td>
</tr>
<tr>
<td>DPB</td>
<td>143.1</td>
<td>150.3</td>
</tr>
<tr>
<td>TEPB</td>
<td>91.4</td>
<td>133.0</td>
</tr>
</tbody>
</table>

It was observed that the butylene-propylene random co-polymer, DPB had the highest crystallinity, as well as Tm and Tc. The ethylene-containing co-polymers were very similar in terms of Tm and Tc, although there were differences in the shapes of the melting peaks. It appeared that the presence of second co-monomer in TEPB (butylene-ethylene-propylene co-polymer) could cause additional irregularities, which was reflected in its
lowest crystallisation and melting temperature. The presence of a broad peak in its thermogram, in the region of 60 - 100°C (Fig. A7) suggests that it solidified in less crystalline form than the other grades, but the recrystallisation during heating took place. The determination of the co-polymer’s Tgs was very difficult to perform, as can be seen from Fig A8. A very weak transition was observed in the region around ~25°C.

The thermal properties of random co-polymers for possible use in BOPP processing, obtained by DSC, can help in understanding what kind of behaviour should be expected during operation. All co-polymers are completely molten at bubble inflation temperature (160 – 165°C), which is not the case with homo-polymers. That can be very important in terms of the extensional viscosity, which will be discussed later. As mentioned before, the co-polymers provide the coats for the PP film. Apart from changing the surface properties of the film (such as sealability and printability), they could probably enhance film’s flexibility and clarity, due to their low Tg and crystallinity.

5.2.2.2 DSC analysis of MA1 and MA5

Two co-polymer grades, MA1 and MA5 belong to a different class of ethylene-propylene co-polymers. They were manufactured in a way that provided formation of a rubbery component (ethylene-propylene rubber, EPR) that was evenly dispersed in a polymer matrix. Although similar in appearance, two grades showed different behaviour in the DSC scans, which could be useful for understanding their rheological properties. While MA1 melting behaviour was similar to the type described for random co-polymers, MA5 showed two distinct peaks (Fig. 5.7). The numerical values of Tm and Tc are given in Table 5.7:

<table>
<thead>
<tr>
<th></th>
<th>Tm1</th>
<th>Tm2</th>
<th>Tc</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA1</td>
<td>140</td>
<td></td>
<td>99.2</td>
<td>37.5</td>
</tr>
<tr>
<td>MA5</td>
<td>123.5</td>
<td>164.1</td>
<td>108.1</td>
<td>75.5</td>
</tr>
</tbody>
</table>

The melting peaks detected for MA5 correspond to LLDPE (Tm1) and PP (Tm2). It was unclear whether the grade was an intimate blend or a block co-polymer, since both could yield similar DSC trace.
Figure 5.7 DSC melting curves of MA1 and MA5

In crystallisation, multiplicity was observed, as a difference to the random co-polymers where only the iPP was the crystallisable component. In Fig. A9, the second peak for MA1 was noticed. It was very weak, at around 73°C, which suggested that the PE block or phase was present in the crystallisable form. The main crystallisation peak of MA1 at around 99°C could be assigned to PP, with total crystallinity calculated as equal to 18%. This was the lowest level of crystallinity observed in the grades tested. The possible explanation would be that the EPR phase in MA1 was dispersed in the matrix of a random E-P co-polymer. In case of MA5, two phases or blocks were probably present in similar amount, as apparent from Fig. 5.7. The main crystallisation peak at 108.1°C in Fig. A9 could be assigned to eutectic PP/PE blend; it was interesting that the crystallisation started at higher temperatures, around 120°C, similar to pure polypropylene. This portion of PP probably crystallised from a PP-rich phase; after the inflection at around 113°C, the main peak was observed. During further cooling, the PE crystallisation occurred, creating a peak at 86°C. The percentage crystallinity of MA5 was as high as 36%. From a practical point of view, two different applications could be found for the above grades: MA1 could possibly serve as a coat with special surface properties or as a mid-layer in PE-PP laminates; due to high crystallinity, MA5 is the only co-polymer grade expected to be used as a core polymer, similar to homo-polymers. The advantage expected from a grade like MA5 is producing a flexible film.
5.2.3 DSC study of EP1 and its blends

The modifier grade EP1 was analysed as described in Section 4.2.3.1 and its composition was proved to be iPP/HOCP 50wt%/50wt%. A DSC study was carried out to investigate the influence of different thermal conditions on the PP/resin system. The blends of EP1 with two PP grades (MA3 and MM1) were also studied.

5.2.3.1 Thermal analysis of EP1

The effect of HOCP on BOPP film properties is well known (Section 2.2.5). To avoid problems with mixing, most polymer processors prefer using the master-batches, rather than pure resin. EP1 is such a master-batch, supplied in a granular form. The initial DSC tests on EP1 revealed that its melting temperature was below 160°C, which was significantly lower than for any pure PP grade. The Tg of EP1 was determined to be around 45°C and the percentage of PP crystallinity was around 20%, which was approx. half of the expected PP crystallinity. Since the % crystallinity was determined from the specific heat of melting (ΔH*, J/g), it appeared that HOCP did not effect the crystallinity of polypropylene, knowing that the weight fraction of PP in EP1 was one half, too. In other words, all crystallisable PP was normally able to crystallise, driven by thermodynamics of the process; due to the dilution of PP with an amorphous component, one could expect that the kinetics of the crystallisation would change. This was apparent from a very low Tc measured for EP1, around 112°C. The next important observation was the occurrence of a multiple melting peak in the second heating run. It was obvious that the presence of HOCP had a significant impact on the polypropylene’s behaviour in EP1. The DSC study described in Section 4.2.3.2 was conducted in order to gain better understanding of the influence of different thermal histories on EP1.

In Fig. A10, the first heating runs of four quenched samples are shown. Several comments could be made: -both samples quenched from 250°C showed broad, weak exothermic peaks in the region of 90° - 110°C that corresponded to the transition of mesomorphic to crystalline α- form (recrystallisation); such transitions were not obvious for the samples quenched from 200°. -The glass transition was much more intensive in the samples quenched from 250°C than in the later two; for the sample quenched in liquid nitrogen, the Tg was found to be approx. 24°C and for the sample quenched in water approx. 43°C (Fig.
5.8). The presence of only one Tg can be considered as an indication of miscibility in the EP1 melt at temperature of 250°C. It can be assumed that quenching from 250°C to liquid nitrogen forced most of the PP to remain in the amorphous state, where it was mixed with HOCP. Therefore, the Tg agreed well with the theoretical value calculated by Fox equation (2.17), using -10°C for the Tg of PP and 80°C for HOCP. In case of EP1 quenched in water, due to lower cooling rate and low thermal conductivity of PP, a portion of PP could have enough time to crystallise; that would lower its concentration in the amorphous phase and shift the Tg to higher value.

![Graph of Heat Flow vs Temperature](image)

**Figure 5.8 Glass transition region in the DSC scans of quenched EP1 samples**

The sample quenched from 200°C to water showed two glass transition peaks, which were expected for a phase-separated melt, but have never been detected previously (list of literature in Section 2.2.5). The two Tgs were at around 7°C (Tg₁) and 45°C (Tg₂). The sample quenched from 200°C to liquid nitrogen showed very similar DSC curve, with both glass transitions in the similar regions. This phenomenon can be accepted as a confirmation of the immiscibility in the EP1 melt at 200°C. Two Tgs can be explained by the formation of two amorphous phases: one polypropylene-rich (Tg₁) and the other HOCP-rich (Tg₂). The detection of such weak transitions was probably achieved due to the combination of two experimental conditions: -quenching from the appropriate temperatures provided sufficient amounts of amorphous phase and -high sensitivity of the modulated DSC technique allowed using the low scan rates without losing the resolution.
The above experiments had an important implication on the experimental procedures that were employed for the study of EP1 blends with PP grades: - the low scan rate was chosen (4°C/min); - samples were prepared by relatively fast cooling; - the glass-transition temperatures and single TmS were recorded in the first heating runs; - after crystallisation, the second heating runs were performed and the occurrence of multiple peaks was related to the blends’ compositions. Although the grade EP1 itself would not be used in BOPP processing, it was expected to use it as an additive to PP homo-polymer grades, i.e. as a blend; the relevance of the following study was to relate the changes in polypropylene’s behaviour to the blend’s composition.

5.2.3.2 DSC analysis of EP1 blends with MA3 and MM1

The blends of MA3 and MM1 with EP1 were prepared and investigated as described in Section 4.2.3.3. The results are shown in Table A3. The influence of blend’s composition on its Tg is represented in Figure 5.9:

![Graph showing Tg vs %EP1 for MA3/EP1 and MM1/EP1 blends with a linear trend line labeled Fox Eq.]

Figure 5.9 Glass-transition temperatures of the blends in dependence on composition

The plot in Fig. 5.9 is very similar to the one obtained in reference [Cimmino, et al., (1991)] (Fig. 2.23). One can see that the Tg was not influenced by the nature of PP component, but only by the percentage of EP1 (or HOCP). The experimental values were higher than those calculated from Fox equation (2.17). In terms of existence of two Tgs
(previous section), it can be assumed that in the blends only the $T_g$, which corresponds to the HOCP- rich phase, was measured.

The influence of EP1 concentration in blends on $T_m$ and $T_c$ is shown in Figure A11, and on percentage crystallinity in Figure A12. The drop in melting and crystallisation could be explained by kinetic factors, due to the dilution of PP in the melt. From Figure A11, it appears that the drop was more sudden at EP1 concentration of 50%. The total crystallinity (Fig. A12) was decreasing in a rather linear fashion with increasing EP1 concentration. As explained in the previous section, the crystallinity was calculated for the whole sample mass, which contained decreasing amount of PP with increasing %EP1. It can be shown that the crystallinity of PP itself was not affected, which could lead to a conclusion that the blends were either miscible or the PP could crystallise from both separated phases.

![DSC curves](image)

Figure 5.10 DSC curves (2nd heating run) for MA3/EP1 blends

Figures 5.10 and 5.11 show the melting behaviour of the blends during the second heating runs. It can be seen that pure PP grades and low concentration blends melt in the similar way as in the first run, i.e. the same type of crystals was formed regardless of crystallisation rate. With increasing EP1 concentration, the shape of the curves changed, and the multiple peaks occurred at EP1 concentration of 50%. Since all the samples were
prepared in the same way and the tests were run under the same conditions, it could be concluded that the difference between the samples was in the immiscibility for EP1 content of 50% and higher. As assumed before, during cooling, the PP from both phases could crystallise, but with different rate. Due to dilution, the PP in the HOCP-rich phase would crystallise slowly, which would allow more nucleation sites to be formed and the resulting crystals would be thinner than those formed in the PP-rich phase. Such crystals would melt at lower temperature and the crystals formed in the PP-rich phase would melt at higher temperature. This explains the splitting of the melting peaks; such behaviour could be noticed only with slow cooled samples, where such processes had enough time to happen. In the fast cooled samples, most of the PP would remain in mesomorphic phase that would recrystallise during heating and only a single melting peak would be observed.

Figure 5.11 DSC curves (2nd heating run) for MM1/EP1 blends

The tests presented above were found to be very useful in characterisation of PP blends with amorphous resins. From the practical point of view, the addition of such modifiers as EP1 would be in a small concentration, due to its cost. According to the results of this study, for the EP1 concentrations of up to 30-50%, the miscible blends would be obtained. The total crystallinity of such blends would be lower, as well as their Tm and Tc. The size of the crystals would also be affected, which would have implications on the polymer behaviour at the temperatures of bubble inflation in the process.
5.3 HOT-STAGE OPTICAL MICROSCOPY OF EP1 BLENDS

Thin films of EP1 and its blends were investigated using the hot-stage optical microscopy (HS-OM), which allowed visual observation of their melting, crystallisation and phase separation. In case of EP1, the unhomogeneity of the melt was observed. In Fig. 5.12, the phase separated melt became miscible during heating to 260°C; during cooling, the phase separation occurred again, in the form of droplets.

![Figure 5.12 HS-OM images of EP1: melt at 220°C (left); miscible melt at 250°C (middle) and phase separation during cooling (190°C, right)]

Further cooling led to crystallisation, shown in Fig. A13. The last two images in Fig. A13 were taken in polarised light, which allowed only the PP spherulites to be seen. The amorphous phase remained dark. The blends with low EP1 concentration showed no phase separation, as shown in Fig. 5.13 (MA3/EP1 85/15) and Fig. A14 (MM1/EP1 80/20). Similar behaviour was observed with the other blends of EP1 with its concentration of up to 30%. In the blends with %EP1 50 and higher, the phase separation was observed, similar to the image in Fig 5.12 (right).

![Figure 5.13 HS-OM images of MA3/EP1 85/15: 180°C (left) and room temperature (right)]

The optical microscopy runs were performed using the same heating and cooling rates as employed for the DSC tests. This allowed the visualisation of the effects hypothesised in
Section 5.2.3. Although it was employed as a qualitative technique, the HS-OM allowed confirming the phase separation of the following melts: MA3/EP1- 50/50 and 30/70, MM1/EP1- 50/50 and 30/70 and pure EP1. In case of miscible melts (%EP1 ≤ 30), it was noticed that the onset of crystallisation occurred at temperatures that decreased with increasing %EP1. There was also an impression that the amount of amorphous regions (dark areas in polarised light) increased and the size of the crystals decreased with increasing EP1 concentration. In general, the observation from optical microscopy agreed well with the conclusions from the DSC study of EP1 blends.

5.4 STEADY SHEAR RHEOLOGY OF PP GRADES AND BLENDS

Shear characterisation of polypropylene homo-polymers, propylene co-polymers and EP1 blends was carried out as described in Section 4.4. The flow properties of the grades were compared and related to their structure. The implications of the shear characteristics of the polymers on their possible use in BOPP processing were also mentioned in this section.

5.4.1 MFI testing of PP grades

The MFI, as defined in Section 4.4.3.1, is a single-point parameter that characterises the melt flowability. Most often, it is the only shear characteristic given in the product specifications supplied by the manufacturer. Although insufficient for any complete shear viscosity study, the value of the MFI can give an indication of what magnitude of viscosity can be expected at the conditions of MFI testing (temperature, moderate to high shear rate). For that reason, the MFI values obtained from the manufacturers were listed wherever they were available. In addition, the MFIs were determined experimentally for PP grades (Table A4). The melt density at the temperature of experiments (230°) was also determined (Eq. 4.6). Most of the grades had an MFI around 9.0; from Table A1, one can see that all these grades (MM1, TN1, TN2 and MA2) had very similar \( M_w \) (around 280,000). It was expected to observe lower MFI for MA3, due to its higher \( M_w \), which was confirmed experimentally (Tables A1 and A4).
The limitations of using the MFI values for prediction of polymer's molecular characteristics became evident in case of MA1 and EP1. From the empirical relationship between MFI and \( M_w \) (higher \( M_w \) – lower MFI), one can expect MA1 to have higher value than eg. MM1; also, EP1 could be expected to have the MFI similar to MA3. Experimental evidences were completely opposite, which can be explained by the role of another level of structure – morphology: MA1 is a heterophase PE-PP system, where the E-P rubber phase is dispersed in the polymer matrix, which increases the viscosity. In case of EP1, the high MW PP component is diluted with a low MW oligomer (HOCP); the melt is phase-separated and the viscosities of both phases (PP- rich and HOCP- rich) are lower than the hypothetical viscosity of pure PP. As a consequence, an extremely high MFI was measured for EP1.

### 5.4.2 Steady shear viscosity of polymer grades

Shear viscosity curves were obtained for polymer grades by combining the results of rotational and capillary rheometer measurements (Sections 4.4.2.2 and 4.4.3.2). Typical results are shown in Fig. 5.14:

![Figure 5.14 Steady shear measurements of MA3 at 230°C: symbols- data points; line- Cross model](image)

Figure 5.14 Steady shear measurements of MA3 at 230°C: symbols- data points; line- Cross model
The rotational rheometry results were corrected for parallel-plate geometry (Burger’s correction, Fig. 4.10); the capillary data were corrected for both non-Newtonian (Rabinowitsch-Mooney) and elastic (Bagley) effects (Fig. 4.11). The confidence in the accuracy of the measurements was gained by overlapping of the viscosities measured with three different dies (shear rate region of 10 - 1,000 s⁻¹). The most inaccuracy was present in the shear rate region of approx. 1 - 10s⁻¹. The reason for that was predominantly less sensitivity in the low-pressure readings with the capillary rheometer.

To obtain viscosity as a smooth function of shear rate, the simplified Cross model (Eq. 2.63) was applied to experimental data (line in Fig. 5.14). This allowed the estimation of the zero shear viscosity, \( \eta_0 \); the infinite shear viscosity region (Fig. 2.28) was not reached for any of the materials tested. The values of Cross model parameters, \( \eta_0, K \) and \( m \) are listed in Table A5. The tests were initially conducted at temperatures 190°, 210° and 230°C. Additionally, the measurements were carried out at the temperature of 250°C, because of the relevance of higher temperatures (230° - 250°C) for the polymer extrusion in BOPP processing. The effect of temperature on viscosity of MA3 can be seen from Fig. 5.15 and for the rest of the homo-polymer grades in Figs. A15 - A18:

![Viscosity vs Shear Rate](image)

Figure 5.15 Shear flow curves of MA3 at temperatures 190°, 210°, 230° and 250°C (full symbols - SR200, open symbols - capillary, line - Cross model)
With increasing temperature, the viscosity decreased. The Newtonian plateau was found to be wider at lower temperature, as the polymer melts became more liquid-like. This can be expressed quantitatively by the Cross model parameter $K$ that decreased with temperature, which shifted the onset of shear thinning towards higher shear rates. The slope of the viscosity curve, expressed by the parameter $m$ of the Cross model, was relatively constant at all temperatures for all polymer grades. This phenomenon caused the flow curves in Fig. 5.15 to remain parallel with change in temperature.

5.4.2.1 Comparison between viscosity curves of PP homo-polymer grades

A comparison between shear viscosity curves of PP homo-polymer grades at 230°C is presented in Fig. 5.16 and at other temperatures (190°C, 210°C and 250°C) in Figures A19-A21:

![Figure 5.16 Shear viscosity curves of PP grades at 230°C](image)

Several conclusions could be made: -the most viscous polymer in the low shear rate region, at all testing temperatures was MA3, followed by MA4; the other PP grades (TN1, TN2 and MM1) showed very similar viscosities. The order of zero shear viscosities could be expressed with the following list: MA3 » MA4 »(TN1 ≡ TN2) ≥ MM1. The grades showed different degree of shear thinning; those with the highest $\eta_0$ were also the most
shear thinning. Thus, the difference between viscosities at high shear rates was less pronounced. The difference in shear thinning behaviour was reflected in different values of parameter $K$ (Table A5), while the slopes ($m$) were very similar. So, the flow curves looked rather parallel in the high shear rate region (100 - 10,000 s$^{-1}$). The rheological behaviour of PP grades was in a good agreement with their MW parameters obtained from GPC analysis (Section 5.1.1): MA3, the grade with the highest $M_w$ and $M_z$ averages, showed the highest zero shear viscosity. It was followed by MA4, the grade with the second greatest $M_w$ from Table 5.1. Two of the grades with the same MWD (TN1 and TN2) were almost identical in steady shear testings. Small differences between them could be attributed to the experimental error, so the conclusions about the influence of additives (nucleating agent in TN2) could not be made. The similarity between TN1 and MM1 was also apparent: however, with slightly greater MW averages than MM1, TN1 showed slightly higher $\eta_0$ at all temperatures. The qualitative relationship between polydispersity and shear thinning was also valid for PP homo-polymers: the grade with the highest values of $M_w/M_n$ and $M_z/M_w$ (MA3) was also the most shear thinning, followed by MA4. The rest of the grades (MM1 and TN1=TN2) were almost identical in terms of shear thinning. As mentioned before, the shear thinning behaviour was reflected only by the magnitude of parameter $K$, which governs the onset of shear thinning. Due to the errors involved in both experimental procedures and mathematical modelling of viscosity data, there was a reasonable discrepancy in determining $K$ and $m$ parameters given in Table A5. The quantitative correlations between structural and rheological parameters are discussed in Section 5.7 in more details.

5.4.2.2 Shear viscosity of co-polymer grades

Steady shear viscosity of co-polymer grades was measured using the same procedure as for the PP homo-polymers. The tests were conducted at temperatures 190°, 210°, 230°C and 250°C for MA1 and MA2; grade MA5 was tested at temperatures of 180°, 230° and 250°C and the rest of the grades (SEP, DPB and TEPB) at 230°C. The temperature dependence of MA1, MA2 and MA5 viscosity curves is shown in Figs. A22 - A24. As expected, an increase in temperature led to a decrease in viscosity for all co-polymer grades tested at several temperatures. Grade MA2 showed the most similarity to PP grades such as MM1 and TN1; this is reasonable, according to very similar MWDs of the grades mentioned
(Table A1). A comparison between random co-polymers at 230°C is shown in Figure 5.17:

![Graph showing viscosity vs shear rate for different co-polymer grades at 230°C]

Figure 5.17 Shear viscosity curves of random co-polymer grades at 230°C

Unlike the homo-polymer grades, the co-polymers did not completely follow the relationships between MW and rheology. Although the similarities between MA2, SEP and TN1 were evident, TEPB with slightly higher Mw showed lower zero shear viscosity than the former grades. However, DPB, the grade with the lowest Mw and Mz amongst this class of co-polymers, was also with the lowest value of zero shear viscosity. It appears that the other factors of polymer architecture (such as chain configuration and mobility), apart from MW, play a role in determining their rheological behaviour. In case of shear thinning behaviour, it could be concluded that the grade with greatest value of Mw/Mn (SEP) was more shear thinning than the grade with the lowest polydispersity (DPB). The small differences between other two grades (MA2 and TEPB) were more complex to interrelate. It’s worth mentioning that DPB was the grade with the broadest Newtonian region, i.e. the least shear thinning, with parameter $K < 0.2$, which was expected from the only grade with $Mw/Mn < 4$. From the practical point of view, it is important that the combination of structural parameters lead to a good match between viscosity curves of co-
polymers and standard homo-polymers (such as TN1) in the shear rate region of 100 1,000 s$^{-1}$, i.e. at the conditions found during extrusion (Fig. A25).

Different kind of rheological behaviour was found in co-polymer grades MA1 and MA5. Figure A22 shows that the Newtonian plateau was not reached for MA1 at shear rates around 0.01s$^{-1}$, which was only partly possible to explain with higher polydispersity. The Cross model was still applicable, which produced $\eta_0$ much higher than expected from its Mw. A very pronounced shear thinning behaviour of MA1 was reflected in its very high value of parameter $K$; however, the slope $m$ that governs the viscosity at higher shear rates was much lower than for the other polymer grades (an average of 0.56 compared to 0.65 - 0.70 for all other grades). The possible explanation for deviation of MA1 from the relationships between MW and rheological parameters that are valid for other grades could be its morphology, which is supposed to be E-P rubber particles dispersed into polymer matrix. For that reason, the elastic response to applied stress could dominate the rheology of MA1 melt in a greater extent than for the other polymer melts studied.

The viscosity function of MA5 (Fig. A24) was not possible to model by using the Cross model, so the parameters $\eta_0$, $K$ and $m$ could not be determined. A bimodality of an MA5 viscosity curve was apparent, i.e. it appeared as a combination of two simple flow curves; this could be understood if an independent viscoelastic response of either two separated phases or co-polymer blocks (detected by DSC, Fig. 5.7) was assumed. In order to characterise this phenomenon, the steady shear measurements on MA5 melts were performed at the temperature of 180°C, which allowed better instrument precision than at e.g. 230°C, due to the higher torque (rotational rheometers) and pressure measurements (capillary rheometer). The symbols in Fig. 5.18 represent the experimental data, obtained by combination of step-stress and stress-sweep tests on SR200 and capillary measurements. The step-rate tests were also performed using RMS605, but the data were not consistent, due to the low torque resolution of the instrument (Fig. A26). Yet, this test showed that much longer time was required to reach the steady state for MA5 (>100s) than for other grades at similar conditions (30-40s for MA2, Fig. 4.9). However, it was possible to utilise the step stress tests using the SR200 rheometer, which provided better stability and precision, in order to measure the viscosity of MA5 at shear rates below 0.01s$^{-1}$.
Figure 5.18 Steady shear testing of MA5 at 180°C

The line in Fig. 5.18 was plotted by modelling the experimental data to the equation:

\[
\eta(\dot{\gamma}) = \frac{a_1}{1 + a_3 \dot{\gamma}^{a_4}} + \frac{a_5}{1 + a_7 \dot{\gamma}^{a_8}}
\]  \hspace{1cm} \ldots \hspace{1cm} (5.2)

The model was developed by duplicating the Cross model, in order to fit the viscosity function bimodality. In Eq. 5.2, parameters \(a_2\) and \(a_6\) correspond to \(\eta_0\), \(a_3\) and \(a_7\) to parameter \(K\) and \(a_4\) and \(a_8\) to parameter \(m\) of the Cross model. A very good fit was achieved by using the least square method, with \(R^2 > 0.99\).

The comparison between heterophase co-polymers MA1 and MA5 with PP homo-polymer TN1 was given in Figure A27. It was apparent that both co-polymer grades showed higher viscosities at low shear rates than TN1, in spite of the higher \(M_w\) of TN1. The onset of shear thinning was at much lower shear rates for MA1 and MA5 than for TN1, so the modelling of zero shear viscosity was difficult. Additional difficulty in case of MA5 was the shape of its viscosity curve, which made the use of the Cross model unacceptable. The crossover region for all three flow curves was around \(10 s^{-1}\); beyond that region where the viscosities of the grades were similar, an opposite trend was noticed: the viscosity of MA1 was higher than \(\eta\) (TN1), and \(\eta\) (MA5) was the highest. All this suggested that the
differences between the rheological behaviour of PP homo-polymers and heterophasic co-polymers could not be explained by their MW distributions. The higher modulus of MA1 and MA5, as a consequence of the rubber component present, could be the reason for the higher resistance of these grades to shear flow. In terms of processing, it could be noted that both MA1 and MA5 would probably cause more difficulties during extrusion than the standard PP grades, in accordance with the previous discussion.

5.4.2.3 Steady shear testings of EP1 blends

Viscosity curves of EP1 at temperatures of 190°, 210°, 230° and 250°C are shown in Fig. A28. As a blend of an oligomer (HOCP) with a high-MW polymer (PP), the grade EP1 was expected to show an interesting rheological behaviour. In Fig. 5.19, the flow curve of EP1 at 230°C was compared to MA3 and MM1:

![Viscosity curve of EP1 at 230°C compared to MA3 and MM1](image)

Figure 5.19 Viscosity curve of EP1 at 230°C compared to MA3 and MM1 (symbols – exp. data; lines – Cross model: also in Figs. 5.20 and 5.21)

EP1 viscosities at low shear rates were close to MM1, but much lower than MA3; while MM1 had a broad Newtonian plateau, EP1 showed an early onset of shear thinning, similar to MA3. That suggests that the shape of the flow curve was dominated by the PP component of EP1, with a similar M_w to MA3; flow curve of EP1 appeared parallel to MA3’s and shifted down, which could indicate the dilution effect of low-MW component HOCP. There was no indication of the influence of miscibility on EP1 shear flow curves,
as they remained of the same shape in the temperature range of 190°C (immiscible) – 250°C (miscible). The blends of EP1 with MA3 and MM1 were tested in steady shear mode at temperatures 230°C and 250°C, so the effect of EP1 addition to PP grades could be evaluated at processing conditions. As mentioned before (Section 5.2.3.2), all the blends were expected to be miscible at 250°C; the shear behaviour of such blends is shown in Figs. 5.20 and 5.21:

Figure 5.20 Viscosity curves of MA3/EP1 blends at 250°C

Figure 5.21 Viscosity curves of MM1/EP1 blends at 250°C
The viscosity functions of the blends presented in Figs. 5.20 and 5.21 were assumed to be the result of the combination of the following two factors: -the MWD of the polypropylene component of a blend was a combination of MWDs of the pure PP grade and the PP from EP1; -with increasing concentration of EP1, the concentration of HOCP increased and the concentration of PP decreased. The later effect (dilution of PP) was the same in both series of blends and it was supposed to lower the viscosity; -the former effect (change in MWD) was different for two series of blends, as discussed in Section 5.1.3. As seen in Fig. A.3, the M<sub>w</sub> averages of PP components remained relatively constant for MA3/EP1 blends, but kept increasing for MM1/EP1 blends with increasing EP1 content. On the contrary, the polydispersity of MA3/EP1 blends decreased with %EP1, while it remained constant for MM1/EP1 blends. From these two observations, the effect of HOCP on the rheology of the blends was deducted: -addition of HOCP to PP lowered the zero shear viscosity significantly and to a certain degree increased the shear thinning behaviour. In MA3/EP1 blends, the effect of HOCP on shear thinning was balanced by the opposite effect of decreasing polydispersity of PP component, so the flow curves remained parallel. In case of MM1/EP1 blends, the effect of HOCP on η<sub>0</sub> was overwhelmed by the increase in M<sub>w</sub> of PP; since M<sub>w</sub>/M<sub>n</sub> of the PP was not changed, the presence of HOCP led to slightly more pronounced shear thinning of MM1/EP1 blends with increasing %EP1. The effects on zero-shear viscosity at 250°C were plotted in Figure 5.22; the complete data can be seen in Table 5.8:

<table>
<thead>
<tr>
<th>Cross model parameters</th>
<th>Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MA3</td>
</tr>
<tr>
<td>η&lt;sub&gt;0&lt;/sub&gt;</td>
<td>8200</td>
</tr>
<tr>
<td>K</td>
<td>1.05</td>
</tr>
<tr>
<td>m</td>
<td>0.68</td>
</tr>
</tbody>
</table>

|                        | MM1    | 20%EP1 | 30%EP1 | 50%EP1 | EP1    |
| η<sub>0</sub>          | 1870   | 1700   | 1760   | 1730   | 1550   |
| K                      | 0.28   | 0.26   | 0.31   | 0.36   | 0.66   |
| m                      | 0.67   | 0.68   | 0.67   | 0.66   | 0.63   |

The tests conducted at 230° showed similar trends, i.e. there were no additional effects that could be related to melt immiscibility (Figs. A29 and A30). From the point of view of BOPP processing, the addition of small amounts of EP1 that are sufficient to modify the
film final properties, would cause small changes in rheological (processing) behaviour. Although not intensive, the changes could be beneficial in terms of lowering the shear viscosity, which means easier extrusion and less built-in stresses in the quenched tube.

![Graph showing the influence of %EP1 on zero shear viscosity of the blends](image)

**Figure 5.22 Influence of %EP1 on zero shear viscosity of the blends**

**5.4.2.4 Influence of temperature on steady shear viscosity of PP melts**

Viscosity measurements for several polymer grades were conducted at four different temperatures, namely 190°, 210°, 230° and 250° C. Their zero shear viscosities (Table A5) were plotted against reciprocal temperature, in order to estimate the activation energy of flow, as defined in Section 2.3.5:

![Graph showing the Arrhenius plot of \( \eta_0 \) vs. 1/T for a PP grade (MM1)](image)

**Figure 5.23 Arrhenius plot of \( \eta_0 \) vs. 1/T for a PP grade (MM1)**
In accordance to Eq. 2.28, the exponent in the exponential fit (Fig. 5.23) was equal to $Ea/R$, which allowed calculating the values of $Ea$ given in Table 5.9:

<table>
<thead>
<tr>
<th>Grade</th>
<th>MA1</th>
<th>MA2</th>
<th>MA3</th>
<th>MM1</th>
<th>TN1</th>
<th>EP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>36</td>
<td>34</td>
<td>34</td>
<td>36</td>
<td>34</td>
<td>49</td>
</tr>
</tbody>
</table>

The values of $Ea$ were very similar for all the grades (34-36 kJmol$^{-1}$), except for EP1 that was more than 30% higher. The estimated values of $Ea$ for PP were in agreement with literature values. An explanation for much higher $Ea$ of EP1 could be in the phase separation of its melt at certain temperatures. This behaviour would be further investigated by using the results of dynamic shear testings, which provided better precision in estimating the $\eta_0$ and the possibility of time-temperature superposition. The practical significance of knowing the effect of temperature on viscosity is the possibility of adjusting the process parameters to suit the nature of polymer, or vice versa. As shown in Fig. A31, the viscosity curve of MA3 that was the most viscous grade, matched with TN1's flow curve at 20°C lower temperature; in other words, manipulating the temperature could be necessary to enable processing of non-standard grades.

5.5 DYNAMIC SHEAR CHARACTERISATION OF VISCOELASTIC BEHAVIOUR OF POLYMER GRADES AND BLENDS

The materials listed in Table 3.1 were characterised by using the dynamic (oscillatory) shear testing; the SR200 rheometer was used, following the procedures described in Section 4.4.4. The method provides a tool to measure the viscoelastic response of a material to applied stress, which can be related to its processability; furthermore, since the tests are conducted in the linear viscoelastic region, where the relaxation processes are well defined by models and equations, the information on polymer structure can be extracted, as well. Results for several grades, tested at 190° and 230°C are shown in Figures 5.24 & 5.25 (190°C) and A32 & A33 (230°C). The complex viscosity plots (Figs. 5.25 and A33) appeared similar to the results of steady shear tests, presented in Section 5.4.2: MA3 was the grade with the highest zero shear viscosity; MM1 had slightly lower viscosity than TN1 and the viscosity of TN2 was almost identical to TN1. The advantage of the complex
viscosity curves, $\eta^*(\omega)$ was in their smoothness and precision, which made comparisons between grades easier.

Figure 5.24 Storage modulus ($G'$) of several polymer grades at 190°C

Figure 5.25 Complex viscosity ($\eta^*$) of several polymer grades at 190°C

The results for a co-polymer grade MA1 and the blend EP1 were plotted on the same graph with PP homo-polymers, so the difference in their behaviour could be noticed. It was found that $G'$ plots were more useful for comparative study of polymer grades: it is known that storage modulus is a relative measure of polymer melts' elasticity; at high frequencies, the response to applied stress is predominantly elastic, so $G'$ curves of different grades of
the same polymer type would tend towards the same plateau modulus, $G^0_\nu$. It was really noticed for PP grades in Figs. 5.24 and A32 that their $G'$ curves were getting closer with increasing frequency. As a contrast to PP homo-polymers, the $G'$ of MA1 and EP1 showed different behaviour: at both temperatures, the storage moduli of MA1 were increasing more rapidly with frequency than for PP grades, so its $G'$ curve crossed-over with MA3; at maximum accessible frequency, MA1 had the highest $G'$ or elasticity. The elasticity of EP1 showed an opposite trend: its $G'$ curve grew less with $\omega$ than for the PP grades, so it crossed-over with their $G'$ curves. At maximum frequency, the elasticity of EP1 was the lowest amongst all tested grades. These findings could be easily understood from the known structure of the polymer grades: as an E-P rubber compound, MA1 was expected to show higher elasticity (in the whole frequency region, which was really noticed at low $\omega$, Figs. 5.24 and A32). In the EP1 melt, the presence of a low-MW component, HOCP had to lower its modulus, which was most apparent close to the plateau region. This could be readily explained using the Eq. 2.51: higher values of $G^0_\nu$ correspond to lower MW between entanglements, and *vice versa*. Since the same type of polymer network was present in MA1, EP1 and PP grades, the number of entanglements was increased in MA1 by addition of EPR, whilst it was decreased in EP1 by dilution of PP with HOCP. Unfortunately, the above analysis could not be performed quantitatively, using the experimental data, since the plateau region was not fully reached. Nevertheless, the relative position of the $G'$ curves could be utilised to conclude about the nature of the compared grades.

Similarly to steady shear testing, the dynamic measurements were performed at temperatures of 190°C, 210°C and 230°C for most of the polymer grades; co-polymers and blends were additionally tested at 250°C. Moreover, two of the grades (MA4 and MA5) were also tested at 180°C, which was close to the lowest limit for shear measurements, due to the crystallinity of PP. The results of the frequency sweeps were utilised to perform the comparisons between the grades, to calculate the important shear parameters, such as zero shear viscosities and flow activation energies and to calculate the relaxation spectra and relaxation moduli that would be correlated to polymer structure.
5.5.1 Dynamic shear characterisation of PP homo-polymer grades

Polypropylene grades MA3, MM1, TN1 and TN2 were tested in oscillatory shear mode at temperatures 190°, 210° and 230°C; their $\eta^*$ and $G'$ curves are given in Figs. A34 - A37; Grade MA4 was tested at temperatures 180°, 190°, 210°, 230° and 250°C (Fig. 5.26):

![Graph showing $G'$ and $\eta^*$ curves](image)

Figure 5.26 Results for dynamic shear testings: $G'$ and $\eta^*$ curves of MA4

Similar to steady shear viscosity, the complex viscosity decreased with increasing temperature. The same trend was noticed for other material functions, i.e. for dynamic moduli ($G'$ and $G''$). The complex viscosity, as a function of frequency [$\eta^*(\omega)$] was decreasing with frequency in a similar manner as steady shear viscosity as a function of shear rate. The results for additional measurements, performed at 250°C for PP grades were plotted in Fig. A37. The plot shows similarity with the steady shear behaviour at the same temperature (Fig. A21): MA3 was the highest, followed by MA4 and then TN1 and MM1. Unlike the steady shear results, the $\eta^*$ curves for TN1 and MM1 were overlapping (in the limits of experimental error). It appeared that the complex viscosity measurements could also be an indication of shear thinning behaviour: all complex viscosity curves tended towards similar values at higher frequency.
The analogy between steady shear and complex viscosity was analysed in the lights of Cox-Mertz rule, introduced in Section 2.3.6. The relationships 2.35 and 2.36 were verified, as shown for MA3 at 190° and 250°C in Fig. 5.27:

Figure 5.27 Comparison between steady shear (line), complex and dynamic viscosities (symbols) for MA3 at 190° and 250°C

It was observed that dynamic viscosity \((\eta' = G''/\omega)\) curve showed more similarity to steady shear data than \(\eta*(\omega)\), especially at higher temperatures. That could be explained as due to more pronounced elastic effects at low temperature, which could have affected the estimation of the viscous component. From the results presented in Fig. 5.27, one can conclude that the dynamic shear data cannot be used for replacing the steady shear characterisation, which is in agreement with theoretical discussion in Section 2.3.6. However, for comparative purposes, either complex or dynamic viscosity could be used, as shown for PP grades (Figs. 5.25, A33 and A37). It was especially beneficial to use dynamic shear data for modelling the zero shear viscosity. The dynamic viscosity curves were modelled using the equation of the same type as Cross model (Eq. 2.63), by replacing shear rate with frequency and viscosity with \(\eta'\). The values obtained are given in Table 5.10. A comparison with data in Table A5 revealed a very good agreement (±5-10%) between \(\eta_0\) obtained from steady and oscillatory shear modes.
Table 5.10 Zero shear viscosities of PP homo-polymers from dynamic data

<table>
<thead>
<tr>
<th>Grade</th>
<th>$\eta_0$ (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180°</td>
</tr>
<tr>
<td>MA3</td>
<td>22060</td>
</tr>
<tr>
<td>MA4</td>
<td>17540</td>
</tr>
<tr>
<td>MM1</td>
<td>5250</td>
</tr>
<tr>
<td>TN1</td>
<td>6240</td>
</tr>
<tr>
<td>TN2</td>
<td>6240</td>
</tr>
</tbody>
</table>

5.5.2 Dynamic shear characterisation of co-polymer grades

Oscillatory shear measurements were conducted on co-polymer grades using the same procedures and conditions as for the PP homo-polymers. The comparison between complex viscosity curves of random co-polymer grades at 230°C is shown in Figure 5.28:

![Complex viscosity curves](image)

Figure 5.28 Comparison between $\eta^*$ of random co-polymers at 230°C

The values for a PP homo-polymer grade TN1 were plotted as a reference on the same graph. The same conclusions could be made from both graphs in Fig. 5.28 and 5.17, i.e. from dynamic and steady shear curves: SEP was the grade with slightly higher viscosity than MA2, which matched entirely with TN1. Viscosity of TEPB was significantly lower.
and the viscosity curve of DPB had the lowest position. Most of the conclusions based on the low shear rate / low frequency region were the same. The difference between two graphs was noticeable in the shear-thinning region: in steady shear, the flow curves were overlapping, whilst there were significant differences in the dynamic mode. There are two possible reasons for that difference: first, there is no theoretical background for equivalence between steady and complex viscosities, especially in that shear rate/frequency region; second, the power law region of the steady shear curves was approx. at 100-10,000 s⁻¹, while the maximum available frequency for complex viscosity data was around 300 rad/s. Similar trends were shown at other temperatures, as shown for 190° and 250°C in Fig. A38. The dynamic viscosity data were modelled as described in the previous section and the values of zero shear viscosity are given in Table 5.11; compared to steady shear data at 230°C (Table A5), a good agreement was found (±5-10%).

Table 5.11 Zero shear viscosities of random co-polymer grades

<table>
<thead>
<tr>
<th>Grade</th>
<th>η₀</th>
<th>190°</th>
<th>210°</th>
<th>230°</th>
<th>250°</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA2</td>
<td>5570</td>
<td>3700</td>
<td>2620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEP</td>
<td>7200</td>
<td>4600</td>
<td>3060</td>
<td>1900</td>
<td></td>
</tr>
<tr>
<td>DPB</td>
<td>3850</td>
<td>2360</td>
<td>1720</td>
<td>1140</td>
<td></td>
</tr>
<tr>
<td>TEPB</td>
<td>4800</td>
<td>3200</td>
<td>2250</td>
<td>1530</td>
<td></td>
</tr>
</tbody>
</table>

Dynamic shear behaviour of heterophasic co-polymers MA1 and MA5 was different from the one observed with the other grades. Grade MA1 was already compared to several polymer grades in Section 5.5 (Figs. 5.24&5.25 and A32&A33) and the explanation for its behaviour was postulated based on its structure. From Fig. A39, one can see that the storage moduli of MA1 showed a positive deviation from the $G' \propto \omega^2$ relationship that provided the linear appearance of $G'$ curves on a log-log graph for other grades. This phenomenon was not that obvious for $\eta*$ curves, but it was certainly present, preventing from accurate modelling of the zero shear viscosities (Table 5.12):

Table 5.12 Zero shear viscosity of MA1 from dynamic data

<table>
<thead>
<tr>
<th>Grade</th>
<th>η₀ (190)</th>
<th>η₀ (210)</th>
<th>η₀ (230)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA1</td>
<td>10050</td>
<td>7140</td>
<td>5190</td>
</tr>
</tbody>
</table>
The values in Table 5.12 were 15-25% lower than $\eta_0$ obtained from steady shear (Table A5), which could be a consequence of lack of the Newtonian region in viscosity curves. That made the $\eta_0$ values uncertain and not useful for the comparisons with other grades.

The above effects were even more pronounced in case of MA5, as shown in Fig. 5.29:

![Figure 5.29 Storage moduli of MA5 at temperatures 180°-250°C](image)

The transition in storage moduli of MA5 was more obvious, in terms of stronger deviation from linearity on the log-log scale; moreover, it occurred at a higher frequency (around 1 rad/s) than that for MA1 (below 0.1 rad/s). The difference in rheological behaviour between MA1 and MA5 could be the consequence of the amount or the nature of cross-linked compound in those grades. That difference was apparent from the DSC curves of the grades (Figs. 5.7 and A9). In case of MA5, the transitions of the flow regimes were visible in its $\eta*$ curves, as well. The experimental data were modelled using the duplicated Cross model (Eq. 5.2), developed in Section 5.4.2.2. Additionally, the higher frequency data were modelled using the conventional Cross model (Fig. 5.30). It was shown that the Eq. 5.2 was applicable for the dynamic shear data in the same manner as for the steady shear viscosity (Fig. 5.18). If the complete separation of the flow regimes could be
assumed, then the low-viscosity component would be also possible to model with a simple Cross model, as shown in Fig. 5.30:

![Graph showing complex viscosity vs. angular frequency](image)

**Figure 5.30 Modelling of the complex viscosity of MA5 at 180°C**

A zero shear viscosity at around 5,000 Pas was obtained, which was even lower than \( \eta_0 \) of other polymer grades at 190°C, suggesting the low MW of MA5. This was in agreement with the GPC data, but no quantitative relationships could be made without more detailed analysis of such polymeric systems.

### 5.5.3 Temperature dependence of viscoelastic properties

Similar to the steady shear viscosity behaviour (Section 5.4.2.4), the viscoelastic material properties analysed by dynamic frequency sweeps were strongly temperature dependent, as seen from Figs. 5.26, 5.29, A34-A36 and A39. The zero shear viscosities obtained from the dynamic shear tests were plotted against reciprocal temperature in order to estimate the flow activation energies, \( Ea \) in the same manner as presented in Fig. 5.23, utilising the Arrhenius-type equation (2.28). The estimated values are given in Table A6. Furthermore, according to the principle of time-temperature superposition (TTS), described in Section 2.3.6, the master-curves were built using the experimental data at various temperatures. The shift factors, \( a_T \), were also utilised to calculate the flow activation energy, using the Eq. 2.29. These values are also shown in Table A6. A very good agreement can be seen
between activation energies determined using three different procedures or source of data: using the shift factors for the TTS, using the \( \eta_0 \) from dynamic shear and \( \eta_0 \) from steady shear testings. It was found that the values of flow activation energy were very similar for PP homo-polymer and random co-polymer grades. Analysis of the data showed that \( E_a \) was equal to 39 \( \pm 3 \) kJmol\(^{-1}\), within 95% confidence limits. The heterophase co-polymers MA1 and MA5 showed lower values, at around 32 kJmol\(^{-1}\). Finally, the activation energy of EP1 was significantly higher than for the other grades, suggesting the influence of phase separation on thermo-rheological properties.

Another important purpose of performing the time-temperature superposition was extending the range of frequencies of experimental data. This is very important for calculating the relaxation properties of a polymer. Due to the low \( E_a \) for PP (around 40 kJ/mol) and the limited temperature range (crystallinity and built-in stresses at \( T<180^\circ \text{C} \), degradation at \( T>250^\circ \text{C} \)), the frequency range could not be extended by much using the TTS (Fig. 5.31):

![Figure 5.31 Master-curves for MA5 at \( T_{Ref} = 210^\circ \text{C} \)](image)

In case of MA5, when temperature of 210°C was chosen as a reference, two sets of data were shifted from each end. Thus, from the original range of 0.01-300 rad/s, the new master-curve was extended to the range of 0.008-500 rad/s, which was not found to be
sufficient for reaching the plateau modulus region. Nevertheless, the TTS was proven to be beneficial for further analysis of the relaxation properties, because of increasing the density of the data and reducing the experimental error introduced by measurement. It can also help reaching the crossover point of dynamic moduli: for MA5, the frequency of the crossover point was not accessible experimentally, but it was determined from a master-curve as equal to 364 rad/s.

The master-curves of several polymer grades are shown in Figs. A40-A42.

### 5.5.4 Dynamic shear rheology of EP1 blends

Blends of EP1 with PP grades MA3 and MM1 showed an interesting rheological behaviour that was characterised at processing conditions in steady shear mode (Section 5.4.2.3). Further study was performed by using the dynamic shear testings and the results were related to the blends’ structure. The complex viscosity curves of MA3/EP1 blends (Figs. 5.32 and A43) showed the same trends as the steady shear flow curves (Figs. 5.20 and A29), i.e. the viscosity decreased with increasing %EP1. The same trend was noticed with the dynamic moduli (G’ shown in Figs. 5.33 and A44).

![Figure 5.32 Complex viscosity of MA3/EP1 blends at 190°C](image-url)
The corresponding graphs for MM1/EP1 blends are given in Figs. 5.34 and A45 ($\eta^*$) and 5.35 and A46 ($G'$). The difference between the results for MA3 and MM1 blends was of the same type as noticed in steady shear testing: the $\eta^*$ curves tended to overlap in the zero shear region, but diverged at higher frequencies.
This phenomenon was also apparent in the case of $G'$ curves: while the moduli were parallel in case of MA3/EP1 series, for MM1 blends the $G'$ curves crossed-over at a frequency in the range of 0.5-2.0 rad/s. At high frequencies, the order of $G'$ curves was the same as for MA3/EP1 blends, i.e. the modulus decreased with increasing %EP1. It can be assumed that in the high frequency region, the $G'$ tended towards the plateau zone, which means that the $G_N^0$ of the melts decreased with %EP1 (or dilution of PP) independently of polypropylene’s MWD. At low frequency, the magnitude of $G'$ was apparently dependent on polymer’s $M_w$, as well.

For clarity, most of the graphs show only the results for the blends with EP1 concentration $\geq 30\%$; all the tests were performed for the lower concentrations, as well, and the results were used in modelling the zero shear viscosity and flow activation energy. The values of $\eta_0$ and $Ea$ for both series of blends are compiled in Table A7. The zero shear viscosity data were plotted against %EP1 (Figs. 5.36 and 5.37); the same trends were found as for the steady shear results: the $\eta_0$ of MA3/EP1 blends decreased with EP1 concentration but remained constant for MM1/EP1 blends. The trends were not influenced by temperature, suggesting that only the nature of the PP component and the degree of its dilution played a role in determining the $\eta_0$. 
Several rheological techniques commonly used to detect the melt immiscibility [Dumoulin, et al., 1991] were applied on the EP1 systems. The values of $E_a$ (Table A7) were plotted against EP1 concentration and it was found that both series of blends showed similar behaviour: below EP1 content of 50%, the change in flow activation energy was negligible, but very significant beyond that concentration (Fig. 5.38). It is important to note that these similar trends were found with $E_a$ values extracted from the zero shear viscosities that correlated to %EP1 in a completely different manner for two series of blends. It appears that the trends observed in Figs. 5.36-5.37 provided only insight into $\eta_0$.
dependence on chain structure related factors (MW, dilution), while morphology influenced the temperature effects.

![Graph showing flow activation energies of blends related to their composition](image)

Figure 5.38 Flow activation energies of the blends related to their composition

The significance of $Ea$ is how easily the polymer molecules in the melt can flow at a higher temperature. For blends with $\leq 30\%$EP1 the increase of temperature from $190^\circ$ to $250^\circ$C did not change the morphology of the melt, i.e. it was homogeneous at all tested temperatures. The $Ea$ values of these blends were all very close to $Ea$ of pure PP (35-40 kJ/mol). The change of temperature from $190^\circ$ to $250^\circ$C for blends with 70% and 100%EP1 changed the melt from multi-phase to the homogeneous state. Apparently, the homogeneous melt flowed easier than the immiscible one, where the applied stress should not only ‘move’ the molecules, but also overcome interfacial forces.

As suggested in literature [Dumoulin, et al., 1991], the melts of miscible blends are ‘thermo-rheologically simple’ and the corresponding master-curves of $\eta^*$, $G'$ or $G''$ should be obtained by horizontal shifting of the experimental data. Such behaviour was noticed for the concentrations of EP1 of up to 50% in both series of blends, while horizontal shifting did not give perfect master-curves for MA3/EP1 30/70, MM1/EP1 30/70 and EP1. This was in agreement with the proposed morphology of the melts, i.e. for the above blends immiscibility was expected. However, the ‘perfection’ of master-curves (or ‘the ease’ of matching the curves by shifting) was more a matter of subjective opinion than of quantitative analysis (Figures A47 and A48).
Further analysis of dynamic shear data was performed by plotting Cole-Cole plots (i.e. elastic component of complex viscosity, \( \eta'' \), as a function of its viscous component, \( \eta' \)). It was found before [Dumoulin, et al., 1991] that the shape of the plots was semi-circular for miscible PP/PE blends, but not for the immiscible ones. These authors stated that this behaviour should be expected for other systems, as well. The Cole-Cole plots for MA3/EP1 blends are shown in Figure 5.39a & A49 and for MM1/EP1 blends in Figure 5.39b and A50. For both series of blends, the shape of the curves remained semi-circular for all concentrations. Since the Cole-Cole plots represent a relationship between elastic and viscous response of the melt to applied stress, as a consequence of relaxation properties of polymer chains, one can conclude that the influence of phase separation on the above processes was not predominant for PP/HOCP systems. It appears that only the characteristics and concentration of PP in the studied systems were responsible for the observed quantitative changes in rheological properties (viscosity, elasticity), rather than morphological factors.

![Figures 5.39 a-b: Cole-Cole plots at 190°C – a) MA3/EP1; b) MM1/EP1](image)

5.6 EXTENSIONAL RHEOLOGY OF POLYMER GRADES

For BOPP processing, estimation of polymer extensional properties is of great importance. It was of greatest interest to measure the extensional viscosity of the polymers in their semi-molten state. The extensional flow during extrusion was also analysed.
5.6.1 Cogswell's analysis of converging flow

Converging flow during capillary extrusion was utilised to calculate the extensional viscosity of several polymer grades using Eqs. 2.54-2.56. The procedure is usually referred to as the Cogswell’s analyses (Section 2.3.7). The nature of the results is different from those obtained by using extensional rheometers: the former are supposed to be estimated at steady-state conditions, while the later are transient or time-dependent. Fig. 5.40 shows a typical result for Cogswell’s analysis (Section 2.3.7), compared to the steady shear data at the same conditions (190°C):

![Graph showing extensional viscosity of MA3 at 190°C from Cogswell's analysis](image)

Figure 5.40 Extensional viscosity of MA3 at 190°C from Cogswell’s analysis

Applied to another polymer, MA5 at 180°C, this technique produced results shown in Fig. A51. In case of MA3, the calculated \( \eta_E \) curve was parallel to shear flow curve, with the numerical values approximately equal to three times shear viscosity. With MA5, the shapes of the \( \eta_E \) and \( \eta \) curves were significantly different. It was not possible to determine whether it was a consequence of polymer’s nature, not reaching the steady state in the extensional flow, or the errors in measurements and data analysis. Similar analysis was performed with the co-polymer grades (SEP, DPB and SEP) at the extrusion conditions (230°C) and the results were compared to a homo-polymer grade (TN1). As seen in Fig. 5.41, the PP grade TN1 was represented by the top extensional viscosity curve; the extension-thinning behaviour was also apparent. The order of extensional viscosity curves for co-polymer grades was different from their steady shear viscosity curves, i.e.: TEPB >
DPB > SEP. If the accuracy of the pressure measurement for the zero-length dies is assumed, then the importance of such analysis becomes evident: although all the grades showed similar shear viscosities at high extrusion rates, their extensional properties were different in a manner that could not be predicted from their viscoelastic behaviour. Since the above co-polymers were involved in the co-extrusion during BOPP processing, matching both shear and extensional viscosities of the grades might be an important factor for running the process smoothly.

![Diagram](image)

Figure 5.41 Extensional viscosity of co-polymer grades at 230° from Cogswell’s analysis

### 5.6.2 Direct measurements of transient extensional viscosity of polymer grades

Transient extensional viscosity measurements for the polymer grades were performed using Rheometrics RME and the necessary corrections were applied according to the procedure described in Section 4.4.5. The extensional flow that occurred during the measurements was possible to describe as a start-up flow, characterised by a time-dependent extensional viscosity, $\eta_E$ defined as a stress-growth coefficient (Eq. 2.33). Such measurements can provide two important pieces of information: the first is the quantitative measure of the polymer’s resistance to stretching; another one is the degree of extensibility, or the maximum strain at break. Fig. 5.42 shows a comparison between $\eta_E$ of two PP grades, MA3 and TN1. It can be seen that at any particular time (excluding times
very close to the actual start of the test), higher $\eta_E$ values were obtained for MA3 than for TN1, which was attributed to differences in their molecular weights. The differences could also be noticed between values measured for the same grade at different strain rates. Furthermore, the samples broke earlier at higher strain rates. However, at a chosen strain rate, both samples broke at similar times. In Fig. 5.43, the same extensional viscosity data were plotted against strain. On such graph, it became obvious that for any of the two grades the same $\eta_E$ was reached at the same strain of break for different strain rates.

Figure 5.42 Extensional viscosity of two PP grades: $\varepsilon = 0.1 \text{s}^{-1}$ (open symbols), $1 \text{s}^{-1}$ (filled symbols)

Fig 5.43 Extensional viscosity of two PP grades versus strain.
Temperature was another factor that influenced the extensional viscosity. Its influence was dependent on nature of the polymer, as shown in Fig. 5.44:

![Graphs showing extensional viscosity of polymer grades at 165° and 180°C: MA2 (left) and MA4 (right)](image)

Figure 5.44 Extensional viscosity of polymer grades at temperatures 165° and 180°C: MA2 (left) and MA4 (right)

A decrease in temperature from 180° to 165°C caused a small increase in extensional viscosity for a co-polymer grade MA2, but a huge impact was noticed with the homo-polymer grade, MA4, where the behaviour known as the strain hardening was detected. To characterise the influence of the above factors on the extensional rheology of the polymer grades, they were tested at temperatures of 165°, 170° and 180°C using the strain rates of 1.0, 0.1 and 0.01 s⁻¹ and the results are discussed in the following sections.

5.6.2.1 Extensional viscosity of PP homo-polymer grades

Several factors, such as strain rate and temperature, can influence the results of extensional viscosity measurements, as shown in Figs. 5.42 and 5.44. For that reason, for each grade, the results of measurements at different conditions were compiled and compared on the graphs as shown in Fig. 5.45 for the grade MA4. For the rest of the PP grades, the results are presented in Figs. A52 - A55. At the temperature of 180°C, the \( \eta_e \) curves obtained at strain rates 0.01 and 0.1 s⁻¹ overlapped completely for most of the grades, showing that the tests were conducted reproducibly and in the linear viscoelastic region. The curves obtained at the strain rate of 1.0 s⁻¹ showed a small positive deviation at higher times (strains), but overlapped at low and moderate strains. The tests were conducted until the samples broke; as seen for MA3 in Fig. A56, the rupture occurred when similar values of strain and extensional viscosity were reached for different strain rates.
The decrease in temperature caused an increase in extensional viscosity. Two types of temperature effects could be noticed: as long as the samples were completely molten, the temperature dependence of their $\eta_e$ curves was governed by the flow activation energies, similar to shear viscosity (Section 5.4.2.4). As soon as the crystallinity was present in the samples, a different type of results was obtained. In Fig. 5.45, the curves for temperature of 170°C were of the same shape as for 180°C, but shifted to higher magnitudes of $\eta_e$. A further decrease in temperature for only 5°C caused a qualitative change in the extensional behaviour. The values of $\eta_e$ were an order of magnitude higher at 165°C than at 170°C. Furthermore, the strain hardening behaviour was obvious. Generally, it can be stated that in the temperature range of 170°C-165°C, the transition in extensional behaviour of PP occurred, that can be understood as a change from a linear polymer melt to a rubbery material. Such behaviour was only recently reported in literature [Rauschenberger, V., (1998)]: similar to the results in Fig. 2.37, the top curves that showed strain hardening corresponded to a semi-molten state with a network of PP chains that interconnected the crystals. The samples at 170°C probably corresponded to a melt with a small amount of crystallites that were not connected and could act as filler. According to the discussion in Section 2.4.5, the early rupture of all PP samples at 170°C was comprehended.
The above discussion can be supported with the DSC results for the PP grades (Table 5.4, Fig. 5.5): the temperature of 165°C was located near the melting peak of the PP grades. A close look at the DSC melting curves suggested that the melting was not completed at 170°C. A HS-OM study also revealed that the crystals could remain in the melt at temperatures beyond the $Tm$ for PP (165° - 170°C), as shown in Fig. A57. From these findings, it became obvious that the thermal history of polypropylene could play an important role in its crystallinity and, hence extensional viscosity.

All the homo-polymer grades except MA3 showed similar behaviour in terms of transition between two extensional regimes in the temperature range 170 - 165°C. With MA3, the strain hardening was observed at temperature 170°C, indicating that it existed in the rubbery state at higher temperature than the other grades (Fig. A52). Even more, it was not possible to conduct the measurements for MA3 at temperature 165°C, due to the high forces and slippage during stretching. It appeared that the MA3 samples were ‘more solid’ than the rest of the grades. This could not be concluded from its DSC results (Section 5.2.1). It could be possible that MA3 contained larger crystals that would remain unmelted at temperature 170°. Its behaviour at that temperature was interesting for another reason: at low strains, the $\eta_e$ values were not much higher than expected for the molten regime, similar to the other grades. However, at strains beyond 1, the strain hardening occurred, i.e. the transition to stretching from a rubbery state was apparent during the deformation. It can be assumed that this was a consequence of strain-induced crystallisation, which induced formation of permanent network of cross-linked crystallites.

The practical implication of the above phenomenon is that the RME measurements at temperatures close to the processing ones can distinguish whether the polymer can be processed or not. For MA3, one can anticipate that it would not be processable at the same temperature as the other grades, but the stretching would become possible if the temperature was increased. The optimal temperature would be determined from a series of RME tests, which is more cost-effective than the plant trials for the BOPP processing.

The results obtained for the samples in the fully molten state showed similar trends as the shear viscosities at such conditions. In Figs. 5.46 and A58, the top $\eta_e$ curves belonged to MA3, followed by MA4 and the overlapping curves for TN1, TN2 and MM1. The position of MM1 curves were slightly lower than TN1’s, which was the same order
observed for their zero shear viscosities. It shows that the transient extensional viscosity was measured in the linear viscoelastic region, where the viscosity was proportional to the polymer's molecular weight (Eq. 2.59), which was also observed by matching the extensional and three-fold shear start-up curves (Fig. 4.18).

![Graph](image)

Figure 5.46 Comparison between $\eta_e$ curves for PP grades at 180°C and strain rate of 0.1s$^{-1}$

Except for MA3, which behaviour was described above, trends similar to that at 180°C were continued at temperature of 170°C. However, the data were more scattered and the repeatability of the results was reduced. As mentioned before, at these conditions the remaining crystallites were dispersed randomly through the melt; small differences in testing conditions and sample preparation could yield the observed behaviour. The most important finding was that the samples broke at lower strains than at other two testing temperatures. This shows that the described melt morphology would be undesirable for the BOPP processing.

The most important results for assessment of the grade suitability for BOPP processing are presented in Fig. 5.47:
Figure 5.47 Extensional viscosity of PP grades at 165°C and strain rate 1 s⁻¹

It can be seen that the order of the $\eta_E$ curves was changed in comparison to temperatures 180° and 170°C. The top one belonged to TN2, at both strain rates, which showed that the crystallinity was the most important factor for extensional viscosity of the semi-molten samples, rather than molecular weight. As known (Table 3.1), TN2 is a nucleated modification of TN1; the size and amount of crystals formed in TN2 was apparently different from the crystalline structure of TN1, which caused more crystallinity to remain at the temperature of measurements. At strain rate of 1 s⁻¹, the lower curve belonged to TN1 and at strain rate of 0.1 s⁻¹ the lowest was MM1. It can be assumed that the small differences in testing conditions (eg. time spent for sample loading) could cause the mixed order of the curves. Although the curves showed diversity at low and moderate strains, they all tended to similar values of extensional viscosity at higher strains. Video monitoring of the runs confirmed reasonably uniform drawing, as a contrast to the tests at 170°C. It was possible to conduct the runs until the approximate strain of 3, due to the large forces developed. It was observed that all the extensional viscosity curves reached similar $\eta_E$ values at that strain. The possible reason for this was the strain induced crystallisation, which eventually formed the same morphology in all the samples that were initially different. When the data were plotted against strain (Fig. A62), it was observed that higher extensional viscosity was reached at lower strain rate; this can be explained by 10 times longer time that samples were stretched, which allowed more crystalline structure to be formed.
To allow quantitative analysis of the polymers’ strain hardening behaviour, a ratio of extensional viscosities at values of strain 3 and 1, respectively, was introduced as the Extensional Viscosity Index (EVI):

\[
\text{EVI} = \frac{\eta_E^+ (\varepsilon = 3)}{\eta_E^+ (\varepsilon = 1)}
\]

Equation 5.3 is a modification of the definition of EVI [Jones and Kurtz, (1982)], adjusted for different nature of PP compared to LDPE. The EV indices were calculated from experimental data and presented in Table A8. It was accepted that an EVI ≤ 2 represented a transient extensional behaviour with no strain hardening. For EVI in the range of 2 – 3, a weak strain hardening can be assigned to a polymer. With EVI > 3, the polymer exhibits a strong strain hardening behaviour. At temperature of 180°C, no PP grade showed any strain hardening. The EVI could not be estimated for PP homo-polymer grades at 170º, due to the early break of the samples. The exception was MA3 that was stretched uniformly and showed a strong strain hardening. However, at temperature of 165ºC, the rest of the PP homo-polymer grades exhibited very strong strain hardening, with EVI between 6.1 and 14.5. In all cases, the EVI determined at a higher strain rate (1.0 s\(^{-1}\)) was greater than EVI at 0.1s\(^{-1}\). These observations revealed the most important extensional characteristics of PP in BOPP processing: -high levels of extensibility and strain hardening in semi-molten PP are provided by a permanent network of cross-linked crystallites, which structure depends on temperature and previous thermal history and -the strain hardening effects are stronger at higher deformation rate.

### 5.6.2.2 Extensional viscosity of co-polymer grades

The transient extensional viscosity measurements were conducted with both random- and heterophase co-polymers, following the same procedure as for the PP grades. As shown in Table A8, none of the random co-polymer grades showed any strain hardening. This was in accordance with the previous discussion on the effects of crystallinity on extensional behaviour. It was shown by DSC analysis (Section 5.2.2.1) that all random co-polymer grades were completely molten at all testing temperatures. Due to the low extensional viscosity of the melts, the measured force was low, what caused \(\eta_E\) curves to
be more noisy than for the homo-polymer grades. Decrease in temperature raised the extensional viscosities by the amount expected from the known flow activation energies. Typical results for random co-polymers are shown in Fig. 5.48 (MA2 at various temperatures and strain rates):

![Graph showing extensional viscosity vs. time for different temperatures and strain rates]

*Figure 5.48 Temperature and strain rate dependence of $\eta_E$ (MA2)*

Comparison between $\eta_E$ curves for random co-polymer grades at 180°C is shown in Fig. 5.49. The tests at all temperatures were conducted at strain rate of 0.1 s⁻¹; in addition, the strain rate of 1 s⁻¹ was employed at temperature of 165°C (Fig. A65). The rest of the results are given in Figs. A63-A64. The results of the measurements performed at 180°C revealed a great degree of overlapping of the $\eta_E$ curves, especially at low times (strains); at high strains, the curves diverged and the order of extensional viscosities was: (SEP $\approx$ MA2) $>$ (TEPB $\geq$ DPB). This was similar to the trends of their zero shear viscosities, which suggested that the same molecular parameters (MW and chain mobility) governed both shear and extensional rheology of the co-polymers. The testing conditions closest to the BOPP processing situation (lowest temperature and highest strain rate) were utilised to compare extensional behaviour of co-polymers to a homo-polymer (Fig. A65). It could be seen that the homo-polymer grade (TN1) in the semi-molten state could reach more than two orders of magnitude higher extensional viscosity than any of the co-polymer melts.
This finding suggested that the extensional properties of co-extruded co-polymer layers would be irrelevant for the process operation.

![Figure 5.49 Comparison between $\eta_E$ curves for co-polymer grades at 180°C](image)

Figure 5.49 Comparison between $\eta_E$ curves for co-polymer grades at 180°C

Other two co-polymer grades, MA1 and MA5 showed behaviour significantly different from the random co-polymers, as shown in Fig. 5.50:

![Figure 5.50 Extensional viscosity of MA1 and MA5 at 165°C](image)

Figure 5.50 Extensional viscosity of MA1 and MA5 at 165°C

MA1 was the only grade for which a certain degree of strain hardening occurred in completely molten state. Fig. A66 shows that at all temperatures and strain rate of 0.1 s$^{-1}$,
the extensional viscosity increased considerably beyond the strain of two (time = 20s at strain rate 0.1s⁻¹). This behaviour was of a different type from the strain hardening of semi-molten PP grades that started at strain of 1 - 1.5. The late onset of strain hardening of MA1 was probably the reason for low values of its EVI in Table A8. Another heterophase co-polymer grade, MA5 showed a similar behaviour to polypropylene (Fig. A67). This was expected, since it contained a distinguished PP component that melted at around 164°C. For that reason, plot in Fig. A67 can be readily explained: low Ea of MA5 was the reason for a small difference between extensional viscosities at temperatures of 180° and 170°C. Due to remained crystallinity, MA5 showed strong strain hardening at 165°C (Table A8); the magnitudes of its $\eta_e$ curves were still much below those of homo-polymer grades, probably because of its lower $T_m$ and %crystallinity (Table 5.7). This suggests the possibility of processing MA5 as a BOPP grade at lower temperatures, which should be a subject of further optimisation.

5.6.2.3 Extensional viscosity of EP1

Temperature dependence of extensional viscosity of the modifier grade EP1 is presented in Fig. 5.51:

![Figure 5.51 Extensional viscosity of EP1](image-url)
Due to the low $T_m$ and crystallinity of EP1 in comparison to pure PP (Table A3), only a weak strain hardening was noticed at the temperature of 165°C. The measurements were hard to perform, due to the low force readings and the sticky nature of molten EP1. The comparison with PP grades MA3 and MM1 at 180°C revealed the similarity to the shear behaviour of the compared grades: the MA3 curve was the top one, followed by MM1 and then EP1; however, at higher strains, there was a cross-over and the final measurements for the $\eta_e$ of EP1 were higher than for MM1 (Fig. A68). That was in agreement with the order of zero shear viscosities of the grades, i.e. MA3 > EP1 > MM1. The measurements confirmed that adding the HOCP to PP could change its extensional rheology; the effect was due to the change in polymer’s crystallinity and melting temperature. Polymer with an addition of HOCP (or blended with EP1) should be processed at lower temperature than the pure PP grade, since the presence of HOCP lowered the crystallinity and consequently, the onset of strain-hardening behaviour.

5.7 RELATIONSHIPS BETWEEN STRUCTURE AND RHEOLOGY OF POLYMER GRADES

Main goal of this study was to find the most suitable relationships between structural parameters (such as chemical composition, molecular weight distribution and morphology) and rheological behaviour of the grades for possible use in BOPP processing. The results obtained for shear (in both steady and dynamic modes) and extensional flows were analysed in regards to the MWDs of the grades. The use of MDSC technique for assessing the melts morphology and co-polymer characterisation was of great benefit for understanding several ‘anomalies’ found.

5.7.1 Shear viscosity in relation to molecular weight

The differences between shear flow curves of polymer grades can be noticed in both Newtonian region ($\eta_0$) and shear thinning (power law) region. It appeared from the results (eg. Fig. 5.16) that the slope of the curves in the power-law region was very similar for PP grades. At low shear rates, the differences between grades were significant; the following order of zero shear viscosities was established: MA3 > MA4 > (TN1 ≈ TN2) ≥ MM1. This was in qualitative agreement with their weight-average molecular weights. Since the
grade TN2 represented the nucleated modification of TN1, with the same MWD, it was ignored in further studies. A quantitative relationship between $\eta_0$ and $M_w$ was found from a plot shown in Fig. 5.52. The values for two co-polymers, MA1 and MA2 were also plotted in order to establish the validity of the possible relationship for co-polymers:

![Graph showing relationship between $\eta_0$ and $M_w$](image)

Figure 5.52 Zero shear viscosity in relation to weight-average MW

A very good fit of power law type ($\eta_0 \propto M^\alpha$) was found for the PP homo-polymer grades; the random co-polymer MA2 fitted well to the relationship, while the heterophase grade MA1 did not obey it. For that reason, the values for other random co-polymers were included on the next plot (Fig. A69), where the similar values of $\alpha$ for different temperatures were found. As mentioned in Section 2.4.2, the commonly accepted equation 2.59 was postulated for narrow polymer species; in case of polydisperse polymer melts, values of $\alpha$ different from 3.4 can be expected. For polymer grades in this study, an average of $\alpha = 4.7$ was found. A possible reason for that is the dependence of zero shear viscosity not only on $M_w$, but also on polydispersity indices (Eq. 2.61). From the later analysis, it can be stated that there was a clear correlation of $\eta_0$ to $M_w$ of PP and random co-polymer grades. As shown in Section 5.5.1, the zero shear viscosities estimated from the dynamic shear tests were in a good agreement with steady shear $\eta_0$. That provides possibility to utilise the dynamic tests for a quick assessment of PP grades. From a previously established plot of $\eta_0$ vs. $M_w$, the zero shear viscosity can be predicted for a grade with a known $M_w$ and vice versa.
Zero shear viscosity is not a sufficient parameter that characterises the flow of polymer melts. Different degree of shear thinning was found in polymer grades (eg. Fig. 5.19). The inspection of Table A5 showed that most of the polymer grades had very similar values of parameter $m$ of the Cross model, but the onset of shear thinning was different, which was reflected in different values of parameter $K$. In order to classify the shear thinning behaviour of polymer grades, it was convenient to plot their steady shear data in the reduced form, i.e. as $(\eta/\eta_0)$ vs. $\eta_0 \gamma$. It was found that $\eta/\eta_0$ falls off more rapidly with $\eta_0 \gamma$ for the samples with broader MWD [Minoshima, W., et al., (1980)]. The data presented in Fig. 5.19, rearranged to this form are plotted in Fig. 5.53:

![Graph showing reduced viscosity vs. shear rate for different polymer grades](image)

**Figure 5.53** The plot of reduced viscosity $(\eta/\eta_0)$ vs. $\eta_0 \gamma$ for several polymer grades

The former statement is valid for differences between MM1 and MA3, but in case of EP1 one has to consider that it was a blend with a low-MW oligomer. Fig. 5.53 showed that any extreme behaviour on such a plot might suggest different nature of a polymer grade. In case of PP homo-polymer grades, the shear thinning behaviour was related to polydispersity of the grades. It was found that the parameter $K$ increased with polydispersity $(M_w/M_n)$, as shown in Fig. A70. The shape factor, $sf$ defined in Eq. 2.46 was plotted on the same graph. The good correlations were found for both factors; it should be stated here that the values of $K$ are temperature dependent (Table A5) and the
use of such correlations should be restricted to the specified temperature. The possibility of estimating the values of $\eta_0$ (from the relationship shown in Fig. A69) and $K$ (Fig. A70) from polymer's MWD, provides a tool for predicting the whole shear flow curve, using the simplified Cross model (Eq. 2.37) with an average value of $m = 0.67$.

5.7.1.1 Estimation of MWD from shear viscosity curves

The attempt to estimate the complete MWD was pursued by using the Eq. 2.86. For two PP grades, TN1 and MA3 the following parameters were estimated: slope $\nu = -0.65$ and $-0.69$ and critical shear rate, $\dot{\gamma}_c = 1.8$ and 0.33, respectively. The shear data collected at 210°C were taken as most stable. Theoretical value of index $\alpha = 3.4$ was used. The calculated distribution functions are shown in Fig. 5.54, compared to GPC MWD curves.

![Comparison between calculated and experimental MWD curves](image)

Figure 5.54 Comparison between calculated and experimental MWD curves

One can see that the calculated curves are much narrower than the GPC curves. Their relative positions were correct, suggesting that $M_{\text{peak}}$ (MA3) > $M_{\text{peak}}$ (TN1). However, this was most probably a consequence of scaling with $M_w$ (obtained from GPC). The breadth of calculated curves (dotted lines in Fig. 5.54 – log-normal extrapolation of calculated values) was similar for two PP grades, although their MWD curves determined by GPC were very distinct. The polydispersity index $M_w/M_n \approx 1.4$ was calculated using Eqs. 2.3 - 2.5 for both grades, which was opposite to experimental findings. A possible reason for a bad agreement between rheology- and GPC- distribution curves could be a similar slope $\nu$
in the power-law region, as well as a low density of experimental points in the transition zone around critical shear rate. The viscosity function was interpolated in that region, what made it smooth but less accurate. The mathematical manipulation could also introduce some error, in the process of modelling the viscosity functions and while performing the differentiation.

5.7.2 MWD and viscoelastic properties of polymer grades

Dynamic shear testing provides a variety of information on polymer's viscoelastic behaviour. From the results of a dynamic frequency sweep, parameters can be derived that correlate with molecular weight distribution. As discussed before (Section 5.5.1), the zero shear viscosities estimated from dynamic data agreed well with $\eta_0$ from the steady shear. That makes use of the same type of correlation between $\eta_0$ and Mw as described in Section 5.7.1. The dynamic moduli, G' and G" are in relation to the relaxation time spectra via Eqs. 2.92 a and b. Simple procedures to extract some information on polydispersity from these relations were proposed in the forms of rheological polydispersity index, RPI [Zeichner, G.R. and Patel, P.D., 1981] and modulus separation index, Modsep [Yoo, H.J., 1993], given by Eqs. 2.96 and 2.97, respectively. The values for RPI and Modsep were estimated from the experimental data at 210°C and presented in Table A9.

![Rheological polydispersity index vs. Mw/Mn](image.png)

Figure 5.55 Rheological polydispersity index vs. Mw/Mn
It can be seen that the cross-over frequency, \( \omega_c \), was shifted towards lower values for polymer grades with broader distribution. The cross-over modulus, \( G_c \) was consequently lower which yielded a higher \( RPI \) in Eq. 2.59. The correlation between \( RPI \) and \( M_w/M_n \) is shown in Fig. 5.55; relatively good correlation was found for PP homo-polymer grades, but none of the co-polymer types (represented by MA1 and MA2) could fit well. However, the \( Modsep \) index showed a very good correlation to \( M_w/M_n \), even for MA1 and MA2, especially at low modulus (500 Pa), as shown in Fig. A71.

### 5.7.2.1 Relaxation time spectra and relaxation moduli of polymer grades

The most common approach of relating dynamic shear data to MWD is based on the mixing rules, represented by Eq. 2.50. The relaxation modulus, \( G(t) \) is usually calculated from the relaxation time spectra (Eq. 2.27) that can be extracted from the dynamic moduli, using Eq. 2.55 (a and b). The plateau modulus, \( G_N^0 \) is usually estimated from the experimental \( G' \) data, by fitting an appropriate equation (eg. 2.55a). There are several problems one can encounter in practicing the above procedure: 1) plateau region is usually not accessible in experiments, due to the limited frequency; 2) estimation of relaxation time spectra from the dynamic moduli is an ill-posed problem and 3) another ill-posed problem is encountered when estimating the MWD from the relaxation modulus. It was recently proposed to avoid problem (3) by direct calculation of the distribution function from the relaxation time spectra [Thimm, et al., (1999)], using Eq. 2.56. For that purpose, the relaxation time spectra were calculated for the polymer grades, using the data obtained by time-temperature superposition of the experimental dynamic moduli.

The calculations were performed by using the Rheometrics Rhios\textsuperscript{®} Software, which provided a choice of three computational methods: least squares, non-linear fitting and Tikhonov regularisation. To choose the most suitable technique, spectra for one of the grades (MA1) were calculated using all three methods. The comparison (Fig. A72) showed that the differences between methods were reflected only at low relaxation times, which is the most important area to be related to MWD. The recalculation of dynamic moduli from the relaxation spectra (Fig. A73) showed that the non-linear fitting method failed to replicate the \( G'' \). As a purely iterative technique, the least-squares method produced the spectrum that was recalculated to dynamic moduli identical to the experimental ones. The \( G'' \) recalculated from the relaxation spectrum produced by
regularisation method deviated at high frequencies from the experimental loss modulus, but the method was accepted for further calculation because of the shape of the relaxation spectrum obtained by this technique, which is recommended for use in estimating the MWD from the relaxation data [Honerkamp and Weese, (1993)]. Relaxation spectra for several polymer grades estimated at the temperature of 190°C are shown in Fig. 5.56. The spectra in Fig. A74 were calculated for the temperature of 210° (co-polymer grades compared to TN1).

Figure 5.56 Relaxation spectra of polymer grades at 190°C

The relaxation times of polymers (for a specified relaxation strength, H) are dependent on both molecular weights (Eq. 2.53) of the relaxing chains and the polydispersity, or the MW of the surrounding chains. With increasing MW, the relaxation times increase, as seen for PP grades in Fig. 5.56. The species that could not be detected by GPC analysis (such as cross-linked high-MW chains in MA1) can also shift the relaxation times, which would cause disagreements in correlations between viscoelastic properties and MWD. A very strong effect of that type was noticed in the relaxation spectra of MA5 (compared to MA4 in Fig. A75), which explains the difficulties in reaching the zero shear viscosity: the times required to relax the low stresses were increased in comparison to MA4. The effect of temperature on relaxation times can also be seen in Fig. A75. In accordance to discussion in Section 5.5.3, the decrease in temperature shifted the relaxation times towards higher values along the horizontal axis. Using the relaxation spectra, the relaxation moduli, $G(t)$ of polymer grades were calculated (Figs. 5.66 and A76):
The temperature dependence of relaxation moduli is shown in Fig. A77. It can be seen that $G(t)$ was estimated as a smooth function of time, which indicated the validity and precision of experimental data and computational techniques.

5.7.2.2 Calculation of the relaxation moduli from the MWD

In order to apply Eq. 2.56 for calculating the MWD from the relaxation time spectra, one has to determine the generalised mixing parameter $\beta$. As mentioned in Section 2.4.3, the values of $\beta$ in the range of 2 - 3.84 were used. A suitable way to estimate its value for polypropylene was to calculate the relaxation modulus from the experimental MWD using Eq. 2.54 and compare it with experimental $G(t)$. Another parameter that required adjustment during this procedure was the plateau modulus, $G_N^0$. Its value was estimated as $\approx 60,000$ Pa by using the Rhios® software, which was far too low compared to literature value of around 380,000 Pa [Eckstein, et al., (1998)]. For that reason, the $G_N^0$ for PP grades was estimated by applying two methods: fitting the Cross model-type equation to $G'$ as a function of $1/\omega$ and from the relaxation spectra, by using Eq. 2.58. The value of $G_N^0 = 130,000$ Pa was accepted as the most accurate for the available data. Eq. 2.52 was used as the kernel function $F(t,M)$. The MW-time scaling was performed by using the Eq. 2.90. Parameters $K$ and $\alpha$ were also adjusted during the procedure. The best fit, shown in
Fig. 5.58 was obtained with the following values: $K = 6.2 \times 10^{-13}$, $\alpha = 3.2$ and $\beta = 3.6$. However, a relatively good fit could be obtained by using the literature value for $G_N^0 = 380,000$, with the parameters $K = 8.0 \times 10^{-15}$, $\alpha = 3.4$ and $\beta = 2.8$.

![Graph showing comparison between relaxation moduli of MA4 calculated from viscoelastic data (line) and MWD (symbols)](image)

Figure 5.58 Comparison between relaxation moduli of MA4 calculated from viscoelastic data (line) and MWD (symbols)

Since there were many parameters in the equations that had to be determined, the method could be regarded as a relative one. Fig. A 78 shows that a good fit could be obtained for MA3 with a different set of parameters: $G_N^0 = 80,000$ Pa, $K = 1.0 \times 10^{-13}$, $\alpha = 3.4$ and $\beta = 3.84$. The attempt to use $\alpha = 4.7$, determined in Section 5.7.1 did not give useful results. It appears that $\alpha$ in the relation given by Eq. 2.53 was the parameter valid for the monodisperse fractions; hence it followed the theoretical value of $\approx 3.4$.

5.7.2.3 Calculation of the distribution function from the relaxation spectra

The equation 2.56 was applied to the relaxation spectra of several PP grades, using the parameters determined in the previous section. Fig. 5.59 shows that the use of $G_N^0 = 80,000$ Pa produced a better agreement between calculated and GPC distribution curves for a polymer grade (MA4). It can be noticed that the distribution curve calculated from the relaxation time spectra was broader than the curves calculated from the viscosity functions, given in Fig. 5.54 ($M_w/M_n \approx 2$, compared to 1.4 for the former curves).
Figure 5.59 Comparison between GPC and calculated MWD curves (bars- $G_N$=380,000, crosses- $G_N$=130,000 Pa, full line- GPC, dashed- log-normal extrapolation)

It appeared from the results presented in Fig. 5.59 that the use of experimentally determined values could produce more accurate results than using the literature values for different PP grades. The importance of adequate determination of parameters in the Eq. 2.56 can be seen from Fig. A79: the curve calculated using $\beta = 3.84$ was broader (and closer to the GPC curve) than the curve calculated with $\beta = 2$ (quadratic mixing rule). The most important verification of the applied methods is presented in Fig. 5.60: the comparison between MWD curves of MA3, MA4 and TN1 calculated from the viscoelastic data showed that the applied procedure maintained the information on the broadness of distribution, which was not achieved by using the viscosity function in Section 5.7.1.1. The polydispersity indices calculated from the distribution functions (Fig. 5.60) for MA3, MA4 and TN1 were 2.2, 2.0 and 1.9, respectively, which was in a correlation to the GPC data given in Table 5.1, as shown in Fig. A80. Such proportionality can be utilised to obtain the more realistic polydispersity measures from this method. It can be seen from Fig. 5.60 that the lack of accuracy was most significant for the low MW end, while the calculated curves appeared very similar to the GPC curves at molecular weights $> M_w$. This phenomenon was probably a combination of two factors: the principal one - higher sensitivity of rheological parameters to high MW chains and - the frequency limits of the dynamic shear measurements.
5.7.3 Molecular structure and extensional properties of polymer grades

When the extensional viscosity measurements are performed in the linear viscoelastic region, the results are supposed to follow three-fold shear stress-growth function (Eq. 2.51), as shown for MA3 in Fig. 4.18, as well as for MA5 in Fig. 5.61:

Figure 5.61 Transient extensional viscosity of MA5 at 180°C compared to three-fold shear stress-growth functions: from step-rate test (solid line) and viscoelastic data (Eq. 2.64)
Since the step-rate test involve many experimental errors (Section 4.4.2.1), a choice for obtaining the $3 \times \eta^*(r)$ using the Eq. 2.64 was utilised. As seen in Fig. 5.61, a good agreement was found between ‘extensional viscosity’ curves obtained from different sources, in the strain range of 1 - 3. As a viscoelastic property, the transient extensional viscosity would tend towards a plateau at high strains, according to Eqs. 2.35 & 2.36. The results discussed in Section 5.6.2 confirmed a good agreement between shear and extensional viscosities. From these findings, it can be expected that the extensional viscosity plateau would be at the magnitude of $3 \times \eta_0$, which is proportional to a power of $M_w$. In this work, the slope of the transient viscosity curves, or the rate of the stress growth, was related to polydispersity. It was found that the stress-growth was steeper for the grades with broader distributions (eg. Fig. 5.46). From the plot given in Fig. 5.62, it can be seen that the steepness of the extensional viscosity curves depended strongly on $M_z/M_n$, which is probably a consequence of the significance of the high molecular weights on the relaxation spectra:

![Graph showing the relationship between slope and polydispersity](image)

**Figure 5.62** Slope of the $\eta_E$ curves as a function of polydispersities, $M_w/M_n$ and $M_z/M_w$

The non-linear effects in the extensional rheology, such as strain hardening, were also found for polypropylene, but only in the semi-molten state. As discussed in Section 5.6.2.1, these effects were predominantly influenced by morphology of the polymers, rather than their MWDs.
6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

* Two PP grades were blended with a commercial modifier; this was the first study on the blends of different PP grades with a commercial modifier based on hydrogenated oligocyclopentadiene (HOCP). For the first time, it was possible to observe two glass-transition temperatures (Tg) for the PP/HOCP system, which was an additional confirmation of immiscibility.

  - the multiplicity of the melting peaks for slowly crystallised samples was observed and reported for the first time for PP/HOCP system; this phenomenon was successfully utilised as a tool for detecting the phase separation of such blends in this study
  - in both series of blends (MA3/EP1 and MM1/EP1), the phase separation was assigned to the blends containing ≥ 50%EP1; the MWD of the PP grades did not show any influence on blends’ morphology and thermal behaviour

* The heterophasic co-polymers, MA1 and MA5 showed a rheological behaviour which was a consequence of the presence of ethylene-propylene rubber dispersed in the polymer matrix. A modification of the Cross model was proposed in order to model the viscosity of MA5.

* Different rheological behaviour was found for the two series of EP1 blends. The mechanism of the action of EP1 on the viscosity of PP was assumed to be dual: -the effect of HOCP component was represented by lowering the shear viscosity, due to its low Mw; - the effect of the PP component of EP1 was modifying the MWD of the polypropylene in the blend, in comparison to the original MWD. Depending on the MWD of the PP grades, different combinations of effects could be achieved.

* The viscoelastic behaviour of the EP1 blends was thoroughly examined. The effects of HOCP and PP components on shear viscosity, found in steady shear mode, were confirmed by dynamic shear testings. Additionally, the morphological factor was related to the dynamic shear properties. The use of Cole-Cole plots, previously reported as a tool for
detection of immiscibility, was not successful in case of EP1 blends. The time-temperature superposition was found to be less successful in case of the blends with \( \% \text{EP1} \geq 50 \) than for the systems with lower EP1 concentration. That was assigned to the phase separation, i.e. such blends were not thermorheologically simple. The most significant rheological indicator of phase separation was the sudden increase in flow activation energy for the blends with \( \geq 50\% \) EP1.

* The transient extensional viscosity (extensional stress growth coefficient), \( \eta^*_e(t) \) was measured using the RME extensional rheometer. It was found for all polymer grades that the melt extensional viscosity (at 180\(^\circ\)C) followed the three-fold shear transient viscosity, which could be determined experimentally or calculated from the relaxation time spectra. Decrease in temperature to 170\(^\circ\)C caused an increase in viscosity. The difference between PP homo- and co-polymers was noticed: PP grades showed lower extensibility, which was explained by occurrence of crystals that acted as filler particles. One of the PP grades, MA3 showed a strong strain hardening behaviour, which was characteristic for the rest of the grades at temperature of 165\(^\circ\)C. This type of behaviour of semi-molten PP samples was assigned to the existence of permanent network built by crystallites connected with the PP chains. The new parameter was introduced in order to characterise the strain hardening behaviour of PP: extensional viscosity index, \( EVI \) that was a ratio of extensional viscosities at strains 3 and 1, respectively.

* Both shear and extensional behaviour of tested polymer grades were strong functions of their molecular weight distributions. The dependence of the zero shear viscosity on the weight- average MW followed the power law, with the exponent of 4.7, which was different from the usually quoted value of 3.4; this was not regarded as disagreement, since the power of 3.4 was only proven to be valid for the monodisperse species, while in the broad commercial polymers the polydispersity (expressed by \( M_w/M_n \) and \( M_z/M_w \)) could play an important role. The influence of polydispersity on the onset of shear thinning was found, i.e. the \( K \) parameter of the Cross model increased with increasing \( M_w/M_n \) in a linear fashion. The above correlations could be utilised to predict the viscosity of a polymer grade from its known \( M_w \) and \( M_w/M_n \).
The MWDs of two PP grades were estimated from their steady shear viscosity curves by inversion of the blending laws. The method was not found suitable for these polymer grades, since it did not provide information about broadness of the distribution.

From the viscoelastic data, two parameters were extracted that correlated well with polydispersity. Rheological polydispersity index, calculated from the modulus at the cross-over point ($RPI = 10^5 / G_c$) correlated to $M_w/M_n$ less accurately than the modulus separation index (Modsep), which was extracted at low values of modulus. It was significant that both types of co-polymers followed the Modsep- polydispersity correlation, what was not the case for the RPI. Relaxation time spectra $H(\tau)$ and relaxation moduli, $G(t)$ of the polymer grades were calculated from their master-curves. Attempts were made to estimate the generalised mixing parameter, $\beta$ for PP. The value of $\beta = 3.6$ was found to be most suitable for the grades tested. In combination with plateau modulus estimated at around 130 kPa, that made possible calculation of $G(t)$ from the MWD.

The recently proposed analytical relationship between relaxation spectra and MWD was applied to several PP grades. It was found that the obtained curves were narrower than corresponding GPC curves. However, the relative position and broadness of the distribution curves were in agreement with the GPC results.

The influence of molecular weight distribution on the extensional viscosity of PP at 180°C was found to be based on the general principles of linear viscoelasticity. The transient extensional viscosity curves tended towards the three-fold zero shear viscosities at high strains, which means they could be related to $M_w$. Polydispersity was found to have an influence on the slope of the curve, which was for the first time related to both $M_w/M_n$ and $M_z/M_w$. The stronger influence of the higher moment of distribution, $M_z/M_n$ was shown.

The morphology of the samples was found to have a huge influence on the polymers’ extensional rheological behaviour. Two types of semi-molten polymer states were defined: one above the melting temperature, which appears molten but it contains remained crystallinity; and the second one - the rubbery state, just bellow $T_m$, in which the polymer appears solid, but it is soft and possible to stretch. The existence of the later allows both
high drawability and sufficient extensional viscosity required for stable operating of the BOPP process.

### 6.2 RECOMMENDATIONS

- Produce a reliable set of steady shear flow curves for PP grades of different known MWDs that will allow calibration of Cross model parameters, \( \eta_0 \) vs. \( M_w \) and \( K \) vs. \( M_w/M_n \). This would allow the shear behaviour of new grades to be predicted on the basis of their molecular characteristics.

- Produce a reliable set of dynamic shear results and MWD curves for different PP grades that will allow estimation of \( M_w \) and polydispersity for a new grade according to the correlations proposed in this work.

- Prepare a program in a suitable software package that will make the conversion of viscoelastic data into MWD via relaxation time spectra even less time-consuming. Apply the program to a large set of polymers and investigate whether a calibration is possible between the rheological and GPC distribution curves.

- Prepare the procedure that would allow extensional viscosity measurements near \( T_m \) to be utilised for the estimation of optimal BOPP processing window.
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MAJOR PUBLICATIONS AND PRESENTATIONS ARISING FROM RESEARCH


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Table A1 Molecular weight averages and polydispersities of analysed polymer grades

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<th>St.dev. (°%)</th>
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### Table A2: Comparison between GPC results obtained at RMIT University, Australia and in Waters Laboratories, USA

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Figure A1 The MWD curves of MA3/EP1 blends (PP component)
Figure A2 The MWD curves of MM1/EP1 blends (PP components)
Figure A3 Mw averages and polydispersities (Mw/Mn) of the EP1 blends
(squares- MA3, diamonds- MM1; open symbols- Mw (primary axis), filled symbols- Mw/Mn (secondary axis)
Figure A4 DSC crystallisation curve of a random co-polymer (M42)
Figure A5 First heating runs in DSC analysis of co-polymer grades
Figure A6 DSC crystallisation curves of co-polymer grades
Figure A7 DSC melting curves of co-polymer grades (second run)
Figure A8 Determination of Tg from the cooling DSC scans for co-polymers
Figure A9: Crystallisation behaviour of MA1 and MA5
Figure A10 DSC tests on EP1 samples prepared under different quenching conditions
Table A3 Results of the DSC study on the EP1 blends with MA3 and MM1

### EP1/MA3 Blends

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<th>Tm (2)</th>
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### EP1/MM1 Blends

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<th>Tm (2)</th>
<th>Te</th>
<th>%cryst.</th>
<th>ΔH* (J/g)</th>
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Figure A11 Melting and crystallisation temperatures of the blends in relation to their composition
Figure A12 Percentage crystallinity of EP1 blends with MA3 and MM1 related to their composition
Figure A13 Optical micrographs of EPI during crystallisation

115°  100°  25°C
Figure A14 HS-OM images of MM1/EPI 80/20 blend
Table A4 Results of MFI measurements for PP grades (230°C, 2.16 kg load)

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<th>Grade</th>
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* @190°C, 2.16 Kg
<table>
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<th>230°C</th>
<th>250°C</th>
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<td>K</td>
<td>m</td>
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<td>0.63</td>
<td>3500</td>
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<td>3500</td>
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<td>TEPB</td>
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*Table A5 Cross model parameters for polymer grades*
Figure A15 Steady shear viscosity curves of MA4 (symbols- experimental, line- Cross model)
Figure A16 Steady shear viscosity curves of TN1 (symbols: experimental, line: Cross model)
Figure A.17: Steady shear viscosity curves of TN2 (symbols: experimental, line: Cross model)
Figure A18 Steady shear viscosity curves of MM1 (symbols - experimental, line - Cross model)
Figure A19 Shear viscosity curves of PP grades at 190°C
Figure A20 Shear viscosity curves of PP grades at 210°C
Figure A21 Shear viscosity curves of PP grades at 250°C
Figure A22 Steady shear viscosity curves of MA1 (symbols- experimental, line- Cross model)
Figure A23 Steady shear viscosity curves of MA2 (symbols- experimental, line- Cross model)
Figure A24 Steady shear viscosity curves of MA5
Figure A2.5: Viscosity of copolymers compared to TN1 at 200°C
Figure A26 Step rate test (transient shear viscosity) of MA5 at 180°C and 0.012s⁻¹
Figure A27 Grades MA1 and MA5 compared to TN1 at 230°C
Figure A29 Viscosity curves of MA3/EP1 blends at 230°C
Figure A30: Viscosity curves of MM1/EP1 blends at 230°C
Figure A31 Matching viscosities of MA3 and TN1 at different temperature (MA3 - 250°C, TN1 - 230°C)
Figure A32 Storage modulus (G') of several polymer grades at 230°C
Figure A33 Complex viscosity ($\eta^*$) of several polymer grades at 230°C

![Complex viscosity plot of polymer grades at 230°C](image)
Figure A34 Results for dynamic shear testings of MA3: $G'$ and $\eta^*$ curves at 190°, 210° and 230°C
Figure A36 Results for dynamic shear testings of TNI: $G'$ and $\eta^*$ curves at 190°, 210° and 230°C
Figure A36a Results for dynamic shear testings of TN2: $G'$ and $\eta^*$ curves at 190º, 210º and 230ºC
Figure A37 Comparison of complex viscosity curves for PP grades at 250°C
Figure A38 Comparison between complex viscosities of random co-polymer grades at 190°C and 250°C
Figure A39 Complex viscosities and storage moduli of MA1 at 190°C, 210°C and 230°C
**Table A6 Flow activation energies (Ea, kJmol⁻¹) of polymer grades**

<table>
<thead>
<tr>
<th>PP Grade</th>
<th>MA3</th>
<th>MA4</th>
<th>MM1</th>
<th>TN1</th>
<th>TN2</th>
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Figure A40 MM1 master-curves at $T_{ref} = 210^\circ$C

$G', G''$ (Pa)

$\eta^*$ (Pa.s)

$T_r = 210^\circ$C

$a_T \omega$ (rad/s)
Figure A41. M44 master-curves at $T_{ref} = 210^\circ$C
Figure A42 $G'$ master-curves of co-polymer grades (compared to TN1) at $T_{ref} = 210^\circ C$
Figure A43 Complex viscosity of MA3/EP1 blends at 250°C
Figure A44 Storage moduli of MA3/EP1 blends at 250°C
Figure A45 Complex viscosity of MM1/EP1 blends at 250°C
Figure A46 Storage moduli of MM1/EP1 blends at 250°C
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Figure A47 Master-curves of MA3/EP1 blends
Figure A48 Master-curves of MM1/EP1 blends
Figure A50 Cole-Cole plots for MM1/EP1 blends at 250°C
Figure A51 Extensional viscosity of MA5 at 180° from Cogswell's analysis
Figure A52: Extensional viscosity of MA3 at different temperatures and strain rates
Figure A53 Extensional viscosity of MM1 at different temperatures and strain rates
Figure A54 Extensional viscosity of TN1 at different temperatures and strain rates
Figure A55 Extensional viscosity of TN2 at different temperatures and strain rates
Figure A56: Extensional viscosity of MA3 versus strain at 180°C

[Graph showing extensional viscosity (Pas) plotted against strain (-) with symbols for different strain rates: MA3 0.01s⁻¹, MA3 0.1s⁻¹, MA3 1s⁻¹]
Figure A57 Hot-stage optical micrographs of TNI samples during melting, at temperatures (from left to right): 140°, 160° and 170°C
Figure A58 Comparison between extensional viscosities of PP grades at 180°C and strain rate of 1 s⁻¹
Figure A59 Comparison between extensional viscosities of PP grades at 170°C and strain rate of 0.1 s⁻¹
Figure A60 Comparison between extensional viscosities of PP grades at 170°C and strain rate of 1 s⁻¹
Figure A61 Comparison between extensional viscosities of PP grades at 165°C and strain rate of 0.1 s⁻¹
Figure A62 Comparison between extensional viscosities of PP grades at 165°C (vs. strain)
Table A8 Extensional Viscosity Indices (EVI) for polymer grades

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<td>1 s⁻¹</td>
<td>0.1 s⁻¹</td>
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Figure A63: Extensional viscosity of copolymers at 170°C, strain rate = 0.1 s⁻¹
Figure A65 Extensional viscosity of copolymers at 165°C and strain rate of 1 s⁻¹, compared to TN1
Figure A68 Comparison of extensional viscosities of MA3, MM1 and EP1 at 180°C and strain rate 0.1 s⁻¹
Figure A69 Zero shear viscosity in relation to weight-average MW

\[
y = 1 \times 10^{-23} x^{4.8259} \\
R^2 = 0.9045
\]

\[
y = 9 \times 10^{-22} x^{4.4737} \\
R^2 = 0.9887
\]
Figure A70 Parameters $K$ and shape factor related to polydispersity ($M_w/M_n$)

\[ y = -1.0877x + 11.134 \]
\[ R^2 = 0.9359 \]

\[ y = 0.1893x - 0.5197 \]
\[ R^2 = 0.9569 \]
Table A9 Polydispersity parameters from GPC and dynamic shear testings for several polymer grades

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<th>Mw/Mn</th>
<th>Mz/Mw</th>
<th>ωc (230C)</th>
<th>RPI (210C)</th>
<th>Modsep (1000Pa)</th>
<th>Modsep (500 Pa)</th>
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<td>3.7</td>
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</table>
Figure A71: Modulus separation index versus Mw/Mn

- For 500 Pa:
  \[ y = 0.2883x + 5.7672 \]
  \[ R^2 = 0.91 \]

- For 1000 Pa:
  \[ y = 0.2385x + 4.878 \]
  \[ R^2 = 0.9439 \]
Figure A72 Relaxation time spectra of MAI using different computational methods
Figure A73 Recalculation of dynamic moduli from the relaxation time spectra
Figure A74 Relaxation time spectra of co-polymer grades and TN1 at 210°C
Figure A76 Relaxation moduli of co-polymer grades and TN1 at 210°C
Figure A77 Relaxation moduli of MA4 at temperatures 180°C, 210°C and 250°C
Figure A78 Relaxation moduli of MA3 calculated from viscoelastic data (line) and MWD (symbols)
Figure A80 Comparison between polydispersity indices from GPC and calculated MWD curves

\[ y = 0.1042x + 1.3526 \]

\[ R^2 = 0.9973 \]