Deformation and failure of semi-crystalline polymer systems: influence of micro and molecular structure
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DOI:
10.6100/IR563142

Published: 01/01/2003

Document Version
Accepted manuscript including changes made at the peer-review stage

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Download date: 27. Jan. 2019
Deformation and failure of semi-crystalline polymer systems

influence of micro and molecular structure

NUR 971
Trefwoorden: semi-kristallijne polymeren / deformatie / faalgedrag / slagvastheid / intrinsiek gedrag / microstructuur / stromingsgeïnduceerde kristallisatie / hard filler particles
Subject headings: semicrystalline polymers / deformation / failure / toughness / intrinsic behaviour / micro structure / flow-induced crystallization / hard filler particles

Printed by the University Press Facilities, Eindhoven, the Netherlands.

Cover illustrations: Small and Wide Angle X-ray Scattering patterns of flow induced oriented polypropylene (front) and polyethylene (back).
Cover design: Judith van Overbruggen (Foto Finishing Shop Eindhoven)

This research was financially supported by the Dutch Polymer Institute (DPI; project #164).
Deformation and failure of semi-crystalline polymer systems

influence of micro and molecular structure

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van de
Rector Magnificus, prof.dr. R.A. van Santen, voor een
commissie aangewezen door het College voor
Promoties in het openbaar te verdedigen
op vrijdag 4 april 2003 om 14.00 uur

door

Bernardus Antonius Gerardus Schrauwen

geboren te Oud en Nieuw Gastel
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr.ir. H.E.H. Meijer
en
prof.dr. P.J. Lemstra

Copromotor:
dr.ir. L.E. Govaert
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Summary

This thesis is composed of four papers in the field of deformation and failure of semi-crystalline polymer systems. The main goal is to identify the relationship between mechanical properties and internal micro and molecular structure, which strongly depends on processing conditions applied. In order to achieve this, three main experimental aspects are addressed: (1) morphological characterization, by means of X-ray scattering techniques, (2) determination of intrinsic deformation behaviour, from true stress-strain measurements in uniaxial compression tests, and (3) the macroscopic response in tensile and impact toughness tests.

In Chapter 2 the influence of crystallinity, lamellar thickness and molecular weight on intrinsic properties, like yield stress, strain softening and strain hardening are studied for three semi-crystalline polymers: poly(ethylene terephthalate), polyethylene and polypropylene, differing in glass transition temperature relative to ambient temperature. The yield stress is found to be proportional to lamellar thickness and the strain softening is found to be a property of the amorphous phase. Although a direct measurement of the number of entanglements in the solidified polymer is absent, the strain hardening modulus appears to be related to the chain entanglement density. Indications for this relation are found from the influence of crystallization temperature from the melt on the strain hardening behaviour. A decrease in strain hardening is found when higher melt crystallization temperatures are applied. These higher temperatures allow more pronounced reeling in of the polymer chains upon crystal growth, decreasing the number of trapped entanglements. The fact that the maximum strain hardening modulus found for the poly(ethylene terephthalate) samples equals that of its amorphous sample, indicates a similar relationship as known for the amorphous class of polymers, where strain hardening is proportional to network density. The observation that crystallinity does not influence the strain hardening modulus appears to be related to the fact that, in the polymers investigated, the crystals yield at large deformation, allowing chain transfer and slip without giving a network contribution. Molecular weight and processing conditions are, therefore, found to be the main aspects determining the post yield behaviour.

The importance of this intrinsic behaviour on the macroscopic deformation and failure behaviour is demonstrated in Chapter 3, where uniaxial tensile and impact toughness
tests are performed on similar polymer samples as studied in Chapter 2. Stability of
deformation is qualitatively predicted using a straight-forward analytical modeling
approach. Ductile-to-brittle transitions are found either by an increase in yield stress,
due to an increase in lamellar thickness, or by a decrease in strain hardening and/or
tensile strength, as a result of a lower chain entanglement density. In impact tough-
ness, no brittle-to-ductile transitions were found and only small variations in impact
toughness were observed as a result of variations in intrinsic yield stress and strain
hardening.

In these chapters quiescent processing conditions were used resulting in isotropic struc-
tures. In practice, however, semi-crystalline polymers are often subjected to flow in
processing conditions, like e.g. injection moulding and extrusion. This results in flow-
induced oriented crystalline structures, which influence the deformation and failure
behaviour of polymers. In Chapter 4 injection moulding and extrusion techniques
are used to introduce oriented structures in polyethylene and polypropylene samples.
These oriented structures are characterized along the thickness and flow path of the
samples, subjected to different processing conditions (e.g. temperature and flow rate).
Deformation is found to be anisotropic and related to the oriented structure. For all
polymers studied an increase of extended chains (shish) in the loading direction is
proposed to cause an increase in yield stress, and a lamellar structure oriented per-
pendicular to loading direction leads to an increase in strain hardening. The varia-
tions of yield stress and strain hardening from these oriented structures are capable
to induce brittle-to-ductile transitions in impact toughness on the moulded samples.
Impact toughness enhancement in polyethylene is found to be most efficiently with in-
creasing strain hardening. The effect of orientation on toughness was less pronounced
in polypropylene.

Using the relations between deformation behaviour and crystalline micro-structure, as
identified in the previous chapters, the impact toughness behaviour of calcium carbon-
ate filled polyethylene and polypropylene systems is studied in Chapter 5. Again, the
results indicate an influence of flow history on structure development and on resulting
mechanical properties. The highest impact toughness, observed in this study, was ob-
tained from injection moulded bars, with intermediate filler content, tested close to the
injection gate in flow direction. This behaviour is explained by the presence of an ad-
ditional flow-induced oriented structure along the sample thickness. This orientation
increases strain hardening in flow direction, and, thus decreases localization of strain
in the ligaments between the particles. As a result, more energy can be dissipated and
toughness is enhanced. The fact that polypropylene is less sensitive to impact improve-
ment by orientation, as found in Chapter 4, explains its modest impact improvement
for the calcium carbonate filled blends.
Chapter 1

Introduction

Although polymers are, nowadays, widely used in many structural products given their low costs and ease of processing, the end use in engineering applications is often restricted by their macroscopic mechanical performance. Among the advantages of semi-crystalline polymers, compared to amorphous ones, is that their maximum use temperature is set by the melting temperature rather than of the glass transition temperature. A disadvantage is that the impact toughness of most of the polymers is low, but capable for improvement. The common technique to increase impact toughness is rubber modification. The disadvantage of adding rubber to a polymer system is, however, the further decrease in stiffness. In search for ultimate properties it was recognized that, for some semi-crystalline polymers, the addition of rigid particle leads to an enhancement of both stiffness as well as impact toughness. Using common sense, the increase in elastic modulus of these filled systems is easily recognized, when considering the high stiffness of hard fillers and adhesion between the two materials. The impact toughness behaviour is, however, not fundamentally understood. In fact, one would rather expect a decrease in impact toughness when using rigid particulate fillers, as observed in amorphous polymers. To explain variations in deformation and failure behaviour between different polymer systems, the internal structure of the polymer product has to be taken into account, since the properties are determined by the micro and molecular structure. In the past decade, considerable knowledge was developed on the relationship between molecular structure and mechanical behaviour of amorphous polymers. Although some of these concepts are also applicable to semi-crystalline polymers, the presence of a two phase, crystalline-amorphous structure yields more complex relationships, in which not only molecular constitution is important, but also micro-structural aspects, like e.g. degree of crystallinity, crystal size, spherulite size and crystal orientation. These crystal micro-structures depend on molecular constitution, presence of nucleating agents, and most strongly on processing conditions, i.e. the thermal-mechanical history experienced by the polymer in the process. Consequently, the relationships between all these aspect are most important
in order to understand the final properties of a product. However, many of these underlying relations are still not clear due to the complex mutual interaction of many parameters. The objective of this study is to contribute to this last issue by investigating the deformation and failure behaviour of semi-crystalline polymer systems, and rationalize this from their internal micro structure.

**Survey of the thesis**

This thesis is based on four papers. The goal is to understand the fundamental aspects in the ultimate properties of hard particle filled semi-crystalline polymer systems. This is studied in the final chapter, Chapter 5, where polyethylene and polypropylene samples filled with calcium carbonate particles are subjected to impact toughness tests. The addition of the fillers used, indeed results in an increase in impact toughness, but the behaviour strongly depends on processing conditions applied.

As discussed in the first part of this introduction, processing conditions influence the micro-structure of a product and, thus, determine the final properties. Therefore, it is important to know the relationship between micro-structure and mechanical behaviour, and the influence of processing conditions on the structure. The crystalline structure, like e.g. crystallinity, lamellar size and crystal orientation, can be characterized using suitable techniques, like e.g. X-ray diffraction. Since macroscopic deformation and failure is considered to be directly related to the intrinsic materials’ behaviour, in Chapter 2 the relation between micro and molecular structure and intrinsic properties is studied. The internal morphology (crystallinity and lamellar thickness) of polyethylene, polypropylene and poly(ethylene terephthalate) is varied using quiescent processing conditions, and characterized with wide and small angle X-ray scattering techniques. Uniaxial compression tests are used to determine the true stress-strain behaviour and the intrinsic properties: yield stress, strain softening and strain hardening. The well understood behaviour of amorphous polymers is used to explain the differences in strain hardening behaviour.

In Chapter 3 the same polymer samples are subjected to tensile and impact fracture tests to determine their macroscopic response. Stability of neck drawing is explained with a simplified analytical model approach using the intrinsic true stress-strain behaviour. Trends in brittle-ductile transitions are qualitatively explained from the internal micro and molecular structure.

In these two chapters, quiescent processing conditions were used resulting in isotropic structures. In practice, however, semi-crystalline polymers are subjected to flow in processing conditions, like e.g. injection moulding or extrusion casting, resulting in different crystalline structures. Chapter 4 deals with the deformation and failure of such oriented samples. Flow-induced oriented structures are introduced by injection moulding and extrusion techniques. Distribution and type of oriented structures are characterized with X-ray scattering and microscopic techniques. Anisotropy in macroscopic deformation and failure is studied by tensile and impact testing in flow and perpendicular to flow direction.

Finally, as mentioned before, in Chapter 5 the impact toughness behaviour of calcium carbonate filled polyethylene and polypropylene is studied. The influence of flow history on structure development and, thus, on mechanical properties is recognized and the dependence of impact toughness on processing conditions is explained, using the
knowledge of the previous chapters. At the end of this thesis the main conclusions are summarized in Chapter 6, together with the recommendations for future work, which should substantiate the conclusions given here and explain some still unresolved questions.
Chapter 2

Intrinsic deformation behaviour of semi-crystalline polymers

The influence of crystallinity and lamellar thickness on the intrinsic deformation behaviour of a number of semi-crystalline polymers is studied: a poly(ethylene terephthalate) and two different molecular weight grades of polyethylene and polypropylene. The crystallinity and lamellar thickness are altered by varying the rate of crystallization from the melt and by cold crystallization (annealing) at elevated temperatures above $T_g$ but below the melting point. Crystallinity and lamellar thickness are determined by Wide Angle X-ray Diffraction and Small Angle X-ray Scattering measurements. Uniaxial compression tests are performed to obtain the large strain intrinsic deformation behaviour, e.g. yield stress, strain softening and strain hardening modulus. The yield stress is found to be proportional to lamellar thickness, whereas the strain hardening modulus is shown not to depend on crystallinity or lamellar thickness. Over the strain range experimentally covered, the strain hardening modulus appears to be well described by a simple neo-Hookean relation, and appears to be related to the chain entanglement density. An affirmation for this relation arises from the observation that slowly melt crystallized samples exhibit a lower strain hardening, resulting from a lower chain entanglement density, which is expected to be caused by reeling in of the molecular chains in a slow crystallization process. The similarity in the results observed on all polymers tested supports the conclusion that the crystalline phase does not contribute to strain hardening, which is primary controlled by the chain entanglement density.

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Intrinsic deformation behaviour of semi-crystalline polymers
2.1 Introduction

The search for a relationship between molecular structure and mechanical properties of semi-crystalline polymers has been a motive for extensive studies in the past. The problems in understanding the deformation of semi-crystalline polymers arises from the presence of a two-phased structure and a tendency exists in concentrating primarily on the behaviour of the crystalline regions. Elasticity (Young’s modulus) appears to be understood, in a qualitative sense, in terms of a relation between volume fraction of crystalline and amorphous domains [1,2], but extensive discussion proceeds in finding an explanation of the effect of crystallinity on yield stress and strain hardening. Both properties have been studied on a wide range of semi-crystalline polymers, but are concentrated mainly on polyethylene and ethylene based copolymers. In achieving an as large as possible variation in crystallinity and lamellar thickness, characteristics like number of branches, molecular weight and type of comonomer were varied. The type of crystallization procedures were changed, ranging from solution to melt crystallization and annealing processes at different concentrations, cooling rates and temperatures. Generally all these parameters were changed to find an explanation for the influence of one parameter only: the crystalline structure. Maybe this caused the various hypotheses that were presented to explain the behaviour observed.

Strain hardening of a number of thermoplastic polymers was studied by G’Sell et al. [3, 4], who constructed true stress-strain curves from tensile experiments performed at a local constant strain rate, controlled by in-situ measurement of the diameter in the neck. The strain hardening was found to behave according to the Gaussian relation proposed by Haward and Thackray [5] who used a constitutive model in which a rubber-elastic response was incorporated. The Gaussian description of the strain hardening modulus proved to be valid for all thermoplastic polymers studied in a review by Haward [6] and was also successfully used to describe the strain hardening up to high draw ratios (λ = 3) in amorphous PC [7] and in cross-linked PS and blends of PS and PPO [8]. In the Gaussian theory, the strain hardening is proportional to the network density and absolute temperature. The proportional relation between the strain hardening modulus, measured in compression, and the entanglement (network) density observed by Van Melick et al. [8] for PS/PPO blends is in agreement with these earlier findings. A physical support for the rubber-elastic approach is the reversibility of plastic deformation when deformed amorphous polymers are brought above their glass transition temperature [9]. On the other hand, a disagreement with the Gaussian behaviour of rubber-elasticity is the observed negative temperature dependence [8,10], since the modulus of a true entropic spring would increase with temperature. The negative temperature dependence was suggested to be, at least partly, related to the stress induced segmental mobility of chains [8]. For this reason, neo-Hookean behaviour is preferred over Gaussian behaviour.

Large strain deformation of semi-crystalline polymers is usually discussed in terms of the molecular network, represented by trapped chain entanglements in the amorphous phase and crystallites acting as physical cross-links [12–14]. The influence of the number of trapped entanglements on ultra-drawability of high molecular weight polyethylene was considered in studies by Smith and Lemstra [15–17]. The maximum attainable draw ratio was found to increase with decreasing initial polymer concentration in so-
lution crystallized films and was discussed in terms of a reduced entanglement density in the solid state [15, 16]. Furthermore, a pronounced concomitant decrease in strain hardening was observed in the nominal stress-strain curves of the solution crystallized films [16]. True stress-strain curves showed that the strain hardening modulus of melt crystallized films was significantly larger than observed for solution cast films, and partially remelting of the solution cast film resulted in an intermediate level of strain hardening [17]. Also a decrease in strain hardening was found for increasing testing temperatures.

All tensile tests on these high molecular weight polyethylene samples were performed in a temperature range above the $\alpha$-relaxation temperature, where crystals are known to yield readily, and an influence of crystallites acting as physical cross-links (i.e. the contribution of tie molecules on the network) was considered to be absent [16]. Hiss et al. [13] studied the true stress-strain behaviour at room temperature, obtained by video controlled tensile tests, up to large strains of various polyethylenes and related copolymers. They also used the neo-Hookean model to determine the strain hardening modulus. An increase in strain hardening was observed with increasing crystallinity, which was rationalized by an effective contribution, to the network density, of chains anchored in adjacent crystallites. However, the degree of crystallinity was not the only parameter that was varied in the study concerned, as also molecular weight and branching where varied in order to obtain the differences in crystallinity. It can be expected that these differences in molecular structure also influence the strain hardening. For example, the number of entanglements per molecule increases with molecular weight, and should therefore also be considered to effect the strain hardening. Studies by Kennedy et al. [18, 19] on linear polyethylene and random copolymers of ethylene with narrow molecular weight distributions, indeed indicate a relation between entanglement density and strain hardening modulus. The influence of molecular weight, branch content and branch type was investigated, but a less strenuous mechanism, being strain-induced crystallization, was presented in explaining strain hardening. From all reviewed results, the exploitation of the concept of the rubber elasticity theory, i.e. strain hardening being proportional to entanglement density, seems to be most plausible for semi-crystalline polymers.

Concerning the yield stress in semi-crystalline polymers, there still doesn’t seem to be a perfectly understood qualitative explanation in terms of morphological characteristics. In the early days, a dependency of yield stress on the degree of crystallinity was recognized. Since a glassy amorphous phase also exhibits yielding, most of the studies focus on polyethylene tested above the glass transition temperature, with the amorphous part exhibiting rubber-like behaviour, hence displaying no yield. Popli and Mandelkern [20] reported a linear relation between lamellar thickness and yield stress. In their study, molecular weight and spherulitic superstructure were found not to have any influence on the yield stress. The proportional relation between lamellar thickness and yield was assigned to the process of partial melting and recrystallization [21]. Another, more accepted, approach in explaining the yield stress in semi-crystalline polymers, follows from the classical ideas of crystal plasticity, considering that nucleation and propagation of dislocations control yielding. Young [22, 23] developed a model in which the yield stress is determined from the energy to nucleate a screw dislocation within the crystalline lamellae, resulting in a direct model relation between lamellar
thickness and yield stress. A number of authors [18,19,24–29] validated this model by experimental testing, using experimental and theoretical obtained values for the unknown parameters from literature. While some authors only found the theory to predict a correct order of magnitude of the experimentally obtained yield stress [18,19,24], others showed a good agreement between theory and experiments [25–27]. It is probably the inconsistency in the use of several of the parameters of the model which caused these differences. But the above approaches in understanding the yield mechanism are not based on kinetic aspects, and some discussion in the use of several ’unknown’ parameters and the explanation of observed results is present. A new approach to the model of nucleation of screw dislocations was brought up by Séguéla [30], who proposed that the driving force for nucleation and propagation of dislocations relies on the thermally activated conformational (chain twist) defects.

The use of uniaxial compression tests, performed at constant logarithmic strain rate, looks a promising route [8] to measure the large strain behaviour of polymers. The motivation of this study is finding a relationship between the crystalline structure and the intrinsic mechanical deformation of semi-crystalline polymers, measured in compression. A set of three different polymers is chosen to be investigated: high-density polyethylene, polypropylene and poly(ethylene terephthalate). Crystalline structures are mainly changed by annealing processes of quenched samples, also called cold crystallization for poly(ethylene terephthalate). Highlight of this study is the strain hardening behaviour of the polymers under investigation, whereas yielding will only be investigated for the most commonly studied polymer: polyethylene. The results should mainly supply a basis for a proper understanding of the strain hardening behaviour.

2.2 Experimental

Materials

The semi-crystalline polymers used in this study can be distinguished in three types regarding their glass transition temperature ($T_g$): High-density Polyethylene (HDPE), with $T_g \ll T_{room}$, Polypropylene (PP), with $T_g \approx T_{room}$ and Poly(ethylene terephthalate) (PET), with $T_g \gg T_{room}$. For PE and PP two grades were selected differing in molecular weight, as given in Table 5.1. All polymers were supplied by DSM, The Netherlands. The Arnite-D PET grade is a post-condensated product of the commercial grade D00-300 and contains 2 mol% isophthalic-acid, resulting in a decrease of crystallization rate facilitating the control in degree of crystallinity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>$M_w$ [g mol$^{-1}$]</th>
<th>$M_n$ [g mol$^{-1}$]</th>
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<tbody>
<tr>
<td>PE-1</td>
<td>Stamylan HD 9089S</td>
<td>70.000</td>
<td>11.000</td>
</tr>
<tr>
<td>PE-2</td>
<td>Stamylan HD 8621</td>
<td>210.000</td>
<td>7.000</td>
</tr>
<tr>
<td>PP-1</td>
<td>Stamylan P 17M10</td>
<td>260.000</td>
<td>57.000</td>
</tr>
<tr>
<td>PP-2</td>
<td>Stamylan P 13E10</td>
<td>500.000</td>
<td>84.000</td>
</tr>
<tr>
<td>PET</td>
<td>Arnite-D</td>
<td>76.000</td>
<td>36.200</td>
</tr>
</tbody>
</table>

*Table 2.1: Characteristics of polymer grades used in this study.*
**Sample preparation**

The materials were compression moulded between brass plates and aluminium foil into a mould of 150x75x5 mm³ at suitable temperatures (200°C, 220°C and 280°C for respectively HDPE, PP and PET), imposed by the two heating plates of the press. The polymer pellets were first completely melted under atmospheric pressure and subsequently the pressure was increased stepwise to a maximum pressure of approximately 500 kPa. Degassing, by means of releasing the pressure, was not applied to prevent contact of the surrounding air to the polymer melt, which increases the chance of polymer degradation, especially in case of PET. To avoid hydrolysis, PET was dried in a vacuum oven for at least 10 hours at 110°C before moulding. The polymers were kept at the applied pressure and temperature for at least 15 minutes in order to create homogeneous samples, minimizing the effect of thermal history. The samples were subsequently subjected to different crystallization procedures in order to obtain different levels of crystallinity and lamellar thickness. Within these procedures two types can be distinguished: crystallization coming from above and coming from below the melting temperature.

The procedures applied from above the melting temperature for PE and PET consisted of either placing the molten samples in a cold press of 15°C (quenching, Q15) after removing the brass plates in order to achieve the highest possible cooling rate of about 12-22°C/s, or leaving the molten samples in the press turning off the heat source (slow cooling, SC), allowing to cool to room temperature at a rate of about 0.01°C/s. For the PET samples intermediate cooling rates were also applied, placing the samples in a hot press at 200°C (C200), 150°C (C150) and 135°C (C135). Cooling rates for these temperatures were not measured and assumed to decrease for increasing temperature of the hot ‘cooling’ press. With respect to the crystallization temperature these types of ‘fast’ and ‘slow’ cooling of PE and PET can be considered as non-isothermal. The ‘fast’ cooling technique (Q15) was also applied to PP, but for ‘slow’ crystallization the samples were isothermally crystallized by placing the hot melt in a hot press at 140°C for at least 5 hours. Although, these samples are coded as ‘slow cooling’ (SC) it should be considered that this is an isothermal crystallization procedure, since the crystallization of PP now fully takes place at the temperature of 140°C.

The second type of crystallization procedures were all isothermal (isothermal crystallization, IC) and were only applied to the ‘quenched’ samples (cooled at 15°C). For PET this isothermal crystallization procedure is known as ‘cold’ crystallization and for PE and PP it is known as an annealing process. The samples were wrapped in aluminium foil, sealed with adhesive teflon tape and placed in a thermostated silicon oil bath at given annealing temperatures for different times. This annealing of the quenched samples resulted in an increase of the crystalline long period, given by [31]:

\[ D(t) = D_0 + B(T) \ln \left( \frac{t}{t_0} \right) \quad t_0 > 0 \]  

where \( D \) is the long period at time \( t \), \( D_0 \) is the initial long period of the unannealed sample at a corresponding positive but very small time \( t_0 \), and \( B(T) \) is a constant which is a function of temperature \( T \). From this equation it follows that, upon annealing, the crystalline long period depends on the time and temperature of annealing. Times and temperatures of all isothermal crystallization procedures applied are given in Table 3.2. For the uniaxial compression tests, cylindrical samples (Ø 4 mm x 4 mm) were machined.
Crystallinity and lamellar thickness

The degree of crystallinity and the lamellar thickness were measured by wide- and small-angle X-ray scattering experiments, respectively. Samples with a thickness of about 2 mm, cut from the plates, were used to measure simultaneously 2D SAXS and a 1D WAXS patterns at the Dutch-Belgium beamline (DUBBLE, CRG BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The size of the beam was 1 x 0.3 mm², X-ray wavelength was 1.24 Å and sample-to-detector distance for SAXS measurements was 4 m. The 1D WAXS detector was calibrated using the known peak positions of HDPE for the given wavelength using Bragg’s law:

\[ n\lambda = 2d\sin\theta \]  

(2.2)

Figure 2.1a shows an example of a WAXS profile of an amorphous and semi-crystalline PET sample. Both profiles are scaled to the same intensity at a 2-theta angle of 15.5° and background scattering is subtracted in order to determine the degree of crystallinity of the semi-crystalline sample using:

\[ \chi = \frac{C - A}{C} \]  

(2.3)

where \( C \) is the area of the crystalline profile and \( A \) is the area of the amorphous profile. In case of the PET samples the amorphous halo is assumed to be measured for the fast cooled samples, since no peaks are observed on the broad halo of these profiles (see figure 2.1a). The amorphous WAXS halo of polypropylene was obtained from ref. [32] and for polyethylene an amorphous halo was estimated based on experience [33].

The crystalline long period, \( D \), which is related to the distance between lamellae, was determined from the SAXS measurements. The 2D SAXS data were divided by the detector response obtained from uniform illumination of a Cu source, and background scattering was subtracted. Subsequently, the patterns were integrated in radial direction, resulting in 1D SAXS profiles (see for example figure 2.1b). Since sample thickness varied and beam intensity fluctuated during the experiments, a scaled intensity is plotted against the scattering vector \( q \), which is defined as:

\[ q = \frac{2\pi}{D} = \frac{4\pi}{\lambda}\sin\theta \]  

(2.4)

where \( D \) is the lamellar long spacing, \( \lambda \) the X-ray wavelength and \( \theta \) the scattering angle. The scattering angle can be calculated from the position of the scattered intensity on the detector and the sample-to-detector distance, which was calibrated accurately using the scattering pattern of a dry rat tail collagen. The peak position of the SAXS profiles are taken to calculate the average lamellar thickness from:

\[ L_e = \chi \cdot D \]  

(2.5)

where \( \chi \) is the degree of crystallinity obtained from the WAXS profiles.
Figure 2.1: WAXS profiles of amorphous (A, $T_{mc}=15^\circ C$) and crystalline (C, $T_{mcip}$) PET (a) and SAXS profiles of several PE-1 samples (b).

Mechanical testing

Compression tests were performed on a servo-hydraulic MTS Elastomer Testing System 810 at room temperature. Cylindrical specimens ($\varnothing 4 \text{ mm x 4 mm}$) were compressed at a constant logarithmic strain rate of $3 \times 10^{-3} \text{s}^{-1}$ between two parallel, flat steel plates. The friction between the sample and steel plates was reduced by an empirically optimized method: onto the sample a thin film of PTFE tape (3M 5480, PTFE skived film tape) was applied and the surface between steel and tape was lubricated by a soap-water mixture. During compression tests no bulging or buckling of the samples was observed, indicating that the friction was sufficiently reduced. To achieve a true logarithmic strain rate the displacement of the steel plates was controlled by an extensometer. True stress-strain curves could be contructed from the measured force and displacement, by assuming that the deformation applied was volume invariant.

2.3 Results and discussion

Crystallinity and lamellar thickness

The crystallinity $\chi$, long spacing $D$ and lamellar thickness $L_c$, for each sample are shown in Table 3.2. As expected, the degree of crystallinity was found to be lowest for the quenched (Q15) samples and highest for the slowly cooled samples (SC) for all polymers used. The isothermal crystallization procedures were applied to successfully obtain intermediate levels of crystallinity and lamellar thickness for the PET and PE-1 samples. For the longest annealing times, the maximum lamellar thickness depends on the annealing temperature, which was also anticipated from the term $B(T)$ of equation 3.8. Although the annealing temperature applied to the PET samples was not sufficient to get a lamellar thickness equal to the slowly cooled melt crystallized sample (PET SC), for the low molecular weight HDPE, a complete range in crystallinity and lamellar thickness was reached. Here isothermal crystallization at $125^\circ C$ for 48 hours resulted in almost similar values as the slowly cooled samples. But it should be considered that the isothermal crystallization temperature of $125^\circ C$ is very close to the melting temperature of HDPE and therefore it could well be possible that these samples
Table 2.2: Characteristics of crystallization procedures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Cooling melt</th>
<th>Isothermally</th>
<th>$\chi$ [%]</th>
<th>$D$ [nm]</th>
<th>$L_c$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
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<td>-</td>
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<tr>
<td></td>
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<td>4h @ 100°C</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>24h @ 100°C</td>
<td>11.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>IC100h72</td>
<td>15°C</td>
<td>72h @ 100°C</td>
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<td>10.5</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>IC110m15</td>
<td>15°C</td>
<td>15min @ 110°C</td>
<td>21.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>IC110h4</td>
<td>15°C</td>
<td>4h @ 110°C</td>
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<td>11.9</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
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<td>54h @ 110°C</td>
<td>29.1</td>
<td>10.2</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
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<td>16.1</td>
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<td>8h @ 100°C</td>
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<tr>
<td></td>
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<td>24h @ 100°C</td>
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<td>19.4</td>
</tr>
<tr>
<td></td>
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<td>48h @ 100°C</td>
<td>73.3</td>
<td>29.4</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
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<td>15°C</td>
<td>72h @ 100°C</td>
<td>73.8</td>
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<td>21.8</td>
</tr>
<tr>
<td></td>
<td>IC110h8</td>
<td>15°C</td>
<td>8h @ 110°C</td>
<td>72.3</td>
<td>29.0</td>
<td>21.0</td>
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<tr>
<td></td>
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<td>48h @ 110°C</td>
<td>73.5</td>
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<td>21.7</td>
</tr>
<tr>
<td></td>
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<td>8h @ 120°C</td>
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<td>31.4</td>
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<tr>
<td></td>
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<td>24h @ 120°C</td>
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<tr>
<td></td>
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<td>48h @ 120°C</td>
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<td>32.7</td>
<td>25.0</td>
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<tr>
<td></td>
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<td>8h @ 125°C</td>
<td>75.6</td>
<td>34.7</td>
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</tr>
<tr>
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<td>48h @ 125°C</td>
<td>76.6</td>
<td>35.9</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>in press</td>
<td></td>
<td>76.7</td>
<td>36.7</td>
<td>28.1</td>
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<td>PE-2</td>
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<td>15°C</td>
<td></td>
<td>68.4</td>
<td>29.9</td>
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</tr>
<tr>
<td></td>
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<td>48h @ 125°C</td>
<td>72.9</td>
<td>40.2</td>
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</tr>
<tr>
<td></td>
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<td></td>
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<td>40.5</td>
<td>29.9</td>
</tr>
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<td></td>
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<td>19.2</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>IC140</td>
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<td>4h @ 140°C</td>
<td>72.8</td>
<td>22.6</td>
<td>16.5</td>
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<td>73.5</td>
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<td>PP-2</td>
<td>Q15</td>
<td>15°C</td>
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<td>69.9</td>
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<td></td>
<td>SC</td>
<td>5h @ 140°C</td>
<td></td>
<td>73.4</td>
<td>25.2</td>
<td>18.5</td>
</tr>
</tbody>
</table>

were partially re-melted and crystallized at this elevated temperature from melt. An indication for this can also be found in figure 2.1b, where the SAXS profiles are plotted for several PE-1 samples. Here it can be seen that not only the average long spacing, but also the deviation in long spacings for these two crystallization procedures is fairly similar. Comparison of the intensity levels of the different SAXS profiles for proper interpretation is dangerous, since the sample thickness was not constant and influences the intensity due to absorption.
A relation seems to be present between the degree of crystallinity and lamellar thickness for each polymer. For the low crystalline PET samples the lamellar thickness could not be obtained from the SAXS patterns. The highest isothermal crystallization temperature of 110°C applied to the PET samples, was not sufficient to reach a maximum level of crystallinity, as obtained for the slow crystallized samples. So, unfortunately, the isothermally crystallized samples do not cover the complete possible range of crystalline characteristics. Nevertheless, PET is an attractive polymer to investigate, since the variation of the crystallinity obtained is relatively large, ranging from completely amorphous to 42.6% crystalline. Therefore, the intrinsic behaviour of PET will be briefly discussed first in the following section, since the differences between semi-crystalline and amorphous behaviour of PET can be easily observed.

### Intrinsic behaviour

The intrinsic compressive behaviour of three different PET samples, with different degree of crystallinity obtained via isothermal crystallization procedures, is given in figure 2.2. For the amorphous PET sample (χ = 0 %) a behaviour typical for glassy polymers is observed; an initial elastic region followed by a yield stress after which intrinsic strain softening (‘yield drop’) and strain hardening occurs. Increasing the crystallinity results in an increase in yield stress and a decrease in yield drop. Apparently the crystalline domains contribute more to the yield stress than the amorphous part, resulting in a larger total yield stress of the material. Moreover, if the amount of amorphous polymer decreases, the yield drop, which is an amorphous property, is observed to decrease.

![Figure 2.2: Compressive behaviour of isothermally crystallized PET samples, having different degree of crystallinity (χ).](image)

### Strain hardening

PET

From the true stress-true strain compression curves the strain hardening moduli can be determined at large strains and following a neo-Hookean description, which was
found to be valid for most polymers [6,11], at large strains the stress should be proportional to $\lambda^2 - \lambda^{-1}$. In figure 2.2 the true stress is plotted versus this strain measure and the strain hardening modulus is defined as the slope at large strains ($\lambda \sim 2$), drawn as the dashed lines. Considering the Gaussian background of the neo-Hookean behaviour, the strain hardening modulus is related to the entanglement (network) density, which was experimentally proven to be valid for amorphous polymers [7, 8], including PET, see figure 2.2. Crystallizing the amorphous PET, by isothermal ('cold') crystallization, increases the connectivity in the polymer, resulting in an increase of the yield stress. However, the strain hardening modulus of the crystallized samples is found to be equal to that of the amorphous sample and is clearly not related to the degree of crystallinity. Apparently, after yield the crystallites no longer form physical junction points and essential chain transport through the crystal is possible. As a result, a similar relationship between entanglement density and strain hardening is suggested for semi-crystalline polymers as found for amorphous polymers. The crystalline domains have a viscous contribution, but no entropic network contribution at large strains.

\[
\frac{\dot{\lambda}}{A0} \text{BE} \frac{\dot{\lambda}}{A0} \text{BD}
\]

Figure 2.3: Compressive behaviour of PET samples crystallized with different non-isothermal procedures as given in table 3.2 (a) and strain hardening modulus $G_R$ of all PET samples versus degree of crystallinity $\chi$ (b). Filled symbol represent C and SC samples and open symbols Q15 and IC samples.

The maximum degree of crystallinity obtained by isothermal crystallization was approximately 30%, but higher levels were measured for the slowly cooled samples given in table 3.2. In figure 2.3a the compression curves with its strain hardening (dashed line) are given for several of these non-isothermal crystallization procedures: cooled in the press at 15$^\circ$C (Q15), 150$^\circ$C (C150) and switching of the heating of the press (SC). In figure 2.3b the strain hardening moduli are plotted against the degree of crystallinity for all PET samples tested. The postulated hypothesis, that crystallinity has no contribution to the strain hardening modulus, seems to be invalid at first sight from figure 2.3b, since the strain hardening modulus decreases above a certain degree of crystallinity. However, it should be considered that the samples with the higher crystallinity were obtained from the non-isothermal crystallization procedures (C and SC), indicated in figure 2.3b with the filled symbols. The strain hardening modulus is found
to decrease with decreasing cooling rate, figure 2.3a. An explanation originates from
the fact that crystallization from the melt allows for rearrangement of the chains dur-
ing chain folding. This ‘reeling in’ of chains during crystallization leads to disentan-
glement of the chains from the melt [34–36], more pronounced for lower cooling rates,
resulting in a lower entanglement density and consequently a lower strain hardening
modulus. On the other hand, when isothermal annealing temperatures are applied, the
chain mobility is sufficient for the crystallites to grow, but not sufficient to disentangle
amorphous polymer coils and hence strain hardening is preserved. Similar trends in
the effect of entanglement density, caused by different crystallization processes, on the
strain hardening behaviour was already mentioned in the introduction, regarding the
observations in the study on polyethylene films of UHMW-PE [16, 17]. Here a more
pronounced effect of entanglement density on strain hardening can be found in com-
paring melt crystallized and solution crystallized UHMW-PE samples, where the first
exhibits a large strain hardening, due to the large entanglement density, and the latter
shows almost no strain hardening, since entanglement density is extremely low. Par-
tially recrystallization of the solution crystallized samples results in intermediate level
of strain hardening [17] and complete remelting shows the reversibility of the mech-
anism, indicating the relation with number of entanglements rather than molecular
consitution [37]. Similar trends in drawability, dependent on entanglement density,
were also found in the comparison of slow cooled samples with quenched samples of
melt crystallized polyethylene [14].

![Figure 2.4: Compressive behaviour of: (a) isothermally crystallized PE-1 samples, having
different degree of crystallinity (\(\chi\)), and (b) PE-1 samples crystallized with different
non-isothermal procedures.](image)

**HDPE**

The intrinsic compression behaviour of several PE-1 samples is shown in figure 2.4. In
figure 2.4a the compressive stress-strain relation is plotted for three samples with
different crystallinity, obtained from isothermal (annealing) procedures, and in figure
2.4b the behaviour is plotted for different non-isothermal crystallization procedures.
Figure 2.5 shows the resulting strain hardening modulus of all PE-1 samples tested.
Similar trends as for the PET samples are found, since the strain hardening modulus
does not depend on crystallinity when isothermal annealing is applied, and only seems to drop when a sample is slowly cooled (crystallized) from the melt. It is interesting to note that the highest degree of crystallinity of the annealed PE-1 sample (IC125h48) is of the same level as the slowly crystallized (IC) PE-1 sample, which proves that the drastic decrease in strain hardening modulus of the latter can only be explained by the type of crystallization procedure and not by crystallinity itself.

![Figure 2.5: Strain hardening modulus, $G_R$, of PE-1 samples versus degree of crystallinity ($\chi$). Filled symbol represent SC samples and open symbols Q15 and IC samples.](image)

For the different samples of the higher molecular weight grade (PE-2), again the strain hardening modulus only drops when the sample is cooled slowly from the melt and not upon annealing of the sample, as can be seen in figure 2.6. Another observation favorable for the relation between entanglement density and strain hardening arises by comparing figure 2.5 and 2.6b. It is found that the strain hardening moduli of the higher molecular weight PE-2 samples are larger and that the drop in strain hardening by slowly cooling from the melt is lower than for the lower molecular weight sample PE-1. A high molecular weight polymer is likely to have a higher chain entanglement

![Figure 2.6: Compressive behaviour of PE-2 samples crystallized with different procedures as given in table 3.2 (a) and strain hardening modulus $G_R$ of these PE-2 samples versus degree of crystallinity $\chi$ (b). Filled symbol represent SC samples and open symbols Q15 and IC samples.](image)
density for both crystallization procedures, since ‘reeling in’ of the long chains is more difficult, because of a relatively higher viscosity related to molecular weight.

The increase in entanglement density and the decreasing difference effected by cooling rate for increasing molecular weight was also observed in the investigation of natural draw ratio [14]. Similar trends in the effect of molecular weight and cooling rate on the strain hardening behaviour were also found in literature [18–20]. In these studies no influence of super-molecular structure was observed, e.g. spherulitic size and structure. The observed differences were attributed to level of crystallinity [20]. The effect of cooling rate was only observed indirectly in ref. [19], since they used tensile experiments, where brittle failure was observed for the lower molecular weight, slowly cooled samples. In macroscopic tensile behaviour localisation and failure phenomena can not be overcome as in the compressive measurements of this study. The relation between intrinsic strain hardening and macroscopic tensile behaviour will be discussed in the following chapter.

**PP**

Figure 2.7 shows the results of compression tests on the PP samples. Similar to the PET and PE samples, the strain hardening decreases whenever the samples are slowly crystallized from the melt (SC) compared to quenching from the melt (Q15) and stays at the same level when the samples are annealed. Also similar to the observation in the two molecular weight grades of PE is that the decrease upon slow crystallization is more pronounced for the lower molecular weight polymer grade and that the difference in yield stress between the quenched and annealed low molecular weight PP sample (PP-1) is less than for the higher molecular weight PP samples (PP-2), due to the higher mobility of the lower molecular weight polymer.

![Figure 2.7](image)

**Figure 2.7:** Compressive behaviour of PP-1 (a) and PP-2 (b) samples crystallized with different procedures as given in table 3.2.

The measured strain hardening moduli for the PE ($G_R \approx 1.6 - 4.6$) and PP ($G_R \approx 2.2 - 3.9$) samples correspond with those found by Haward (PE: $G_R \approx 1.7 - 4.4$, PP: $G_R \approx 4.1$) [11]. A conclusion that can be drawn from the results in this study, obtained from three different semi-crystalline polymers, is that strain hardening of semi-crystalline polymers can be described with a neo-Hookean relation originating from
the rubber-elasticity theory, which is also valid for amorphous polymers. There is no observation of any contribution of the crystalline domains to the strain hardening, and an indication towards a relationship with entanglement density exists. For this reason, it can be assumed that studies relating crystallinity to strain hardening are ambiguous when investigation of this relationship is based on different polymer grades, e.g. ref [13]. Also experimental work, using different crystallization techniques, should be discussed carefully, taking in mind the effect of crystallization rate on overall entanglement density.

**Yield stress**

The observations of the compressive behaviour of all tested samples already showed an increase in yield stress with an increasing degree of crystallinity. Since the experiments were performed at room temperature, and PET is situated in the glassy state, the changes in the yield stress of PET have to be contributed to both a change of the crystalline yield stress and the amorphous yield stress. In PP softening was observed, so here an amorphous contribution is also present at the applied deformation rate and temperature. This coupling between amorphous and crystalline yield stress brings an extra parameter in investigating the relation between yield stress and crystallinity.

![Figure 2.8](image)

*Figure 2.8: Observation of 1\textsuperscript{st} ($\sigma_{y1}$) and 2\textsuperscript{nd} ($\sigma_{y2}$) yield stress (a) and schematic representation of fine chain slip at the first yield stress followed by coarse chain slip at the second yield point.*

Therefore a further investigation of this relation is only performed for HDPE, with its glass transition temperature far below room temperature, resulting in a rubber-like behaviour (no yielding) of the amorphous phase. Regarding yielding, two characteristics can be distinguished: the existence of two yield points (double yield) and the relation between crystallinity and yield stress. In this study, all PE samples tested showed the existence of double yield, see figure 2.8a. Time-resolved small- and wide angle X-ray experiments were performed by Butler et al. [38–41] during deformation of PE in both tensile [38, 39, 41] and compression tests [40] and they concluded that double yield exists in both deformation modes. Further occurrence of double yield has been reported mainly in engineering stress-strain curves [42–44]. The deformation mechanisms of both yield points are generally associated as fine chain slip combined with
a martensitic type of transformation within the lamellae at the first yield point and a process of coarse chain slip resulting in lamellar fragmentation at the second yield point [39–41, 45], as schematically presented in figure 2.8b.

![Figure 2.9](image_url)

**Figure 2.9:** Relationship between lamellar thickness ($l_c$) and the two yield stresses.

A proper model for the relation between crystallinity and level of yield stress does not yet exist. Most of the previous studies find the crystal lamellae thickness to be the controlling parameter in the activation of yield in polyethylene [18–20, 23–27] and polypropylene [28, 29]. Figure 2.9 gives both yield stresses, determined as shown in figure 2.8a, as function of lamellar thickness. Independent on the type of crystallization procedure applied, a proportionality is found between lamellar thickness and yield stress, indicating that both yield stresses are activated by similar mechanisms. The most commonly used model that describes the yield stress dependence of lamellar thickness is the one first proposed by Young [22], later refined by Shadrake and Guiu [46]. This model assumes that yield involves the thermal activation of screw dislocation with the burgers vector parallel to the chain axis.

![Figure 2.10](image_url)

**Figure 2.10:** Schematic representation of a screw dislocation in a lamella.

A schematic representation of a screw dislocation with a Burgers vector $b$ and growth over a distance $d$ from the edge is given in figure 2.10, where $l_c$ is the crystal thickness and $\tau$ is the applied shear stress. According to the theory developed, the change in Gibbs free energy, $\Delta G$, associated with the formation of such a dislocation is given by:

$$\Delta G = E - W = \frac{l_c K b^2}{2 \pi} \ln \frac{d}{\tau_0} - l_c d \tau b$$ (2.6)
Here the first term \( (E) \) relates to the elastic strain energy, with \( r_0 \) being the core radius of the dislocation, \( b \) the Burgers vector at distance \( d \) from the edge of the crystal, \( l_c \) the crystal thickness, and \( K \) a function of the crystalline shear modulus. The second term \( (W) \) relates to the work performed by external shear forces, expressed in the shear stress \( \tau \) applied. A dislocation will be activated for a critical value \( d_c \) obtained from the maximum in \( \Delta G \), resulting in:

\[
d_c = \frac{Kb}{2\tau \pi}
\] (2.7)

In this approach a core energy contribution is neglected. Recently Brooks and Mukhtar [27] modified the model, including an extra term representing the core energy, \( (E_0) \), in equation 2.6. Another adjustment, when applying the model to polyethylene, is that the chain axis, and therefore the burgers vector, lies at a tilted angle of 34.5° to the fold surface normal [47]. The lamellar thickness \( l_c \) in equation 2.6 is better replaced by the stem length, \( l \). From these adjustments the following equation results:

\[
\Delta G = E + E_0 - W = \frac{lKb^2}{2\pi} l \ln \frac{d}{r_0} + E_0 - ld\tau b
\] (2.8)

All authors [22–24, 27, 46] assumed that a Tresca yield criteria is valid, i.e. \( \sigma_y = 2\tau \), and combining equation 2.7 with 2.8 resulted in the following expression for the yield stress:

\[
\sigma_y = \frac{K}{\pi} \alpha(T) \exp \left[ -\frac{2\pi \Delta G_c}{lKb^2} + 1 \right]
\] (2.9)

Where

\[
\alpha(T) = \frac{b}{r_0} \cdot \exp \left[ \frac{2\pi E_0}{Klb^2} \right]
\] (2.10)

The Gibbs free energy, \( \Delta G_c \), is assumed to be in the range 40kT-60kT [46], with \( k \) the Boltzmann constant and \( T \) the absolute temperature. Taking a value for \( \Delta G_c \) of 60kT, Brooks and Mukhtar [27] used this approach to fit an optimal value for the temperature dependent parameter, \( \alpha(T) \), for a range of polyethylene grades and found a linear relation for \( \alpha(T) \) for a strain rate of \( 10^{-2} \text{s}^{-1} \). The value of \( K \), taken as a geometric mean of the shear moduli, \((C_{44}, C_{55})^{0.5}\), is also dependent on temperature and was taken from theoretical work by Karasawa et al. [48]. Further, the value for the Burgers vector, \( b \), is generally suggested to be the value of the c-axis of the polyethylene unit cell, being 2.54 Å, and \( r_0 \) is thought to be in the order of 2\( b \). Applying the theory to the results of this study, taking \( \alpha(T) = 0.1481 \), obtained from ref. [27] and \( K = 2.359 \text{ GPa} \) taken from ref. [48] for the involved temperature of 22°C (=295K), shows a relation between stem length within the lamellae and yield stress as indicated in figure 2.11 by the dashed lines using a value of \( \Delta G_c \) of respectively 40kT and 60 kT.

The calculated values of the yield stress as a function of lamellar thickness are in fair agreement with the experimental results of the first yield stress. The second yield stress could possibly be better fitted by using a decrease in the value of \( \Delta G_c \), which is, however, incorrect since a lower value than 40kT is not realistic [46]. This observation doubts the validation of Young’s slip model moreover, since a screw dislocation can be
associated with lamellar fragmentation and should therefore actually be proportional to the second yield point and not to the first yield point, which is believed to be a reversible deformation mode [38–40, 42, 43]. Though it should be emphasized that the current selections of $b$, $K$ and $\alpha(T)$ ($\eta_0$ and $E_0$) are taken from literature, where also some inconsistency in these values was found, no further attempts were made to fit these parameters to match the experimental results. Reason is that, apart from our own criticism of the model, other indications for the notion that the above described model is not perfectly reliable, result from the observation that for example fold surface morphology also seems to effect the yield behaviour [49]. In the investigation of double yield in polyethylene, some authors [44, 50] discussed the observed temperature or strain rate dependence of double yield in terms of viscoelastic ($\alpha$) relaxation in the crystals. A combination of the kinetic aspects of $\alpha$-relaxation and the dislocation model presented above looks a promising route [30]. Another indication for the suggestion that $\alpha$-relaxation should be considered in the explanation for plastic flow, results from the deformation behaviour of oriented UHMW-PE fibres [51]. The irreversible, plastic flow contribution in the deformation was here related to translational motion of chains within the crystal, which is governed by a fast exchange in gauche defects and is accepted to be the origin of the $\alpha$-transition in polyethylene [51, 52]. A detailed investigation in the effect of temperature and strain rate is necessary to draw further conclusions and is beyond the scope of this work.

### 2.4 Conclusions

Uniaxial compression tests proved to be a successful method for characterization of large strain deformation at room temperature of semi-crystalline polymers, regardless of their glass transition temperature. Annealing of quenched samples was shown to have a significant effect on the degree of crystallinity and lamellar thickness. For poly(ethylene terephthalate) the degree of crystallinity was in the range between 0 % and 30 % and for polyethylene in the range of 68 % to 76 % upon applying isothermal crystallization procedures, but for both polymers no effect of annealing on the strain
hardening modulus at large strains ($\lambda \sim 2$) was observed. Long time annealing at high temperature, but still below the melting temperature, of polyethylene resulted in a crystallinity equal to the crystallinity obtained when a slow crystallization process from the melt was applied. The slow crystallization (slow cooling) procedures from the melt, resulted in a lower strain hardening modulus for all polymers tested. However, the decrease in strain hardening, if present, does dependent on the molecular weight and is less for the higher molecular weight polymers. Considering the effect of cooling rate in the crystallization process of a high or low viscous melt, on the number of trapped entanglements in the solidified polymer, strain hardening is expected to be proportional to entanglement density, irrespective of the degree of crystallinity. This relationship between strain hardening and entanglement density is in analogy with a rubber-elastic response. From the fact that a neo-Hookean description indeed holds for all results in this study, it can be concluded that strain hardening primarily depends, at least at large strains, on entanglement density. The absence of crystallites acting as physical cross-links, leads to the suggestion that, after yielding, crystallites have a high mobility. The yield stress at which slip of crystalline lamellae is reached was shown to be dependent on crystallinity, or better lamellar thickness. A fair correlation was obtained between the measured yield stress in polyethylene and that predicted by a mechanism involving the nucleation and propagation of screw dislocations, as found in literature. Still, we think an investigation of the activation of yielding with a kinetic approach, considering the role of stress on the $\alpha$-relaxation chain mobility, is justified.

Acknowledgments

The authors wish to acknowledge Ronald Schellekens of DSM Research for his support and supply of materials, Wim Bras for the availability of the X-ray facilities at the Dubble beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and the financial support provided by the Dutch Polymer Institute (DPI) (project #164).

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Intrinsic deformation behaviour of semi-crystalline polymers

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Chapter 3

Macroscopic deformation and failure of semi-crystalline polymers

The tensile and impact fracture behaviour of poly(ethylene terephthalate) and two different molecular weight grades of polyethylene and polypropylene is studied. Crystallinity and lamellar thickness were altered by varying initial crystallization conditions, such as crystallization rate from melt and annealing at elevated temperature below melting point. The differences observed in macroscopic deformation and failure are qualitatively explained with a simplified analytical model approach using the intrinsic true stress-strain behaviour. Intrinsic material properties were obtained from uniaxial compression tests, performed in Chapter 2 [1]. Stability of neck drawing is found to be dependent on the ratio between intrinsic yield stress and strain hardening modulus and tensile strength. Brittle failure in tension was found to be induced by either an increase in yield stress, due to an increase in crystallinity, or a decrease in strain hardening, due to a lower chain entanglement density, caused by slow crystallization conditions. The importance of tensile strength on fracture behaviour was emphasized by the results of notched high speed impact tensile tests. Slow crystallization from the melt, which is believed to encourage disentanglement, drastically reduced the fracture strength. An increase in crystallinity through annealing was found to increase impact toughness for all polymers tested.

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Relationship between intrinsic and macroscopic deformation and failure in semi-crystalline polymers

Chapter 3

3.1 Introduction

The macroscopic tensile behaviour of semi-crystalline polymers has been a challenging topic in research, since it establishes a basis for the end use of the polymer. Besides characteristics like the elastic modulus and yield (or breaking) stress, which can often be seen as the most important criteria in engineering applications, post yield phenomena, such as drawability and necking, are also of considerable interest. In Chapter 2 [1] it was demonstrated how uniaxial compression tests can be used to measure the true intrinsic deformation behaviour of semi-crystalline polymers and mechanical properties were related to structural parameters. Yield stress was found to increase with crystal thickness and strain hardening modulus was independent from crystallinity, dependent on molecular weight and on the initial crystallization conditions. Therefore, yield stress is controlled by a crystalline parameter, whereas strain hardening is suggested to be dominated by the resulting number of entanglements.

Macroscopic deformation is generally associated with localisation phenomena like necking, voiding or crazing, and fracture. The onset of these phenomena has been shown to be closely related to the intrinsic post yield behaviour of the polymer [2–4]. In the present investigation it will be attempted to use this relation to link the macroscopically observed behaviour with the structural parameters mentioned above. The experimental techniques used are conventional tensile and impact or fracture toughness tests.

In an investigation on the tensile properties of a wide range of linear polyethylenes and random ethylene copolymers by Kennedy et al. [5, 6], all the copolymers and the higher molecular weight grades of the linear polyethylenes showed ductile behaviour, whereas a ductile to brittle transition was observed in the lower molecular weight linear polyethylenes. To reveal the origin of this brittle to ductile transition, the authors focused mainly on the influence of crystallinity and supermolecular (spherulitic) structure. Embrittlement of the material was, subsequently, assigned with an increase in crystallinity, and the failure behaviour observed proved to be independent of the size and perfection of spherulites or the lamellae arrangement. A similar relation between crystallinity and brittleness was found in a study by Mandelkern et al. [7] on four different molecular weight linear polyethylenes (53.000<Mw<120.000), and the absence of a relation between morphological factors and attainable draw ratio was also found in other studies on a range of ductile polyethylenes [8] and ethylene copolymers [9].

In their search for a plausible explanation of the effect of degree of crystallinity on the drawability observed, the authors also noticed an effect of additional parameters, like molecular weight and tie molecule density, but the focus was on the absolute degree of crystallinity. The influence of the crystallization procedures applied to vary the degree of crystallinity were not systematically taken into account, despite the fact that to increase crystallinity not only annealing procedures were used, but also cooling rates were decreased. The effect of a lower crystallization rate causing embrittlement in semi-crystalline polymers is not an uncommon observation [10–13]. For example, Butler et al. [10, 11] presented a study of the deformation of polyethylene using in-situ small- and wide-angle X-ray scattering experiments and, according to their observations, the onset of cavitation occurred at lower strains in case of slowly cooled samples, resulting in brittle failure of low molecular weight HDPE.
The tensile strength of a polymer is determined by its coherence and, thus, the influence of tie molecules and entanglements can be recognized. The importance of initial crystallization conditions on these parameters was shown by Brown and Ward [12] who studied ductile-brittle transitions in slowly cooled and quenched HDPE. They proposed that the brittle fracture stress at low temperatures (\(< 100K\)) depend primarily on the number of tie molecules which hold the crystals together, since the stress necessary to yield the crystals is not reached and chain slip is suppressed. Although there are no direct observations of tie molecules, it is to be expected that their number increases with molecular weight and decreases with decreasing cooling rate from the melt, due to more perfect chain folding and reeling in.

A comparable explanation of similar trends, observed in experiments with POM, was given by Plummer and Kausch [14, 15]. The difference in their argumentation on the observed decrease in fracture toughness with decreasing cooling rate is the fact that they considered a loss of effective entanglements, instead of tie molecules, to be responsible, since the number of true tie molecules in POM was anticipated to be much lower than the number of entanglements [14]. Chain entanglement density is the dominant parameter for tensile strength in amorphous polymers where tie molecules are absent, and the tensile strength is proposed to increase with the number-average molecular weight [16]. Considering this concept, loss in coherence in a material can be expected to be caused by chain slip and disentanglement, independent of crystallinity, or chain breakage. A decrease in chain entanglement density for slow cooling conditions was found in the true stress-strain measurements [1], where the strain hardening modulus, related to entanglement density, decreased upon slow cooling from the melt. This relation between strain hardening modulus and chain entanglement density is the most interesting, since the level of strain hardening is the determining factor for stress build-up in a material and thus important for the maximum draw ratio at which the tensile strength is reached. Thus, a decrease in number of entanglements both decreases the tensile strength and strain hardening. The fact that both tensile strength and strain hardening are related to the entanglement density, complicates an unambiguous understanding of observed brittle to ductile transitions. Although it seems plausible that yield stress, strain hardening and tensile strength are decisive for brittle to ductile transitions to occur, parameters such as temperature and strain rate, which affect these material properties, are often used to invoke brittle to ductile transitions [12, 19]. Nevertheless, the degree of crystallinity and entanglement density seem to be the most interesting parameters in understanding the deformation behaviour in tensile tests.

In impact fracture tests, fracture is invoked by high strain rates and induced localization and failure occurs at low macroscopic overall strains. Dependent on polymer grade the type of failure in these tests can either be of a brittle or ductile type (figure 3.14). Brittle to ductile transitions are usually observed by a change of testing temperature or by a change in initial crystallization conditions [14, 20, 21]. Similar to the explanation used in tensile tests, the degree of crystallinity and chain entanglement density are the two major parameters in understanding the level of absorbed energy upon failure.

Reports on the effect of crystallinity on the impact toughness are, however, controversial. For polyethylene an increase in impact toughness was found with increasing crystallinity upon annealing [13, 22], whereas for polypropylene the opposite was found [23, 24]. Changes in degree of crystallinity are for many crystallization condi-
tions associated with changes in spherulitic size, but both an increase in spherulite size at constant crystallinity as well as a reduction by the use of a nucleating agent resulted in an increase in brittleness of polypropylene [23]. Therefore, spherulite size was assumed not to be important for fracture toughness, which was also proved to be the case in high-density polyethylene [25]. In an investigation of fatigue crack propagation [26] crystallinity and tie molecule density were changed using both annealing conditions below and above the melting temperature. Crystallinity was found to increase relatively more than the tie molecule density upon annealing below the melting temperature and the opposite trend was found upon annealing above the melting temperature. Both crystallinity and tie molecule density determine the fracture toughness, and a competing effect between these two parameters was found. A similar explanation was used in a study on the effect of crystallinity on fracture behaviour on a wide range of polyethylenes [27], and the effect of initial crystallization conditions on the tie molecule concentration was recognized. In the last two studies, tie molecule density was measured using the Brown-Ward equation [12] in which the number of tie molecules is suggested to be the dominant factor for fracture toughness. Although this model only gives an estimate value of the tie molecule density, in many studies this model was accepted to stress the importance of tie molecule or entanglement density. The influence of molecular variables, like molecular weight [22, 28, 29], chain branching [29, 30] or degree of cross-linking [31], on fracture strength were extensively studied. The number average molecular weight was found to be one of the most important parameters controlling the tie molecule density and fracture behaviour in polyethylene [22, 29] and polypropylene [28]. The combination of molecular constitution and crystalline parameters, affecting the number of tie molecules, was described by Huang and Brown [32]. The authors reported that the probability of the formation of a tie molecule depends on both the end-to-end distance of a molecule (molecular weight) and the long period. The observation that polyethylene with an average $M_w$ less than 18.000 was extremely brittle [33], was explained with the suggestion that no tie molecules could be formed. The formation of a tie molecule in this model only considers a conventional tie molecule, being a molecule which connects two adjacent crystals. If two molecules of adjacent crystals join together in an entanglement in the amorphous domain, this may also function as a tie molecule. Although the importance of entanglements and true tie molecules in explaining the fracture toughness is clear, it can be questioned whether the total number of tie molecules, responsible for coherence of the material, are mainly dominated by these chain entanglements or by the so called taut tie molecules.

The studies, discussed above, mostly concern the influence of temperature, strain rate, or molecular factors, such as molecular weight, molecular constitution and features of crystalline morphology. This chapter addresses a method to relate the macroscopic tensile deformation and failure and impact toughness to the intrinsic deformation parameters, such as yield stress and strain hardening, measured in compression. The measured intrinsic deformation and the influence of structural parameters like crystallinity and entanglement density has been presented in Chapter 2 [1].
3.2 Analytical approach

Neck formation in tensile tests

We will use a simple model, originally proposed by Haward [3], to qualitatively predict the stability of macroscopic deformation in tension based on parameters determined in compression tests revealing the materials’ intrinsic deformation. In Chapter 2 [1] for each polymer grade used, the strain hardening and yield stress was studied as a function of crystalline morphology, taking the subjected crystallization procedures into consideration. It was found that for each sample tested strain hardening could be well described with a simple neo-Hookean relation, with a strain hardening modulus $G_R$. In the analytical approach used [3], first, only strain hardening and no strain softening is considered and a true stress-strain curve after yielding can be represented by:

$$\sigma_{\text{true}} = \sigma_y + G_R \left( \lambda^2 - \frac{1}{\lambda} \right)$$  \hspace{1cm} (3.1)

where $\sigma_{\text{true}}$ is the true stress, $\lambda$ the extension ratio, $G_R$ the strain hardening modulus and $\sigma_y$ the yield stress. In this equation the small strain due to elastic deformation is neglected, i.e. yielding starts at $\lambda \approx 1$. In Figure 3.1a several true stress-strain curves are constructed, using different values for the yield stress ($\sigma_y = 18, 24, 30$ and $36$ MPa), taking yielding to take place at $\lambda = 1.1$ and using a constant strain hardening modulus ($G_R = 7$ MPa), all values chosen arbitrary.

Equation 3.1 can be divided by $\lambda$, yielding the engineering stress $\sigma_{\text{eng}}$ strain $\lambda$ curves, see Figure 3.1b:

$$\sigma_{\text{eng}} = \frac{\sigma_y}{\lambda} + G_R \left( \lambda - \frac{1}{\lambda^2} \right)$$  \hspace{1cm} (3.2)
From figure 3.1 it is observed that for an increasing yield stress, the engineering stress-strain curves show a transition from a continuous increasing to a curve exhibiting a decrease in stress after yield. This decrease in stress relates directly to the Considere’s criterium for necking, since the fall in engineering stress, also referred to as geometric softening, leads to localization, whereas a continuously increasing stress results in a homogeneous deformation. Using the condition for necking:

\[
\frac{d\sigma_{\text{eng}}}{d\lambda} = -\frac{\sigma_y}{\lambda^2} + G_R + \frac{2G_R}{\lambda^3} < 0
\] (3.3)

a ratio of yield stress and strain hardening modulus larger than 3 \((\sigma_y/G_R > 3 \text{ for } \lambda \rightarrow 1)\) is found to be the critical value for the transition from homogeneous deformation to necking [3].

The fall in engineering stress is followed by an increase in stress at higher values of \(\lambda\). The inversion point \(\lambda_i\), see figure 3.1b, occurs where \(d\sigma_{\text{eng}}/d\lambda = 0\) and is given by:

\[
\frac{\sigma_y}{G_R} = \lambda_i^2 + \frac{2}{\lambda_i}
\] (3.4)

This condition is required for stable growth of the neck (cold drawing), and was first proposed by Vincent [2]. The condition is met for all stress-strain curves given by equation 3.1 if the strain hardening \(G_R\) is positive and \(\lambda\) is boundless, since after the critical draw ratio at the inversion point the material stabilizes upon further deformation, due to an increasing engineering stress.

**Estimation of the ‘natural draw ratio’**

Haward [3] used the model engineering stress-strain curve to determine an estimation of the draw ratio of the neck or better known as the ‘natural draw ratio’. Ignoring the strain rate sensitivity of the intrinsic deformation behaviour and the strain at the start of the neck, a stable neck is formed when an equilibrium is reached between the load transferred in the neck and that in the undeformed zone. At this point the load in the neck will be large enough to induce yield in the adjacent undeformed material and the estimated draw ratio in neck \(\lambda_n\), see figure 3.2b, is shown to be related to the yield stress \(\sigma_y\) and strain modulus \(G_R\) as follows:

\[
\sigma_y A_0 = \left[\sigma_y + G_R \left(\frac{\lambda_n^2}{\lambda_n} - \frac{1}{\lambda_n}\right)\right] \frac{A_0}{\lambda_n} \rightarrow \frac{\sigma_y}{G_R} = \frac{\lambda_n^2}{\lambda_n} - \frac{1}{\lambda_n - 1}
\] (3.5)

In figure 3.2a, equation 3.5 is graphically represented by the solid line. For a ratio of \(\sigma_y/G_R < 3\) uniform (homogeneous) deformation will be observed and for a ratio above this value necking will occur, with a draw ratio in the neck given by the solid line. The ratio of \(\sigma_y/G_R\) can either pass the value of 3 by an increase in yield stress \(\sigma_y\), as shown in figure 3.1, or by a decrease of the strain hardening modulus \(G_R\). So both changes in the yield stress and the strain hardening modulus can cause a change in the type of deformation behaviour of a polymer, from homogeneous deformation to stable necking or vice versa. Using equation 3.5, studying the post yield behaviour may prove to be a promising way to estimate the strain hardening modulus in a tensile test [34].
Stability of neck drawing

The existence of stable necking and the draw ratio of this neck ($\lambda_n$) can thus be determined as soon as the yield stress and strain hardening are known. The question arises whether this neck is able to bear the transferred load. Taking the tensile strength of the stretched polymer to be a factor $\kappa_t$ larger than the yield stress $\sigma_y$, it follows from equation 3.1 that:

$$\sigma_t = \kappa_t \sigma_y = \sigma_y + G_R \left( \lambda_n^2 - \frac{1}{\lambda_n} \right) \Rightarrow \frac{\sigma_y}{G_R} = \frac{\lambda_n^2 - \frac{1}{\lambda_n}}{\kappa_t - 1} \quad (3.6)$$

This equation is represented by the dashed line in figure 3.2b for (an arbitrary) value of $\kappa_t=5$. Three regions are indicated with the two dotted lines, representing different modes of deformation leading to failure (depicted with the schematic inserts). In region I ($0 < \sigma_y/G_R < 3$) the material starts to deform homogeneously up to a value of $\lambda$ where the dashed line of maximum draw ratio is intersected, resulting in failure. Materials exhibiting values of $\sigma_y/G_R$ in region II, form a stable neck upon drawing, with a draw ratio of the neck given by the solid line. Finally, region III indicates a type of deformation where necking is started at the yield point, but a stable neck can not be formed since the dashed line of maximum draw ratio is reached first. In the area of the transition of region II and III, unstable neck drawing can be expected, influenced by geometrical and material instabilities. For increasing values of $\sigma_y/G_R$, necking rupture will be the observed fracture mode and finally large strain localization occurs at such a small scale that macroscopic brittle failure is observed, without the presence of necking. This localization behaviour in reaching the fracture stress proves that the true intrinsic tensile stress is difficult to measure and that in most cases it is not equal to the measured macroscopic tensile strength of the material.
Effect of strain softening

The application of equation 3.5 was demonstrated satisfactorily for several polymers [3], but is limited to polymers lacking intrinsic strain softening, such as semi-crystalline polymers tested above their glass transition temperature (e.g. polyethylene at room temperature). Semi-crystalline polymers tested below their glass transition temperature (e.g. poly(ethylene terephthalate) at room temperature) are likely to exhibit some degree of intrinsic strain softening, a feature observed in most amorphous polymers. In Chapter 2 [1] it was shown that there can even be a small degree of strain softening in semi-crystalline polymers tested well above their glass transition temperature (e.g. HDPE and PP). Therefore it is important to introduce this true softening into the model, when coupling the measured intrinsic deformation behaviour to the macroscopic tensile behaviour. Van Melick et al. [4] used the above model in studying the localization phenomena in glassy polymers and modified equation 3.5 by taking $\kappa_y \sigma_{y,r}$ for the yield stress in the undeformed zone. Where $\sigma_{y,r}$ is the rejuvenated yield stress and $\kappa_y$ is a multiplier representing the strain softening ($>1$), e.g. caused by ageing in case of amorphous polymers. The equilibrium in stress between the undeformed zone and the neck then yields:

$$\kappa_y \sigma_{y,r} A_0 = \left[ \sigma_{y,r} + G_R \left( \lambda_n^2 - \frac{1}{\lambda_n} \right) \right] \frac{A_0}{\lambda_n} \quad \rightarrow \quad \frac{\sigma_{y,r}}{G_R} = \frac{\lambda_n^2 - \frac{1}{\kappa_y \lambda_n}}{\kappa_y \lambda_n - 1} \quad (3.7)$$

The effect of this increase in yield stress with a factor $\kappa_y$ is schematically presented in figure 3.3 with two arbitrary values of $\kappa_y$. First of all, intrinsic strain softening ($\kappa_y > 1$) causes the equilibrium line to drop initially to zero, meaning that localization is inevitable when the material exhibits strain softening. For this reason, the failure behaviour observed in region I disappears and brittle failure can only be of the type of region III. Secondly, an increase in strain softening (e.g. increase in $\kappa_y$) causes an increase in the draw ratio of a stable neck for similar values of rejuvenated yield stress and strain hardening. This effect was validated in experiments on PC subjected to different thermal and mechanical treatments by van Melick et al. [4]. For semi-crystalline polymers tested below their glass transition temperature, the value of the multiplier $\kappa_y$ is expected to be dependent on the degree of crystallinity, since softening was found to be a property of the glassy amorphous phase (see Chapter 2), and should decrease for increasing crystallinity.

Effect of double yield

A further point of interest, where we will apply the analytical approach, is the observation of double yield in the deformation of polyethylene. Without going into detail on the origin and explanation of the occurrence of the two yield points (see Chapter 2), several true stress-strain curves are schematically constructed in figure 3.4a. For the arbitrary values taken in figure 3.4a, the engineering stress-strain curves are given in figure 3.4b. Both yield stresses are assumed to increase in a similar way, resulting in a constant strain hardening modulus between the two yield points, which is larger than the strain hardening modulus after the second yield point. This type of behaviour was observed in true stress-strain curves obtained from compression tests on high-density polyethylene samples with a different degree of crystallinity in Chapter 2 [1]. A consequence of double yielding is that the second yield point always leads to a sharp
Figure 3.3: Effect of intrinsic strain softening on stability analysis, analogous to [3, 4]: highest reached yield stress is a factor $\kappa_y$ larger than the rejuvenated yield stress $\sigma_{y,r}$ (a). Solid lines represents the equilibrium lines of stable neck growth for polymers exhibiting strain softening, the dashed line represents the tensile strength limits and for each value of $\kappa_y$ two regions of different failure behaviour are observed (b).

neck, whereas the first yield point is associated either with no neck or with only a very shallow neck due to the relatively large strain hardening. As a result, the yield stress observed in a tensile test, defined as a local maximum in stress can either be related to the first yield or the second yield stress as depicted with the arrows in figure 3.4b, and studies using the ‘yield point’ from tensile tests can become less unambiguous. This is illustrated in the experimental results by Brooks et al. [35] and Séguèla et al. [36, 37] in their investigations on double yield of polyethylene and related copolymers. The shape of yielding was found to be similar to the schematic curves of figure 3.4b, for tensile test performed at different temperatures. Besides temperature, strain rate and crystallinity also have an effect on the yield stress.

Figure 3.4: Schematic construction of true stress-strain curves exhibiting double yield according to equation 3.1 (a) and their matching engineering stress-strain curves according to equation 3.2 (b).
Effect of additional parameters

The analysis so far illustrates that deformation and failure of semi-crystalline polymers is strongly dependent on the intrinsic properties: yield stress, strain softening and hardening, and tensile strength. Therefore, the deformation and failure mode is strongly influenced by the parameters related to these properties. For example, most of these properties are strain rate and temperature dependent, some are related to degree of crystallinity (e.g. yield stress) and others to entanglement density (e.g. strain hardening and intrinsic tensile strength). But also, the influence of molecular weight and processing conditions (e.g. crystallization rate) on these properties should be considered. The effects of testing temperature, molecular weight and crystallization rate applied, resulting in various failure types, were demonstrated in a study on ductile to brittle transitions in linear polyethylene by Brown and Ward [12]. Most experiments give results that are consistent with the simple model, e.g. a decrease in fracture strength for decreasing entanglement density [14,15] or a decrease in ‘natural draw ratio’ for increasing molecular weight, due to an increase in strain hardening modulus [38,39]. The influence of strain rate seems trivial, since the yield stress increases with increasing strain rate. However, considering strain rate, the conditions in the neck are different than outside of the neck and the validity of using equations 3.5 and 3.7 becomes questionable. Coates and Ward [40] studied the influence of molecular weight and morphology on the neck profile formation in drawn linear polyethylenes and related the differences to strain hardening and strain rate sensitivity of the materials. In an additional study of the influence of strain rate, Haward [41] argued the inconsistency of applying the model on several results found in literature in which ‘natural’ draw ratio was measured at different strain rates.

Apparently, the importance of strain rate sensitivity should not be neglected and be incorporated in a quantitative study. However, we will show that the model is useful for a qualitative explanation of the observed trends in the tensile deformation and failure behaviour.

3.3 Experimental

Materials and sample preparation

The semi-crystalline polymers used in this study are the same as the ones used in Chapter 2 [1]: High-density Polyethylene (HDPE), Polypropylene (PP) and Poly(ethylene terephthalate) (PET), all supplied by DSM, The Netherlands. Table 5.1 summarizes the type of polymer grade and their molecular weight.

Plates, with dimension 150x75x5 mm³, were compression moulded using the method described in Chapter 2 [1] in order to approximate micro structural properties similar to the compression test samples of that study. This method included two crystallization procedures of the melt, differing in crystallization rate: relatively rapid cooling (quenching), further referred to as Q, and a slow crystallization, referred to as SC. The latter was a slow (non-isothermal) melt cooling technique, by turning off the heat source of the hot press, in case of PE and PET, or an (isothermal) melt crystallization in a hot press at an elevated temperature just below the melting temperature, for PP.

Additionally, crystallinity and lamellar thickness of quenched samples were raised by
Table 3.1: Characteristics of polymer grades used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>$M_w$ [g mol$^{-1}$]</th>
<th>$M_n$ [g mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Arnite-D</td>
<td>76.000</td>
<td>36.200</td>
</tr>
<tr>
<td>PE-1</td>
<td>Stamylan HD 9089S</td>
<td>70.000</td>
<td>11.000</td>
</tr>
<tr>
<td>PE-2</td>
<td>Stamylan HD 8621</td>
<td>210.000</td>
<td>7.000</td>
</tr>
<tr>
<td>PP-1</td>
<td>Stamylan P 17M10</td>
<td>260.000</td>
<td>57.000</td>
</tr>
<tr>
<td>PP-2</td>
<td>Stamylan P 13E10</td>
<td>500.000</td>
<td>84.000</td>
</tr>
</tbody>
</table>

Isothermal crystallization (annealing), coded IC, at elevated temperatures (below $T_m$) for fixed times in a thermostated silicon oil bath. This annealing process causes the crystalline long period to increase, following the relationship [42]:

$$D(t) = D_0 + B(T) \ln \left( \frac{t}{t_0} \right), \quad t_0 > 0$$

where $D$ is the long period at time $t$ and $D_0$ is the initial long period of the quenched samples at a corresponding positive but very small time $t_0$. The value of $B(T)$ is constant for a certain temperature $T$ and strongly depends on the molecular weight. The maximum lamellar thickness that can be reached within a reasonable period of time at a certain temperature is limited, and therefore the annealing times for the impact test samples were not varied in this study, but temperatures were changed. Times and temperatures of all crystallization procedures applied are given in table 3.2. The 5 mm thick plates were machines down to a thickness of 2 mm using a fine surface milling technique, removing 1.5 mm from each side of the plate. For tensile and impact specimens, rectangular bars, with dimensions respectively 75x10x2 mm$^3$ and 75x12.5x2 mm$^3$, were cut out of the plates. Dumbbell-shaped tensile specimens were made according to ISO 527 type 1BA on a milling machine, and Izod impact specimens were notched according to the ASTM D-256 protocol with a notching device. To reduce the number of experiments, for each testing method a selection of the most interesting crystallization procedures was made.

Crystallinity and lamellar thickness

Degree of crystallinity and lamellar thickness were measured by wide- and small-angle X-ray scattering experiments, respectively, performed at the Dutch-Belgium beamline (DUBBLE, CRG BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The method of determining the degree of crystallinity ($\chi$), long spacing ($D$) and lamellar thickness ($L_c$) from the WAXS and SAXS profiles is described in Chapter 2 [1]. The results, partly obtained from [1], are given in table 3.2.

Mechanical testing

The intrinsic deformation was measured in compression tests according to the method described in Chapter 2 [1]. Following the analytical approach, the intrinsic properties required to explain the tensile behaviour, are the yield stress, $\sigma_y$, the softening factor, $\kappa_y$, and the strain hardening modulus, $G_R$. 
<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Cooling melt</th>
<th>Annealing</th>
<th>χ [%]</th>
<th>D [nm]</th>
<th>L_c [nm]</th>
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<td>PET</td>
<td>Q&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15°C</td>
<td></td>
<td>0</td>
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<td>-</td>
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<tr>
<td></td>
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<td>114h @ 110°C</td>
<td>42.5</td>
<td>10.8</td>
<td>4.6</td>
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<tr>
<td></td>
<td>SC&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>42.6</td>
<td>16.1</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>68.4</td>
<td>26.7</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>IC100&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15°C</td>
<td>48h @ 100°C</td>
<td>73.3</td>
<td>29.4</td>
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</tr>
<tr>
<td></td>
<td>IC110&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15°C</td>
<td>48h @ 110°C</td>
<td>73.5</td>
<td>29.5</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>IC120&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>15°C</td>
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<td>32.7</td>
<td>25.0</td>
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<td>30.7</td>
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<td></td>
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<td>19.2</td>
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<td>4h @ 140°C</td>
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<td>73.5</td>
<td>23.8</td>
<td>17.5</td>
<td></td>
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<td>15°C</td>
<td></td>
<td>68.2</td>
<td>19.3</td>
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<td>4h @ 140°C</td>
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<td>5h @ 140°C</td>
<td>73.4</td>
<td>25.2</td>
<td>18.5</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Samples for tensile testing  
<sup>b</sup> Samples for impact testing

**Table 3.2:** Crystallization procedures and morphology characteristics of samples, partly obtained from [1], derived from X-ray scattering techniques.

Tensile tests on the dumbbell-shaped tensile specimens were performed on a Zwick Z010 tensile testing machine, at a constant speed of 10 mm/min, which corresponds to a constant initial strain rate of $3 \times 10^{-3}$ s$^{-1}$ for the applied clamp-to-clamp distance of 55 mm. Although this initial strain rate is equal to the constant logarithmic strain rate in the compression tests, the true strain rate in the tensile tests is not constant and definitely not homogeneous over the sample during a test. Engineering stress-strains curves were constructed from the measured force, clamp displacement and initial cross-section of the specimens. Before testing, all specimens were marked with gauge lines at intervals of 3 mm along their length. In case of ductile behaviour, the tests were stopped at a minimum draw ration of $\approx 2$, where a sufficient length of a stable neck was formed, and the average change in gauge mark separation was used to measure the draw ratio in the neck.

Impact tensile tests were performed on the Izod impact bars at a speed of 1 m/s, using a Zwick Rel hydraulic tensile testing machine. To assure the desired initial speed, a pick-up unit was used to allow the piston to accelerate before loading the specimen. To reduce dynamic effects, the contact area between the pick-up unit and the piston was damped by a rubber pad [43]. Piston displacement and force, using a piezo-electric force transducer, were measured at a sample rate of 250 kHz. The impact toughness energy was calculated by integration of the measured force-displacement curve, di-
vided by the initial cross-sectional area behind the notch. This initial cross-section is
fixed for the geometry of the Izod sample and should therefore be constant (~20.6
mm²), but due to the inaccuracy of pre-experimental machining, width and length of
the crack was measured for each sample. All tests were performed at room tempera-
ture and in four-fold for compression and tensile tests and five-fold for impact tensile
tests.

3.4 Results and discussion

Intrinsic deformation

Table 3.3 gives the results of the intrinsic deformation measured in compression. The
yield stress ($\sigma_y$) and the strain hardening modulus ($G_R$) can be determined adequately
from the compressive true stress-strain curves, but determination of the so called ‘re-
juvenated’ yield stress ($\sigma_{y,r}$), used in equation 3.7, is not straight forward. This stress
is related to the strain softening observed. The value of $\kappa_y$ is be approximated by:

$$\kappa_y = \frac{\sigma_y - \Delta \sigma}{\sigma_y}$$

(3.9)

where $\sigma_y$ is the measured yield stress and $\Delta \sigma$ the drop in stress after yield in the
true compressive stress-strain curves. For the PE samples, which exhibit double yield,
the first yield point is considered to be the yield point which initiates localization be-

Tensile behaviour

In uniaxial tensile testing, deformation phenomena like shear banding, necking draw-
ing and failure can not be circumvented and therefore an engineering stress, defined
as the force divided by the initial cross-section ($F/A_0$), is the measured quantity. The
effect of crystallization procedures on necking and failure is now discussed in terms of
the stability analysis, previously described, considering the necessary intrinsic charac-
teristics, summarized in table 3.3. The engineering stress-strain curves for all PET, PE
and PP samples, measured in tensile, are given in figure 3.5, 3.7 and 3.9, respectively.

In the PET samples (figure 3.5) a ductile neck up to a draw ratio of approximately 1.3 is
observed for the amorphous (quenched) sample (Q), whereas brittle failure takes place
for both crystalline samples (IC110 & SC). Although this indicates that crystallinity
induces a ductile to brittle transition, it is preferable to relate this transition to the in-
crease in the factor $\sigma_y/G_R$, see figure 3.6. Since strain hardening is not changed when
an isothermal crystallization below the melting temperature is applied, the brittle failure of the IC110 sample has to be assigned to the increase in yield stress, which is expected to be related to the lamellar thickness.

The fact that sample Q fails at a draw ratio of 1.3 before the neck is completely developed as schematically shown in figure 3.6 suggest that the Q samples only just survived a stable neck. Since the yield stress is strain rate dependent, a small increase in strain rate would be enough to cause brittle failure of sample Q. This was proven by apply-
Macroscopic deformation and failure of semi-crystalline polymers

Figure 3.6: Qualitative illustration of the relation between $\sigma_y/G_R$ and draw ratio in the neck according to equation 3.6 and 3.7 in the samples of PET. Circles indicate ductile behaviour, x-marks brittle failure.

ing a strain rate of $4.5 \times 10^{-3} \text{ s}^{-1}$ on sample Q. A further increase of $\sigma_y/G_R$, by a decrease in $G_R$, results in an unstable brittle fracture of the slow cooled (SC) sample compared to the cold crystallized (IC110) sample. The lower value of $G_R$ is merely an effect of the lower entanglement density, induced by the lower crystallization rate of the slow cooled sample, since both the slowly cooled and the cold crystallized sample have an equal degree of crystallinity. Of course the lower entanglement density of the slowly cooled sample also causes the tensile strength to decrease, contributing even more to the unstable brittle failure observed. This can be interpreted by lowering the dotted line in figure 3.6, representing the lower tensile strength.

In the intrinsic deformation of the PE samples, strain softening could be neglected ($\kappa_y = 1$), so in principle homogeneous deformation is possible. However, all values of $\sigma_y/G_R$ are larger than 3, so necking will always occur, see figure 3.7. Only the slow cooled sample (SC) of PE-1 shows a brittle type of failure just after yield. Again this is more likely to be a result of the lower entanglement density, accompanying a lower $G_R$, than the slight increase in yield stress. The drastic decrease in strain hardening modulus (from 3.4 to 1.5) gives a $\sigma_y/G_R$ of $\approx 23$, clearly leading to a brittle failure mode as indicated in figure 3.8a.

To support the view that the embrittlement of the SC sample of PE-1 is merely caused by the decrease in strain hardening, again an additional tensile test was performed at a different strain rate. To reduce the yield stress to a value of $\sim 28$ MPa the strain rate was lowered to $3 \times 10^{-4} \text{ s}^{-1}$, but this still resulted in brittle failure just after yielding. The higher molecular weight PE-2 grade shows considerable larger strain hardening moduli and, therefore, low values of $\sigma_y/G_R$ that are decisive for a stable neck as visualized in figure 3.7 and 3.8b. The ‘natural’ draw ratio of the neck, which was measured by marked gauge line intervals, is given in table 3.3. The increase of the ‘natural’ draw ratio for each PE grade coincides with the increase in the value of $\sigma_y/G_R$. Comparison of the values for both PE grades shows a decrease in draw ratio for increasing molecular weight, related to the increase in strain hardening. However, comparing the value of $\sigma_y/G_R$ immediately shows that the model with its assumptions is not capable to give a quantitative result, and that other material properties (like, strain rate sensitivity)
should also be considered.

For the PP samples, the influence of molecular weight on the tensile behaviour is visualized in figure 3.9 and 3.10. The lower molecular weight grade (PP-1) starts to fail upon annealing, whereas annealing of the higher molecular weight grade (PP-2) still results in a stable neck formation. Like shown with PET, failure of the annealed PP-1 sample (IC140) is likely to be induced by the higher intrinsic yield stress, since strain hardening is found to be similar for the quenched (Q) and annealed (IC140) sample. As shown in figure 3.10a the value of $\sigma_y/G_R$ for the Q sample of PP-1 is just below the critical value to cause brittle failure. A small increase in yield stress is suggested to cause the material to reach the critical draw ratio before the one necessary to form a stable neck. This was illustrated with an additional experiment, in which a strain rate of $4.5 \times 10^{-3} \text{s}^{-1}$ caused the sample Q of PP-1 grade to fail just after yield (similar to sam-
Figure 3.9: Macroscopic tensile behaviour of PP-1 (solid lines) and PP-2 (dashed lines) samples, subjected to different crystallization procedures: quenched (a), cold crystallized at 140°C (b) and slow crystallized (c).

Figure 3.10: Qualitative illustration of the relation between $\sigma_y/G_R$ and draw ratio in the neck according to equation 3.6 and 3.7 for PP-1 (a) and PP-2 (b) samples. Circles indicate ductile behaviour, x-marks brittle failure.

Figure 3.11: Photograph of necking-rupture failure behaviour of IC140 sample of PP-1.

ple IC140). The increase in yield stress due to the increase in strain rate is responsible for this brittle failure behaviour. Although, the term 'brittle' is used in failure of the annealed PP-1 sample, the presence of 'real' brittle fracture can be argued. Figure 3.11 shows that type of failure of the IC140 sample of PP-1 is more of a necking rupture type, than a brittle type. This type of failure was already suggested to be the failure mode in the materials exhibiting a $\sigma_y/G_R$ value close to the critical value, as indicated in figure 3.2.
The higher strain hardening and tensile strength of the PP-2 samples, causes the annealed (IC140) PP-2 sample to survive failure and ductile necking is observed. The expected decrease in draw ratio for increasing molecular weight is again present. Whenever a slow crystallization technique is used, unstable brittle failure is observed for both polypropylene grades. This is likely to be not solely attributed to the decrease in strain hardening, but also to a decrease in tensile strength, since the number of entanglements is also expected to be much smaller in slow crystallized samples. This will lower the dotted line in figure 3.10, representing the tensile strength, further.

Two interesting observations are mentioned. The first is the decrease in ‘natural’ draw ratio upon annealing of the PP-2 sample, whereas the value of $\sigma_y/G_R$ increases as a result of the increased yield stress. The explanation lies in the amount of softening ($\kappa_y$), which is less for the annealed sample, resulting in lower values of a stable neck draw ratio as depicted in figure 3.10b. The second is the observation that the yield stress in tensile does not show a considerable increase upon annealing as seen in the compressive true stress-strain behaviour, but seems to be similar in both the Q and IC140 samples. Also the difference between tensile ($\sim 35\,MPa$) and compressive yield stress ($\sim 50\,MPa$) is reasonably large, compared to the other polymers tested.

### Impact toughness

Notched impact toughness was measured by a tensile test at 1 m/s on samples used for conventional Izod impact testing (ASTM D-256). Due to the presence of a notch, deformation and failure is localized at the position of the notch. Impact (fracture) toughness in this study is defined as the necessary energy to break the sample per unit of initial cross-section. The advantage of using a high speed notched tensile test with respect to the conventional pendulum Izod impact test, is that the total initial cross-section breaks and changes in impact toughness can be quantified by the measured stress-displacement curves.

The impact toughness energy for the PE-1 and PE-2 samples is shown in figure 3.12. For both grades the impact toughness increases upon annealing and seems to be proportional to the resulting degree of crystallinity. However, this does not yield the conclusion that impact toughness increases with crystallinity, since the slowly cooled samples show a decrease in impact toughness, whereas the crystallinity is highest. For PE-1, the slow cooled sample even shows the lowest value of all PE samples tested. From the intrinsic and macroscopic deformation behaviour we know that the difference between slowly cooled and annealed samples lies mainly in strain hardening and tensile strength. The increase in crystallinity upon annealing is accompanied by an increase in lamellar thickness and consequently an increase in yield stress. Also, the impact toughness differs strongly for both polymer grades: 5 to 20 kJ/m$^2$ for PE-1 and 60 to 150 kJ/m$^2$ for PE-2. These changes are discussed and rationalized using the measured stress-displacement curves of the high speed impact tensile test and the relation with the intrinsic properties of the sample.

Figure 3.13 gives the impact engineering stress-displacement curves of the first four samples of each grade, shown in figure 3.12: the quenched (Q) and annealed (IC100, IC110 and IC120) samples. The curves show a linear increase in stress up to a maximum where the material behind the notch fails and the stress falls down to zero. The difference in impact toughness between the two polyethylene grades is found in the
shape of the curves after the maximum stress. For both polymers the maximum stress is in the order of the yield stress, but the total displacement before the force has reduced to zero, is much larger for the PE-2 samples. In the PE-1 samples the deformation is strongly localized, whereas in the PE-2 samples ductile behaviour occurs behind the notch, delocalizing the deformation. This difference between a brittle and ductile type of failure is illustrated in figure 3.14. The origin of this difference can be explained with the difference in strength of both polyethylene grades, related to the molecular weight. A higher molecular weight polymer (PE-2) has a higher strength and wants to form a stable neck (region II in the stability analysis), but necking is suppresses and failure is localized by the notch. The lower molecular weight has a lower strength that is (microscopically) reached before deformation can be stabilized (region III), resulting in localization behind the notch and, consequently, a low impact toughness. In other words, the impact fracture of the PE-2 grade is a ductile one, dominated by yielding and strain hardening, whereas the impact fracture of the PE-1 samples is dominated by an unstable brittle failure.

For both polyethylenes, the increase in impact toughness upon annealing is clearly related to an increase in the maximum stress, reached before failure occurs. Although this maximum macroscopic stress is lower than the intrinsic yield stress for the PE-1 samples, it can not be concluded that the yielding of the material is absent, since stresses are localized behind the notch. Increasing crystallinity upon annealing, only increases the intrinsic yield stress, and strain hardening does not change. Therefore, the increase in impact toughness for the annealed samples can be related to the increase in yield stress, since localized yielding of the material requires higher stresses.

In the tensile tests it was found that strain hardening has an important role on the failure. Since the strain hardening was found not to change with annealing conditions [1], it is expected to be equal for all of the samples shown in figure 3.13. Its influence on the impact toughness is illustrated in figure 3.15, where the impact engineering stress-displacement curves of the slow cooled (SC) and annealed at 120°C (IC120) sample are shown.
Figure 3.13: Notched impact tensile stress-displacement behaviour of PE-1 (a) and PE-2 (b) samples for increasing intrinsic yield stress (related to crystallinity, $\chi$) at approximately constant strain hardening. Samples in direction of arrow: Q, IC100, IC110, IC120.

Figure 3.14: Photograph of brittle (left) and ductile (right) impact failure type of respectively PE-1 and PE-2 sample.

Although crystallinity of the slowly cooled samples is higher than in the annealed samples of both polyethylenes (table 3.2), the impact toughness is lower, which is not in agreement with the results presented in figure 3.13. For the brittle PE-1 grades, the lower impact toughness of the slowly cooled sample has to be assigned to an expected decrease in tensile strength, as a result of a lower tie molecule density. For the slowly cooled PE-2 sample, no unstable failure was observed in tension and, in impact, a reasonable high maximum stress is reached. Though, the slight decrease in strain hardening modulus causes a slight decrease in impact toughness energy compared to the IC120 sample.

Figure 3.16 shows the impact toughness of the PP-1 and PP-2 samples. Both samples show a behaviour similar to the polyethylene grades, with an increase in impact energy upon annealing and a decrease when a slow crystallizing technique is applied. All samples showed a brittle failure type like the PE-1 samples, since no distinct deformation took place after the maximum stress. Consequently, the absorbed energy was low, in the range of $2 - 10 \, kJ/m^2$. Similar to the behaviour of PE, the impact toughness
increases upon annealing. The decrease in strength for the slow crystallized samples can be attributed to a lower tie molecule density. A decrease in entanglement density was confirmed by the lower strain hardening modulus measured in compressive true deformation. The increase in tensile strength for increasing molecular weight explains the difference in level of impact energy between the PP-1 and PP-2 grades.

3.5 Conclusions

Uniaxial tensile tests at constant rate of displacement on semi-crystalline polymers, can show ductile necking or brittle fracture before or just after yield. Conditions for stable neck growth can be qualified with the use of a simplified model for true stress-strain behaviour as proposed by Haward [3]. True intrinsic behaviour was measured in Chapter 2 [1] for semi-crystalline polymers with different initial crystallization conditions, including variations in annealing temperature and crystallization rate. Yield
stress, strain hardening modulus and tensile strength are found to be the variable parameters with these crystallization conditions, but they are also found to be the determining parameters for the failure behaviour observed. A qualitative comparison of these intrinsic parameters with the macroscopic tensile behaviour observed, shows that brittle fracture can either be introduced by an increase in yield stress, a decrease in strain hardening modulus, or a decrease in tensile strength. If the tensile strength is low, as is known to be the case for some low molecular weight polymers, brittle failure can occur upon increasing the yield stress by annealing. Applying slow crystallization conditions, results in brittle failure for most of the polymers studied. Both the decrease in strain hardening modulus and fracture strength as a result of a loss of entanglements and tie molecules is considered to be the reason. In case of ductile deformation, the measured ‘natural’ draw ratio in the neck is in agreement with the dependence of the strain hardening modulus on molecular weight.

Notched impact high speed tensile tests are performed to measure the impact toughness energy. In case of polyethylene, ductile fracture is found to be the failure mode for a $M_w$ of 210,000 and brittle fracture for a $M_w$ of 70,000. Both polypropylene samples show a brittle failure mode in impact. For all polymer grades tested the absorbed energy increases upon annealing of the samples, due to an increase in stress at failure. Since the yield stress is the only intrinsic parameter that is changed upon annealing, its increase is responsible for the increase in impact toughness. Slow crystallization conditions in the melt give the molecule more time to gather together upon chain folding, decreasing the strain hardening. A drastic decrease in impact toughness is the result.

Acknowledgments

The authors wish to acknowledge Ronald Schellekens of DSM Research for his support and supply of materials, Wim Bras for the availability of the X-ray facilities at the Dubble beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and the financial support provided by the Dutch Polymer Institute (DPI) (project #164).

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Deformation and failure of oriented semi-crystalline polymers

Deformation and failure of thin, injection moulded and extruded polyethylene and polypropylene samples was studied. Injection moulded samples are loaded in the flow and in the direction perpendicular to flow under both impact and tensile testing conditions, while extruded samples were only subjected to tensile tests. The relation between deformation behaviour and flow-induced crystalline orientation was investigated. The amount of orientation was varied by changing the processing conditions. Distribution and structure of flow induced orientations were characterized by optical microscopy, X-ray diffraction techniques and transmission electron microscopy. Hermans’ orientation functions were either determined from the flat plate wide angle X-ray diffraction patterns or calculated from full pole figures. Deformation was found to be anisotropic and related to the oriented structure. For all polymers studied, an increase of extended chains (shish) in the loading direction is proposed to cause an increase in the yield stress, and a lamellar structure oriented perpendicular to loading direction leads to an increase in strain hardening. In the extruded samples, were a low level of extended chains and a high level of oriented lamellae was found, the resulting combination of yield stress and strain hardening resulted in homogeneous deformation. Brittle-ductile transitions in impact toughness of the moulded samples could also be explained from differences in yield stress and strain hardening. Toughness enhancement was found to be most efficiently with increasing strain hardening and the effect was less pronounced in the polypropylene samples.

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Structure, deformation and failure of flow-oriented semi-crystalline polymers.
4.1 Introduction

Semi-crystalline polymeric products are often manufactured from the molten state, using common processing operations, such as injection moulding or film and sheet extrusion. Within these processes, the molten polymer is subjected to shear and elongational flow, prior to crystallization. The resulting morphology can therefore be quite different from what is observed under quiescent crystallization conditions. Typically oriented crystallite structures like ‘shish-kebabs’ or lamellae row structures are formed if flow and cooling rate are large enough. This is generally the case near the cold walls of the injection mould, sheet extrusion chill rolls and in thin extruded films.

Studies on injection moulding samples of various semi-crystalline polymers, such as PP [1–3, 6], PE [7], PAEK [8, 9], SPS [10] and PEN [11], show a clear multi-phase structure of skin layers and a core when its cross-section is observed with a polarizing microscope. The morphology of these ‘skin layers’ varies with polymer melt properties and moulding conditions [1–3], but also along the flow path of the moulded parts [2, 8–11]. It is clear that the inhomogeneity of such samples affects physical properties like e.g. dimension stability [12, 13], Young’s modulus and tensile strength [14–16].

Zuidema et al. [12, 13] studied the dimensional stability of injection moulded polypropylene and found, in agreement with experimental observations, by numerical modeling that the thickness of the oriented layer decreases with distance from the injection gate, resulting in a different shrinking behaviour. In the line with that work, Peters et al. [17] used numerical modeling with the goal to predict the spatial distribution of spherulites and oriented textures in controlled elongational flows. To complete their model, it should be expanded to distinguish between flow induced line nucleation and flow induced point nucleation. The resulting difference in these two nucleation types is observed in the oriented layer, which generally consists of a part which is nucleated and crystallized in flow, the ‘shear layer’, and a part which is only nucleated in flow, known as the ‘fine grained layer’ [18]. Besides the differences of these structures, the level of shear can also affect the resulting structure, e.g. row structures versus shish-kebabs in polyethylene [19]. For this reason it is important to clarify the structure of this layer in detail.

In the previous two Chapters we discussed how the mechanical properties of semi-crystalline polymers are closely related with their micro-structure, considering isotropic sample only. In this chapter we will focus on the influence of orientation on the mechanical behaviour using conventional injection moulding and extrusion techniques to create such oriented structures. A low amount of orientation, often present in thick moulded samples, does not have a significant effect on the mechanical behaviour [7], see Appendix A. However, if oriented structures percolate through the sample, like observed in thin injection moulded samples [20, 21], extrusion films [22] and certain hard filler modified injection moulded samples [7], the anisotropic nature dominates mechanical properties, e.g. tensile and impact behaviour. For this reason, in literature, push-pull and shear controlled orientation injection moulding (SCORIM) techniques are used to create a higher degree of orientation and an increase in oriented skin layer thickness in order to enhance the mechanical properties [15, 16, 20, 21, 23, 24]. Most studies concerning the deformation behaviour of flow induced oriented semi-crystalline polymers restrict to Young’s modulus and tensile strength [14–16, 23], and only a few focus on the post yield or impact failure behaviour [1, 20, 25].
Structure-properties relationships can only be investigated if a detailed measurement of the distribution of the oriented structures is available and most studies use X-ray scattering techniques in finding process-structure relations [6,8–11,26–29]. These orientation measurement techniques often require cumbersome cutting procedures, whereas direct scanning measurements along the thickness direction in injection moulded parts are reported with birefringence [29–31] and Fourier transform infrared microscopy [32,33] techniques. Although common processing techniques are not the optimal sample preparation methods to study the relationship between oriented structure and deformation, since the polymer experiences a complicated thermal and flow history, sometimes leading to curious orientations [10], injection and extrusion techniques were used in this study to reconcile the deformation and failure behaviour to oriented structures. A detailed measurement of the formed structure was performed by optical microscopy, X-ray scattering techniques and transmission electron microscopy. Differences in oriented structures are related to the tensile and impact toughness behaviour, measured in flow and perpendicular to flow direction, using the correlations of yield, strain hardening and ‘natural draw ratio’, since these were found to be the intrinsic properties determining the deformation and failure behaviour, see Chapter 3.

4.2 Experimental

Materials

The polymers used are an injection moulding and extrusion grade of High-density Polyethylene (HDPE) and Polypropylene (PP), all supplied by DSM, The Netherlands. In the following, these materials will be abbreviated as PE-I and PE-E for the injection moulding and extrusion grade of polyethylene respectively, and PP-I and PP-E in case of the polypropylenes. Table 5.1 summarizes the type of polymer grades used and their molecular weight. All data were provided by the supplier.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>$M_w$: [g mol$^{-1}$]</th>
<th>$M_n$: [g mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-I</td>
<td>Stamylan HD 9089S</td>
<td>70.000</td>
<td>11.000</td>
</tr>
<tr>
<td>PE-E</td>
<td>Stamylan HD 8621</td>
<td>210.000</td>
<td>7.000</td>
</tr>
<tr>
<td>PP-I</td>
<td>Stamylan P 15M10</td>
<td>350.000</td>
<td>64.000</td>
</tr>
<tr>
<td>PP-E</td>
<td>Stamylan P 13E10</td>
<td>500.000</td>
<td>84.000</td>
</tr>
</tbody>
</table>

Table 4.1: Polymer grades used.

Injection moulding

Rectangular plates, with dimension 70x70x1 mm$^3$, were injection moulded on an Arburg 320S / Allrounder 500-150 injection moulding machine. The mould was manufactured by Axxicon Moulds B.V. (Helmond, the Netherlands) and had a V-shaped runner of 5 mm thickness and an entrance of 70x1 mm$^2$, which is similar to the cross-section of the plate cavity. The V-shaped runner caused the material to flow uniformly along the width of the cavity, which was proved by several short shot experiments. The amount of flow induced orientation was varied by applying two extremes in injection
moulding temperature (150°C and 250°C for PE-I and 185°C and 260°C for PP-I) and initial flow rate (10 cm³/s and 100 cm³/s). The extrusion grade of polyethylene, PE-E, was also used for injection moulding. Since the viscosity of this material is higher, injection temperature and flow rate were set to 250°C and 10 cm³/s, respectively. Mould cavity temperature was kept constant at 20°C and holding pressure was 600/400/200 bar for 1/2/5 seconds, respectively, giving a total packing time of 8 seconds. Filling time was obtained from the measured pressure profile in the nozzle, which had a diameter of 3 mm. Table 4.2 gives all variable moulding conditions of the samples produced.

<table>
<thead>
<tr>
<th>Code</th>
<th>Melt temperature [°C]</th>
<th>Nominal flow rate [cm³/s]</th>
<th>Filling time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-I A</td>
<td>150</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>PE-I B</td>
<td>150</td>
<td>80</td>
<td>0.2</td>
</tr>
<tr>
<td>PE-I C</td>
<td>250</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>PE-E</td>
<td>250</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>PP-I A</td>
<td>185</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>PP-I B</td>
<td>185</td>
<td>80</td>
<td>0.2</td>
</tr>
<tr>
<td>PP-I C</td>
<td>260</td>
<td>10</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 4.2: Injection moulding codes and conditions.

For tensile and impact specimens rectangular bars, with dimensions respectively 75x10x2 mm³ and 75x12.5x2 mm³, were cut in flow and perpendicular to flow direction. The specimens perpendicular to flow direction were numbered according to their position from the cavity entrance as PERP-1, PERP-2 and PERP-3, see figure 4.1. The specimens tested in flow direction are abbreviated as FLOW samples. Dumbbell-shaped tensile specimens were made according to ISO 527 type 1BA on a milling machine, and Izod impact specimens were notched according to the ASTM D-256 protocol with a notching device.

Extrusion casting

Oriented polymer sheet samples were manufactured by film/sheet extrusion using the setup given in figure 4.2. A Collin Teach-Line single screw extruder of 20 mm diameter operating at 130 rpm for PE-E and 110 rpm for PP-E was used to establish a constant flow rate of respectively 41.5 g/min and 37.8 g/min. The polymer flow was stabilized in a channel of 15x15 mm² over a length of approximately 250 mm before entering the sheet extrusion die. Temperature of extruder barrel, stabilization channel and die were all set to 180°C in case of polyethylene and 220°C in case of polypropylene. The exit cross-section, \( t₀×w₀ \), of the sheet die was set to 2.1x100 mm² and the distance from die to chill rolls, L, was approximately 150 mm. The chill rolls were water cooled to 20°C and the thickness of the final polymer sheet was controlled by a gap opening, \( t_L \), pressure, P, and speed, \( Ω \), of the rolls.

During sheet extrusion, part of the polymer will be oriented by flow inside of the extrusion die, but most will be oriented in the elongational flow due to drawing by the chill rolls. The speed of the rolls was varied and the draw ratio was determined as the ratio...
of initial and final cross-section of the sheets. Chill roll speed, pressure and draw ratio of the different samples are given in table 4.3. For tensile testing, specimens were cut from the center of the oriented sheets in extrusion direction using a dumbbell-shaped (ISO 527 type 1BA) cutting knife.

**Structure characterization**

**Microscopy**

Two microscopic techniques were used to gain first insight in the oriented structure of the samples. Optical Light Microscopy (LM) was used to visualize the thickness of oriented skin layers. Cross-sections of approximately 3-7 μm were prepared at low temperatures of approximately -130°C, using liquid nitrogen, at a Reichert Ultracut E rotary microtome, equipped with a glass knife. The cross-sections were viewed between crossed polars on an Axioplan imaging microscope and pictures were made.
with the combined Axio Cam camera. Transmission Electron Microscopy (TEM) was used to visualize the crystal lamellae structure in the oriented and non-oriented parts of the samples. Samples were trimmed at low temperature (-130°C) and subsequently treated during 20 hours with a rutheniumtetraoxide (RuO₂)-solution [34]. Ultrathin sections were obtained at room temperature using the microtome, equipped with a diamond knife. TEM was performed on a Jeol JEM 2000 FX microscope, operated at 80 kV. Figure 5.2a shows the direction of viewing and microtoming with respect to flow and sample thickness.

<table>
<thead>
<tr>
<th>Code</th>
<th>Ω</th>
<th>P</th>
<th>w_L</th>
<th>t_L</th>
<th>DR = w_0/l_0</th>
<th>w_L/l_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-E 1</td>
<td>0.4</td>
<td>3</td>
<td>83</td>
<td>1</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>PE-E 2</td>
<td>0.8</td>
<td>3</td>
<td>61</td>
<td>0.65</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>PE-E 3</td>
<td>2.4</td>
<td>5</td>
<td>40</td>
<td>0.3</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>PP-E 1</td>
<td>0.2</td>
<td>1</td>
<td>100</td>
<td>1.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>PP-E 2</td>
<td>2.0</td>
<td>2</td>
<td>40</td>
<td>0.35</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Extrusion conditions.

**X-ray diffraction**

Flow induced oriented structures in the moulded samples were analyzed by recording 2D wide-angle X-ray diffraction (WAXD) film patterns. WAXD experiments were performed at the European Synchrotron Radiation Facilities (ESRF) in Grenoble (France) at the micro-focus beam line (ID13). Since the initial beam size was 5 μm and the collimator-to-sample distance was about 3 mm, the resulting beam size transmitting...
through the sample (TD direction) is less than $10 \, \mu \text{m}$, enabling us to examine the different structures over the thickness of the specimens. Samples of 1 mm width were cut from the middle of the specimens and WAXD patterns were recorded with a 2D-MAR CCD detector (resolution: 2048x2048), scanning the sample with a moving stage over the thickness of the specimen (ND direction). Cutting, scanning and beam direction are illustrated in figure 5.2b. The exposure time was in the order of 1-5 seconds, using a X-ray wavelength of 0.975 Å and a sample-to-detector distance of 150 mm. Scanning was done with steps of 10 $\mu \text{m}$ over half the thickness of the injection moulded samples (0.5 mm) and over the full thickness of the extruded sheets.

Since the resulting X-ray diffraction patterns of the extruded polyethylene samples showed an approximately uniform distribution of orientation over the sample thickness, these samples were used for creating pole figures. Similar samples as shown in figure 5.2b were cut from the extruded sheets. The width of the samples was set equally to the sheet thickness, resulting in square samples, reducing intensity differences due to path length variations. These samples were positioned on a goniometer with the rotation axis being in the middle of the ND-TD plane of the sample and rotated around the machine direction (MD) over $90^\circ$, collecting 2D WAXD patterns every $5^\circ$. Intensities of these collected patterns were taken every $5^\circ$ over the azimuth angle of the 110, 200 and 020 Debye rings and used as input data to create full pole figures in the software program BEARTEX.

Small-angle X-ray scattering (SAXS) patterns were taken at the high-brilliance beam line (ID2) at the ESRF, using a beam size of 300x300 $\mu \text{m}$, a wavelength of 0.995 Å, sample-to-detector distance of 10 m for polyethylene and 5 m for polypropylene samples, and a Frelon CCD camera (resolution: 1024x1024). The larger beam size is too large for accurate scanning over the sample thickness and patterns are only collected with the beam transmitting through the complete sample in ND direction.

**Mechanical testing**

Tensile tests on the dumbbell-shaped tensile specimens were performed on a Zwick Z010 tensile testing machine, at a constant speed of 5 mm/min, which corresponds to a constant initial strain rate of $1.5 \times 10^{-3} \text{s}^{-1}$ for the applied clamp-to-clamp distance of 55 mm. Engineering stress-strains curves were constructed from the measured force, clamp displacement and initial cross-section of the specimens.

Impact tensile test were performed on the Izod impact bars at a speed of 1 m/s, using a Zwick Rel hydraulic tensile testing machine. To assure the desired initial speed, a pick-up unit was used to allow the piston to accelerate before loading the specimen. To reduce dynamic effects, the contact area between the pick-up unit and the piston was damped by a rubber pad [35]. Piston displacement and force, using a piezo-electric force transducer, were measured at a sample rate of 2.5 MHz. The impact toughness energy was calculated by integration of the measured force-displacement curve, divided by the initial cross-sectional area behind the notch. All tests were performed at room temperature and in five-fold.
4.3 Results and discussion

Optical microscopy

Injection moulded samples of semi-crystalline polymers are known to show an inhomogeneous structure, over both the thickness as the length of the sample. Structure and thickness of the ‘skin layers’ varies with the moulding conditions applied: initial flow rate, melt and mould temperature. Figure 4.4 shows optical micrographs of the complete cross-section of sample PE-I A taken from a position close to the injection moulding gate (a), in the middle of the sample (b) and far from the gate (c), as illustrated in figure 4.1. At all positions, several structural layers can be distinguished: a thin ‘skin layer’ (A), a ‘transition layer’ (B), a ‘shear layer’ (C), a ‘fine grained layer’ (D) and an ‘isotropic core’ (E). At the positions near the gate (a) and in the middle (b) the ‘shear layer’ shows a very highly oriented ‘fibre like layer’ (F) which is partly delaminated upon microtoming. The total thickness of the oriented layers (A,B,C,F) is largest at the position close to the gate (a), in the order of 350 $\mu m$, decreases a to approximately 300 $\mu m$ in the middle of the sample (b) and is clearly smallest at the end position (c), $\approx$ 200 $\mu m$.

![Figure 4.4: Optical micrographs of cross-section of injection moulded sample of PE-I A at position close to the gate (a), mid of samples (b) and far from the gate (c) viewed between cross polars at 45$^\circ$ with flow direction, showing difference in thickness of oriented skin layer. We distinguish the ‘skin layer’ (A), ‘transition layer’ (B), ‘shear layer’ (C), ‘fine grained layer’ (D), ‘isotropic core’ (E) and ‘fibre like layer’ (F).](image)

A similar reduction of the oriented layers’ thickness at increasing distances from the injection gate was observed for all injection moulded samples. However, the thickness of the oriented layers strongly depends on molecular weight and moulding conditions applied as shown in figure 4.5 and 4.6. Figure 4.5 shows optical micrographs of cross-sections of the edge, taken from the middle of the samples, of the low molecular weight polyethylene samples PE-I B and PE-I C, which can be compared with the cross-section of sample PE-I A, shown in figure 4.4. For both the sample PE-I B and PE-I C, the total thickness of the oriented layer is found to be in the order of 150 $\mu m$, which is half
Figure 4.5: Optical micrographs of cross-section of injection moulded samples PE-I B (a), PE-I C (b) and PE-E (c), for coding see table 4.2, viewed between cross polars at 0° and 90° with flow direction, showing oriented skin layers.

the thickness observed in sample PE-I A. The higher flow rate applied in sample PE-I B, increases the shear stresses in the polymer and therefore orientation is expected to be larger. However, the total thickness of the oriented layer is observed to be smaller. Increasing the flow rate also decreases the filling time and, consequently, the time that the polymer melt experiences flow stresses. Moreover, orientation is strongest in the melt close to the penetrating solidifying layer (initially this is the cavity wall), where the relaxation times grow high. With increasing filling time the range of this layer is extended and thus the oriented layer. What else can be observed in figure 4.5, is that the distribution of the structural layers, as observed in figure 4.4, is now different. The ‘transition layer’ (B) has completely disappeared, whereas the ‘fibre like layer’ (F), showing delamination upon microtoming, is larger. This is indeed the result of the higher shear stresses near the mould cavity walls due to the higher initial injection flow rate. Increasing the melt temperature at similar flow rate (sample C), decreases the total oriented layer thickness at the cost of the higher oriented ‘shear layer’ (C) and ‘fibre like layer’ (F). A higher melt temperature is accompanied by a lower melt viscosity, decreasing the resulting orientation in the polymer. The effect of melt viscosity is also observed when injection moulding the polyethylene extrusion grade (PE-E), resulting in a thick oriented skin layer as shown in figure 4.5c. Since the melt viscosity of this grade is not in the range of conventional injection moulding grades, the melt temperature used to injection mould this polymer was set at 250°C, still giving a thick oriented skin layer.

Figure 4.6 shows the optical micrographs of half the cross-section of the different injection conditions of the PP-I grade (A,B,C), all taken from the middle of the samples (position 2). Similar to polyethylene, the total oriented layer thickness is found to be largest for the low injection flow rate and temperature (sample A) applied, but a clear appearance of different orientation layers, like observed in polyethylene, is absent in
polypropylene and only one thick oriented layer is observed. The reason for this can be due to a different position of the cross-polars, giving less brightening of the different oriented layers. A more detailed characterization will be given in the X-ray diffraction section, where also the level of orientation in the different layers is determined. Although optical microscopy resembles distribution of orientation in the polyethylene and polypropylene samples, further results on structure and properties of both polymers is reported separately here for clarity of discussion.

![Optical micrographs of cross-section of injection moulded PP-I samples A (a), B (b) and C (c), for coding see table 4.2, viewed between cross polars at 0° and 90° with flow direction, showing oriented skin layer.](image)

**Figure 4.6:**

### Polyethylene

#### WAXD

The 2D WAXD images recorded at the different sample thickness positions for the polyethylene samples typically show patterns as given in figure 4.7. The first pattern, showing full Debye rings of (110), (200) and (020) reflection of the crystal lattice planes, was found in the core of the injection moulded samples. These patterns were nearly completely unoriented, which is consistent with the isotropic spherulitic structure of the polarized micrographs (figure 4.4 and 4.5). The two oriented patterns shown are typical patterns taken from the extruded sheets or from the skin of injection moulded samples. Detailed intensity variation of the second pattern is difficult to observe since orientation is low. For this reason, (110), (200) and (020) reflections were isolated using the FIT2D data analysis software and intensities of these reflections were normalised with the total intensity of each reflection and plotted against the azimuth angle from 0° to 90°, 0° being the equatorial (ND) direction, see figure 4.8a and 4.8d. Keller and Machin [19] showed that the two typical patterns of oriented structure observed in polyethylene (figure 4.7, 4.8b and 4.8e) originate from shish-kebab structures. In flow, the high end tail of the molecular weight distribution, which has the largest relaxation time, is able to orient into fibrous crystals acting as nucleating threads for the lower molecular weight part, which relax much faster during and after flow. Lamellar overgrowth takes place on these oriented threads, resulting in a shish-kebab structure. The
degree of stretch, caused by the strength of the flow, can affect not only the number of nucleating threads (shish), but also the configuration of the transversely growing lamellae (kebabs). In weaker orientating flows, fewer and hence more widely spaced shish are formed and the transverse lamellae (kebabs) show twisting in growth direction due to chain tilting (figure 4.8c), such as is usual in (polyethylene) spherulites. This twisted, oriented lamellae structure is better known as the so called ‘row structure’, as observed in melt extruded polyethylene films [19]. So higher stresses stimulate the formation of shish, but also influence the lamellar development as they will be prevented from twisting, see figure 4.8f.

The method of isolating the different reflections and normalizing the intensity of the WAXD patterns (figure 4.8) is applied to all patterns collected from scanning over half the thickness of the samples. The advantage of normalization is that intensity differences, caused by variations in sample thickness, are circumvented and comparison of different samples and positions can be made. Figure 4.9 shows the normalised intensity of the (110) and (200) reflections as a function of full azimuthal angle (0°-360°) and distance from the edge (0-0.5 mm) of the injection moulded lower molecular weight grade, PE-I. The results of the higher molecular weight grade, PE-E, are given in figure 4.10. The core and skin layers are identified as follows: (I) the core is isotropic, showing no intensity variations over the azimuth angle, giving a normalized intensity of 1 over the complete azimuth angle; (S) strong oriented layers show intensity spots in both reflections at the equator, interpreted by fiber or shish-kebab structures where no lamellae twisting is present (figure 4.8); (R) layer showing a row structure (twisted lamellae) of lower orientation, represented by splitting up of the (110) intensity spots and by (200) spots at the meridian. The distribution of the layers can be compared with the ones observed in the optical micrographs (figure 4.4 and 4.5). Sample PE-I A, which is injection moulded at low temperature and flow rate, shows the largest total oriented layer. Orientation starts with a lower oriented row structure (R), which is visualized as the ‘transition layer’ (B) in figure 4.4, and increases at further distance of the edge forming an untwisted shish-kebab or fiber structure (S), which is visualised as the ‘shear layer’ (C) in figure 4.4. The reason for an increase in orientation for positions further from the edge, is that solidification of the polymer at the edge forms a new wall were shear rate is increased due to a decrease in cross-sectional area of the cavity.

Increasing the initial flow rate (sample PE-I B) is accompanied by higher shear stresses at the cavity wall, resulting in the formation of a highly oriented shish-kebab structure.
Figure 4.8: Normalized azimuthal intensity curves of (110), (200) and (020) reflections (a,d) indicating typical oriented WAXD patterns (b,c) of shish-kebab structures with twisted (c) and untwisted (f) lamellae, according to [19].

directly near the wall. Lower oriented row structures are absent, which was illustrated by the disappearance of the ‘transition layer’ (B) in figure 4.5a. The oriented layer thickness decreases, due to the shorter filling time combined with the limited cooling of the polymer. Increasing the temperature (sample PE-I C) gives a similar distribution of a lamellae row layer (‘transition layer’) and shish-kebab (‘shear layer’) as seen in sample PE-I A, but with a decreased thickness and orientation level, since crystallization rate and stresses are lower in the polymer melt. Injection moulding of the higher molecular weight, PE-E, gives a thick layer of highly oriented structure (S), figure 4.10. Both viscosity and long end tail, promoting the formation of shish, are responsible for this.

Comparison of the layer thickness observed in figure 4.4 and 4.5 with that of figure 4.9 and 4.10 indicates a thicker layer in some samples observed by X-ray scanning. However, a slightly rotational tilt along MD direction of the sample when mounted in the X-ray diffraction setup, can be the reason for this, since the sample dimensions used were relatively large (1 mm). Using a smaller length through which the beam is transmitted, would probably give more reliable results. Furthermore, the ‘skin layer’ (A) observed at the edge in the optical micrographs is difficult to measure with the X-ray diffraction technique, since scattering on the sample edge disturbs the quality
Figure 4.9: Normalized intensity at azimuthal angle of WAXD patterns scanned over half the thickness of samples: PE-I A (a,b), PE-I B (c,d) and PE-I C (e,f). A normalized intensity of 1 over the complete azimuthal scan represents an isotropic spherulitical structure (I), intensity variations indicate the presence of a Shish-kebab (S) or Row (R) structure as indicated in figure 4.8.
of WAXD images and were therefore not used. The results of X-ray scanning along the thickness of the extruded sheets of PE-E are not given here. These samples showed a similar level of orientation over the full thickness and were consequently used to create polefigures, discussed later in this study.

**TEM**

Figure 4.8 proves that WAXD analysis is capable to distinguish between twisted ‘row structures’ and non-twisted ‘shish-kebab’ like structures. However, the highly oriented WAXD pattern shown for the non-twisted structures (figure 4.8d,e) is similar to patterns from PE fibres. The presence of the ‘fibre like layer’ (F), as observed with the delaminated area in the optical micrographs, within the ‘shear layer’ (C) is not directly distinguished from the other layers in the WAXD results. Hence, a more detailed investigation is carried out.

Figure 4.11 gives transmission electron micrographs taken at different different positions in the cross-section of sample PE-I A. The first image is taken from the ‘transition layer’ (B), which is expected to have a row structure. Although a clear row oriented structure is not observed, the majority of the lamellae indeed show a preferential alignment perpendicular to flow (flow is in vertical direction). Part of the lamellae, that are twisted, are viewed in plane direction and are not seen in this transmission mode. The second image shows a clear oriented lamellae structure taken from the ‘shear layer’ (C). Here, the lamellae are not twisted and are all viewed in cross-sectional area. The third image is taken from the ‘fibre like layer’ (F) and again shows a high orientation of lamellae. However, the lengths of the lamellae are shorter than in the previous image, and even shish like patterns are visible. The majority of the polymer is, however, still present in lamellae, so the term ‘fibre like layer’, used so far, should be reconsidered not to indicate a fiber texture. The last image is taken from the core of the sample, showing a random arrangement of lamellae.
Figure 4.11: Transmission electron micrographs of injection moulded sample PE-I showing: (a) low oriented row structure in the ‘transition layer’; (b) highly oriented row structure in the ‘shear layer’; (c) shish-kebab structure in layer F of ‘shear layer’; (d) isotropic structure in the core. Flow is in vertical direction of images.

The image in figure 4.11a is also typical for the structure found in the extruded samples. More convincing evidence that this is a lamellae row structure will be given with the following results of small angle X-ray scattering measurements.

**SAXS**

Since small angle X-ray scattering images were collected at with a beam line of 300x300 μm, and not with the microfocus beam, it is impossible to identify the different layers. Thus, SAXS images were taken with the beam exposing the complete samples thickness in ND direction, and therefore representing the average morphology of the samples. Most interesting is the morphology of the lowest and highest orientation levels as obtained from the WAXD measurements. Figure 4.12 gives, in order of increased orientation, the SAXS patterns of the extruded PE-E 1, PE-E 3 and injection moulded PE-E samples. All images show spots at the meridian, originating from lamellae oriented perpendicular to the flow direction, which is vertical. First of all, this proves the presence of a row structure in all extruded samples, which was difficult to inter-
Figure 4.12: SAXS patterns of extruded PE-E samples, PE-E 1 (a) and PE-E 3 (b), and injection moulded PE-E sample (c) taken in ND direction with the beam going through the complete thickness. Flow is in vertical direction of images.

pret from the TEM images of these samples (figure 4.11a), being more pronounced in the sample subjected to a larger draw ratio. Secondly, in the strongly oriented injection moulded samples the aligned lamellae are still present, indicating that the morphology is definitely not a real fiber texture. However, the strong intensity streak near the beam stop in equatorial direction are a result of the large number of shish present. Finally, the rain drop shape of the intensity spots indicates the variation in long spacing, which is known to be a result of the tapered shape and interlocking of the kebabs [36, 37].

Orientation functions

A quantitative measure of uniaxial orientation, such as present in fibers, can be formalized using the Hermans’ orientation factor ($f_H$). The orientation function is defined as:

$$f_H = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (4.1)$$

where $\phi$ is the angle between the unit within a crystal of interest (e.g. chain axis $c$) and a reference axis (e.g. fiber or machine direction).

$\langle \cos^2 \phi \rangle$ is defined as:

$$\langle \cos^2 \phi \rangle = \frac{\int_{0}^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_{0}^{\pi/2} I(\phi) \sin \phi d\phi} \quad (4.2)$$

where $I(\phi)$ is the pole concentration representing the relative amount of crystalline material having plane normals in the direction of $\phi, \psi$, such that:

$$I(\phi) = \int_{0}^{2\pi} I(\phi, \psi) d\psi \quad (4.3)$$

Regarding the orientation in the polyethylene samples, we are interested in the $c$-axis (chain) orientation in the direction of flow (MD). Assuming a rotational symmetry around the machine direction (fiber symmetry) and defining the angles $\delta, \epsilon$ and $\sigma$ of respectively the $a$-, $b$- and $c$-axis with the machine direction, the orientation functions are given by:

$$f_a = \frac{3\langle \cos^2 \delta \rangle - 1}{2} \quad (4.4)$$
Deformation and failure of oriented semi-crystalline polymers

\[ f_b = \frac{3(\cos^2 \epsilon) - 1}{2} \]  \hspace{1cm} (4.5)

\[ f_c = \frac{3(\cos^2 \sigma) - 1}{2} \]  \hspace{1cm} (4.6)

The a- and b-axis orientation \((f_a, f_b)\) can be directly obtained from the measured (200) and (020) reflections, from:

\[ \langle \cos^2 \delta \rangle = \langle \cos^2 \phi_{200} \rangle \]  \hspace{1cm} (4.7)

\[ \langle \cos^2 \epsilon \rangle = \langle \cos^2 \phi_{020} \rangle \]  \hspace{1cm} (4.8)

Without the pure reflections from the c-axis, Wilchinsky’s [38] method is used to obtain information about the c-axis orientation:

\[ \langle \cos^2 \sigma \rangle = 1 - 0.565 \cdot \langle \cos^2 \phi_{200} \rangle - 1.435 \cdot \langle \cos^2 \phi_{110} \rangle \]  \hspace{1cm} (4.9)

where \(\langle \cos^2 \sigma \rangle\) is calculated from the strong (110) and (200) reflections, using the angle between the normal of the (110) plane and the a-axis \((56.6^\circ\) for PE) and the orthogonality relationship in the orthorombic crystal structure:

\[ \langle \cos^2 \delta \rangle + \langle \cos^2 \epsilon \rangle + \langle \cos^2 \sigma \rangle = 1 \]  \hspace{1cm} (4.10)

When chains are perfectly aligned along the reference axis, \(f_c=1\), whereas \(f_c=-1/2\) for chains aligned perpendicular to the reference axis. For random orientation, \(f_c=0\).

Complete pole figures of the injection moulded samples were not measured, as this is useless, since upon rotation of the sample uniqueness of the different layers is lost. Despite this, we will assume a complete rotational symmetry of each layer along the machine direction and, at the risk of oversimplification, use the measured 2D WAXD patterns to determine the crystalline orientation functions. Figure 4.13 gives the distribution in flow direction over half the thickness (full thickness for PE-E) of the samples, taken at position 2 (figure 4.1). The distribution of the strongest oriented ‘shear layer’ is observed with values of \(f_c\) of approximately 0.5 to 0.75, whereas the b-axis, representing the lamellar growth direction, inclines perpendicular to flow direction \((f_b < 0)\). The core shows an isotropic morphology, since all functions are zero, whereas the lower oriented ‘transition layer’ does not show a clearly interpretable orientation distribution. The latter is due to the row structure of this layer, which is expected not to be of rotational symmetry, and thus determination of the Hermans’ orientation functions on results from single 2D WAXD images does not apply. Nevertheless, the average values of \(f_c\) over the sample thickness are given in table 4.4.

Lindenmeyer and Lustig [22] already pointed out that the technique of using flat plate X-ray diffraction photographs can lead to erroneous conclusions, at least in extruded polyethylene films, and emphasized the importance of pole figures. Since the extruded sheets showed similar orientation patterns along the complete sample thickness, these were used to create complete pole figures, which are presented in figure 4.14. Pole figures of the three principal crystallographic directions are plotted: a-axis (100), b-axis (010) and c-axis (001).
The (010) pole figures of extruded sheets of low melt draw ratio (PE-E 1: DR=2.5, PE-E 2: DR=5.3) indicate that the b-axis is dispersed in the plane perpendicular to machine (flow) direction. The c-axis shows a small tendency towards MD direction, but still shows a strong distribution in normal direction (ND). The a-axis is clearly uniformly dispersed in the plane of the sheet. These findings are in agreement with the row structure presented by Keller [19, 37], since the b-axis is known to be the direction of radial growth, with the a- and c-axis tending to rotate around this growth direction (twisting of lamellae). When the melt draw ratio is drastically increased (PE-E 3: DR=17.5) the c-axis shows the strongest orientation in the direction of flow, whereas both a- and b-axis are almost randomly dispersed in the plane perpendicular to MD (ND-TD plane). This indicates a rotational symmetry of orientation around MD and is consistent with a highly oriented non-twisted lamellae orientation perpendicular to flow direction. Caution should be taken regarding the intensity levels, since the thickness of the samples
is not constant and rotation of the square samples causes both differences in effective volume and path length of the beam. Suitable corrections should be made if the intensities are to be compared. Finally, the average c-axis orientation function was calculated from the complete orientation distributions and summarized in table 4.4.

**Mechanical properties**

In Chapter 3 it was shown that deformation and failure of polymers can be described with a simplified model based on a stability analysis, yielding:

\[
\frac{\sigma_y}{G_R} = \frac{\lambda_n^2 - \frac{1}{\lambda_n}}{\lambda_n - 1} \rightarrow \frac{\sigma_y}{G_R} \sim \lambda_n
\]

where \(\sigma_y\) and \(G_R\) are, respectively, the intrinsic yield stress and strain hardening modulus (from: \(\sigma_{\text{true}} = \sigma_y + G_R(\lambda^2 - 1/\lambda)\)), and \(\lambda_n\) the estimated ‘natural draw ratio’ of the neck. Although it was shown that equation 4.11 is not in quantitative agreement with the materials’ behaviour, a qualitative relationship between \(\sigma_y/G_R\) and \(\lambda_n\) was found to be valid. Although the intrinsic behaviour of the oriented polymer samples can not
be measured, e.g. with uniaxial compression tests, the macroscopic phenomena, like yield stress and 'natural draw ratio', will be investigated and, if possible, results will be interpreted in an average sense.

Since the stress-strain curves of most injection moulded samples tested show similar behaviour with respect to neck drawing, representative curves are plotted only in figure 4.15. Results of yield stress and 'natural draw ratio' of the injection moulded samples are summarized in table 4.5. Figure 4.15a shows the behaviour of the PE-I grade tested in flow direction. Necking starts in all samples at the position far from the gate, where the oriented skin layer was found to be smallest, and the neck grows in the direction of the gate. Apparently, the oriented structure increases the yield stress, and yielding starts for lowest orientation. This relation is also found when testing in perpendicular direction, since for all moulding conditions and materials, the yield stress decreases with increasing distance from the gate. Comparison of the yield stress in flow direction (starting far from the gate) with that in perpendicular direction at the similar position (PERP-3), shows the effect of anisotropy on yield stress. In Chapter 2 it was shown that yield stress is related to lamellar thickness. The differences in yield stress (in figure 4.15a) are therefore expected to be a result of the amount of shish present in the samples. The extended polymer chains which form a shish can be regarded as extremely thick lamellae, which possess a high yield stress. Sample PE-I C was shown to have a much lower orientation giving a lower yield stress than samples PE-I A and B.

![Graph](a)

![Graph](b)

**Figure 4.15:** Macroscopic tensile behaviour of injection moulded samples of PE-I A, PE-I B and PE-I C, tested in flow direction (a) and sample PE-I A, tested perpendicular to flow direction (b) at different distances from the gate (1,2,3).

Strain hardening is also influenced by orientation as the 'natural draw ratio' is found to be lowest upon testing in flow direction. Using the relation given in equation 4.11 and considering that the yield stress is increased in flow direction, the strain hardening modulus, $G_R$, is expected to be higher in flow direction. In sample PE-I A the influence of strain hardening, caused by the thick orientation layer, is evenly pronounced as the draw ratio in the neck, which decreases upon growing in the direction of the gate (see also the increase of stress upon drawing). Sample PE-E A also shows an influence of oriented layer thickness along the flow path when tested perpendicular to the machine direction (figure 4.15), with respect to stability of deformation, as unstable
or even brittle failure is observed when testing samples close to the injection gate. This can be rationalized to be a result of both a higher yield stress as a lower strain hardening (perpendicular to MD).

The influence of both yield and strain hardening is also illustrated in the impact toughness results, presented in table 4.5. In Chapter 3, the intrinsic (isotropic) impact toughness for grade PE-I was found to be in the order of 10 kJ/m². In its brittle failure mode the impact toughness was found to increase with intrinsic yield stress. Considering the impact toughness of the samples tested perpendicular to flow direction, a brittle-ductile transition is now found for a decreasing yield stress. Furthermore, impact testing in flow direction causes a brittle-ductile transition, as a result of the increased strain hardening, yielding ultimate values of 16 times the intrinsic toughness for the sample with the strongest orientation.

The tensile behaviour of the higher molecular weight grade, PE-E, is presented in figure 4.16a. The extruded samples were only tested in flow direction, while the results of the injection moulded PE-E sample, tested in perpendicular direction, are given in table 4.5. Similar to the results of the lower molecular weight grade, both yield stress and strain hardening are affected by orientation. However, the importance of the presence of highly oriented shish’s on yield stress is emphasized, as the injection moulded sample fails in a brittle mode at a stress before yielding is initiated. The highly oriented extrusion sample (PE-E 3), on the other hand, does not fail at low strains and shows a homogeneous deformation before failure. This tendency to deform without necking is also observed in the lower oriented extrusion sheets and, taking a reduction in cross-section to be proportional to the draw ratio, the true stress-strain curves are given in figure 4.16b. Strain is plotted as $\lambda^2 - 1/\lambda$, such that the strain hardening modulus, $G_R$, can be determined. Results of yield stress and strain hardening modulus are reproduced in table 4.6. The yield stress is difficult to determine from the non-necking
samples, but was taken as the value at 7% strain, since this was the strain at yield for all polyethylene samples in intrinsic deformation measured as discussed in Chapter 2. The ratio of yield stress and strain hardening drops down to values of 3 or lower, which is in agreement with the stability analysis presented in Chapter 3. Sample PE-E 1 was also subjected to impact testing and yielded an ultimate impact toughness of 380 kJ/m², which is approximately 6 times the intrinsic impact toughness as found in Chapter 3. The stronger oriented samples, PE-E 2 and 3, were not tested in impact, since the thickness of these samples is below 1 mm, which is expected to change the stress state as indicated in Appendix A.

![Graph](image)

**Figure 4.16:** Macroscopic tensile behaviour of injection moulded sample (PE-E) and extruded sheets of PE-E (1,2,3) tested in flow direction: (a) engineering stress-strain, (b) true stress-strain.

<table>
<thead>
<tr>
<th></th>
<th>PE-E 1</th>
<th>PE-E 2</th>
<th>PE-E 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_y$ [MPa]</td>
<td>22</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td>$G_R$ [MPa]</td>
<td>6</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>$\sigma_y/G_R$ [-]</td>
<td>3.7</td>
<td>3.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

**Table 4.6:** Tensile testing results of extruded PE.

**Polypropylene**

**WAXD**

The WAXD images taken from the different positions along the thickness of the polypropylene samples show typical patterns as schematically illustrated in figure 4.17. In total three Debye rings of unique crystal reflections are visible ((110), (040) and (130)) and one of three interfering reflections ((111), (131) and 041). These reflections are all originated from an $\alpha$ crystalline phase, since no $\gamma$ phase was found. Although a very weak $\beta$ phase was observed in highly oriented structures, this will not be discussed in this study. Differences between these patterns are observed in the (110) and (130)
reflections, and were explained by Fujiyama et al. [6] as follows: when orientation is strong, the morphology is composed of shish-kebabs in which c-axis orientation dominates in flow direction resulting in pattern (c). On the oriented lamellae (kebabs), epitaxial crystallization causes the growth of secondary lamellae of which the chains are perpendicular to the chain axis of the primary component, see figure 4.18a. This orientation, which is also known as lamellar branching, causes an a*-axis orientation in flow.

![Schematic illustration of 2D-WAXD patterns of α-iPP, measured in this study.](image)

*Figure 4.17:* Schematic illustration of 2D-WAXD patterns of α-iPP, measured in this study. Flow direction was vertical. Orientation increases from dominant a*-axis (a) to c-axis (c) orientation. (b) shows an intermediate pattern.

![Lamellar branched shish-kebab structure and method to determine fraction [A*/C]](image)

*Figure 4.18:* Lamellar branched shish-kebab structure (a) and method to determine fraction \([A^*/C]\) from (110) azimuthal scan curve. Both according to Fujiyama et al. [6, 26]. Flow direction is vertical in (a) and at 90° in (b).

A relative comparison between c-axis and a*-axis orientation can be made from calculation of the fraction of a*-axis component, \([A^*/C]\), which can be evaluated from the azimuthal scan curve of the (110) reflection according to Fujiyama’s [6] method:

\[
[A^*] = \frac{A^*}{C + A^*}
\]  

(4.12)

where C is taken as the area around an azimuthal angle of 0° and A* the area around 90°, after substruction of the base line area B, see figure 4.18b.
The WAXD results of the oriented layers in the injection moulded samples showed strong oriented patterns. Therefore, rotational symmetry of the shish-kebab structures was assumed and the $f_c$ and $f_b$ orientation functions were calculated according to equations 4.5 and 4.6 with:

\[
\langle \cos^2 \phi \rangle = \langle \cos^2 \phi_{0\text{-}10} \rangle
\]

\[
\langle \cos^2 \sigma \rangle = 1 - 0.901 \cdot \langle \cos^2 \phi_{0\text{-}10} \rangle - 1.099 \cdot \langle \cos^2 \phi_{1\text{-}10} \rangle
\]

where $\langle \cos^2 \sigma \rangle$ is calculated using Wilchinsky’s [38] method from the (110) and (040) reflections and the angle of 72.5° between the b-axis and the (110) plane. Figure 4.19 gives the distribution of the orientation functions in flow direction over half the thickness of the injection moulded samples. The oriented layer shows values of $f_c$ of approximately 0.5, which are in the same order as found by Lamberti et al. [33] from FT-IR measurements on similar samples. Thicknesses of the oriented layers can be compared with the ones observed form optical micrographs (figure 4.6).

![Graphs showing orientation functions](image)

**Figure 4.19**: Orientation functions, $f_b$ and $f_c$ (a,b,c) and fraction $[A^*]$ (d) in flow over half the thickness of injection moulded samples of PP.

The fraction $[A^*]$ is found to be almost zero at the outer skin, where the cooling rate is highest and secondary nucleation is not possible. The majority of the oriented layer, however, shows a fair amount of lamellar branching, whereas in the core $a^*$-axis orientation seems to dominate. To give an indication in different orientation levels of the injection moulded samples, the average values, $f_{c,av}$ and $[A_{n,av}^*]$, are given in table 4.7.
Scanning of the extruded samples gave uniform results along the thickness and their average values are summarized in table 4.7. The main difference in the extruded samples is found in $[A^*]$ and the value of 0.9 that is found in sample PP-E 1, suggests a completely different orientation than that of sample PP-E 2. Next, results of small angle X-ray scattering we will give a more detailed investigation of the differences in lamellae orientation.

<table>
<thead>
<tr>
<th>Injection</th>
<th>PP-I A</th>
<th>PP-I B</th>
<th>PP-I C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{c,av} [-]$</td>
<td>0.34</td>
<td>0.27</td>
<td>0.25</td>
</tr>
<tr>
<td>$[A^*] [-]$</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Extrusion</td>
<td>PP-E 1</td>
<td>PP-E 2</td>
<td></td>
</tr>
<tr>
<td>$f_{c,av} [-]$</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>$[A^*] [-]$</td>
<td>0.9</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.7:** Average c-axis and relative $a^*$-axis orientations, $f_{c,av}$ and $[A^*]$.

**SAXS**

Figure 4.20 shows the SAXS images of respectively sample PP-E 1, PP-E 2, and PP-I A. The first image shows that only a small amount of lamellae oriented perpendicular to flow is observed in the low elongated extrusion sample, whereas increasing the draw ratio (sample PP-E 2, image (b)) increases this lamellae orientation as seen from the intensity spots at the meridian. The last image, which is typically for all injection moulded PP-I samples, again shows the intensity spots at the meridian caused by oriented lamellae. Similar to what was observed in the SAXS patterns of injection moulded PE, a streak in equatorial direction is visible near the beamstop, indicating the existence of a reasonable amount of shish. Furthermore, the lamellar halo also shows small intensity spots at the equator, which is an evidence for lamellar branching.

![SAXS images](image)

**Figure 4.20:** SAXS patterns of extruded PP-E samples, PE-P 1 (a) and PE-P 2 (b), and injection moulded PP-I sample (c) taken in ND direction with the beam going through the complete thickness. Flow is in vertical direction of images.

**Mechanical properties**

The engineering stress-strain curves of the injection moulded polypropylene samples tested in flow and perpendicular to flow direction are given in figure 4.21. The observed trends in yield stress and strain hardening are similar to the ones observed in
polyethylene: an increase in yield stress and strain hardening upon orientation in flow direction. Yield stress is considered to be increased by the formation of extended crystals (shish) and strain hardening, causing a decrease in natural draw ratio (table 4.8), mainly due to the orientation of lamellae (kebabs). Loading in perpendicular direction shows no considerable differences for all samples produced, and also not for the different positions along the flow path. Testing in perpendicular direction causes craze formation, accompanied by localization and macroscopic yield, in the oriented skin layer.

The impact toughness (see table 4.8) is again found to be highest in orientation direction and related to the degree of orientation. The intrinsic impact toughness of a non-oriented sample of the PP-I grade is $\sim 10 kJ/m^2$, so a maximum increase by a factor of 4.5 was found.

$$\gamma / \beta D / \beta C$$

**Table 4.8: Tensile and impact testing results of injection moulded PP specimens ($x = \text{brittle failure}$).**

<table>
<thead>
<tr>
<th></th>
<th>PP-I A</th>
<th></th>
<th>PP-I B</th>
<th></th>
<th>PP-I C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_y$</td>
<td>$\lambda_n$</td>
<td>Izod</td>
<td>$\sigma_y$</td>
<td>$\lambda_n$</td>
</tr>
<tr>
<td>FLOW</td>
<td>41 [MPa]</td>
<td>[-]</td>
<td>45 [kJ/m$^2$]</td>
<td>39 [MPa]</td>
<td>[-]</td>
</tr>
<tr>
<td>PERP</td>
<td>30 [MPa]</td>
<td>[-]</td>
<td>4 [kJ/m$^2$]</td>
<td>30 [MPa]</td>
<td>[-]</td>
</tr>
</tbody>
</table>

Tensile tests of the extruded samples of PP-E are presented in figure 4.22. Here, the yield stress is found to be lower compared to the injection moulded samples, which indicates a lower amount of extended crystals (shish) as already observed from the SAXS patterns. Localization of the elongated sample PP-E 2 is, however, almost absent, which again proves the effect of oriented lamellae on the increase of strain hardening.
4.4 Conclusions

Flow-induced oriented structures in injection moulded and extrusion casted polyethylene and polypropylene samples were characterized by optical microscopy, X-ray scattering techniques and transmission electron microscopy. The optical micrographs show layers of different level of orientation. Layer thickness in injection moulded samples is found to decrease along the flow path and increase for lower melt temperatures and longer filling times. Wide angle X-ray diffraction patterns taken along the thickness of the sample indicate the existence of several layers, composed of orientation varying from lamellae row structures to highly oriented shish-kebabs. These textures were confirmed by small angle X-ray scattering and transmission electron microscopy images. Since the extruded casted samples did not show a significant variation of orientation along the thickness, pole figures were measured by rotation of the samples along machine direction. Orientation of these samples was found to be dominated by a row structure. For indication of the average level of orientation, Hermans’ orientation functions were either calculated from the flat plate WAXD patterns or from the pole figure results. Most of these characterization techniques were also applied to the polypropylene samples, were lamellae orientation, shish-kebabs and lamellar branching could be distinguished. From tensile tests, performed in and perpendicular to flow direction, the yield stress was found to increase with flow direction and amount of oriented shish, whereas strain hardening was assumed to be mainly increased by chain orientation forming oriented lamellae (kebabs). Since the extruded samples showed low yield stresses and strong strain hardening, these samples tended to deform homogeneous or with a very low draw ratio in the neck. This increase in strain hardening, caused by the lamellae orientation, is also responsible for the observed ultimate impact energy in flow direction. This toughness enhancement is found to be less pronounced for the polypropylene samples.

Acknowledgments

The authors wish to acknowledge Christian Riekel for the availability of the X-ray facilities at the Micro-focus beam-line (ID13) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and the financial support provided by the Dutch Polymer
Institute (DPI) (project #164).

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Chapter 5

Impact behaviour of hard particle filled, oriented semi-crystalline polymer systems

The impact toughness behaviour of CaCO$_3$ filled polyethylene and polypropylene is studied for specimens prepared by compression and injection moulding. The impact toughness is found to be strongly dependent on the processing conditions applied. The highest impact toughness was found when injection moulded polyethylene bars, with intermediate filler content, were tested close to the injection gate and in flow direction. Specimens obtained from injection moulded plates were tested both in and perpendicular to flow direction and impact toughness was found to be anisotropic. The presence of an additional flow-induced oriented structure in the specimen core was observed by optical microscopy and X-ray diffraction techniques. Transmission electron microscopy showed that preferential oriented lamellae grow ‘edge-on’ a particular particle surface. These oriented lamellae increase strain hardening and, thus decreases localization of the strain in the ligaments when tested in flow direction. As a result, more energy can be dissipated and toughness is enhanced. The fact that polypropylene is less sensitive to impact improvement by lamellae orientation, as found in the previous chapter, explains its modest impact improvement by CaCO$_3$ fillers.

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Influence of flow history on impact toughness of CaCO$_3$ filled polyethylene and polypropylene.
5.1 Introduction

Fillers are generally added to polymers to improve their physical properties, like e.g. mechanical behaviour or dimensional stability, with the additional aspect of cost reduction. Regarding the improvement of mechanical behaviour, most semi-crystalline polymers are known to behave ductile under normal testing conditions, and improvement of this is not of progressive interest. However, at high deformation rates, like in an Izod impact test, most polymers start to show brittle behaviour.

It is known that the impact toughness of semi-crystalline polymers can be increased via the addition of a well-dispersed rubbery phase. The toughening of semi-crystalline polymers with rubber particles has been studied extensively and an important toughening criterion was first presented by Wu [1, 2], who showed that the brittle to tough transition in rubber modified PA 6,6 was related to the average interparticle ligament thickness. Since this single parameter is directly related to both rubber concentration and average particle size, it is a useful criterion, but an explanation for its existence was not evident. A morphological explanation was proposed by Muratoglu et al. [3, 4]. Their observations of a preferential oriented crystalline structure of PA 6,6, between the rubber inclusions, were coupled to the local anisotropic mechanical behaviour of the heterogeneous system. Toughening of the total polymer system was suggested to be a result of the reduced resistance to yielding in the interphase of oriented crystalline lamellae around the filler particle. If the interparticle distance is low enough, ‘easy’ shear deformation percolates throughout the structure and toughness is enhanced, due to the significant source of energy dissipation from yielding.

This toughening mechanism was argued to be also valid in semi-crystalline systems filled with hard filler particles [5]. Indeed, there are several studies which report the increase of impact toughness by the addition of rigid particles in e.g. polyethylene [5–11], polypropylene [12–16] or polyamide [17]. In most of these studies the mineral filler used is calcium carbonate and impact enhancement is modest (1.5-3 times improvement). Besides particle size [5–7, 10, 16], dispersion and adhesion are found to be of significant importance [10–13]. For proper dispersion, the particle surfaces are therefore often treated with coupling agents [10, 18]. On the other hand, the increase of polymer-particle interaction increases adhesion, which is found to be a negative effect for impact toughness [12], since debonding of the particle is the primary condition for toughening [5, 19, 20]. The use of surface treatments thus results in competing effects of dispersion and adhesion. For calcium carbonate, a stearic acid surface coating is often used [5, 10, 12, 16] to achieve a proper particle dispersed morphology. Bartuczak et al. [5] even found a maximum increase in impact toughness of approximately 10 times the value of the neat polymer in case of HDPE/ CaCO$_3$ (with calcite stearate coating) modified systems. The mechanism proposed by Muratoglu et al. [3, 4] was considered in their study since a similar effect of interparticle distance was found as observed in rubber filled HDPE [21]. An interparticle distance of 0.6 $\mu$m was found, which was twice the length of ‘edge-on’ lamellae growth observed in thin films crystallized on flat calcite surfaces [22]. Although the onset of toughening at interparticle distances below 0.6 $\mu$m seems to be clear, with respect to particle sizes used, there still was a striking difference in the level of toughness increase. Specimens were prepared via injection moulding a long flexural bar, which was divided into two impact test specimens. For the calcium carbonate filled systems, the specimens from close to the injection gate
showed an increase in impact properties that was twice as high as for the specimens from the far end. Furthermore, Fu et al. [6,7] found a toughness enhancement at an interparticle distance of 5.2 \( \mu m \) when using larger particle diameters and Liu et al. [10] also found the critical ligament thickness to be dependent on particle size. All these differences in results indicate that a commonly accepted view of the mechanism responsible for toughness enhancement in particulate filled semi-crystalline polymer systems is still absent.

This chapter is concerned with the investigation of CaCO\(_3\) filled polyethylene and polypropylene blends, subjected to flow. In the previous chapter it was found that impact toughness is related to flow-induced structures, giving ultimate impact values when samples, with considerable orientation, are loaded in flow direction. Samples are prepared by injection moulding flexural bars and rectangular plates. The presence of oriented structures is characterized using X-ray diffraction techniques and transmission electron microscopy. Differences in impact behaviour are related to the structure development in the samples.

### 5.2 Experimental

#### Materials

The polymers used in this study are a High-density Polyethylene (PE) and an isotactic Polypropylene (PP), both supplied by DSM, The Netherlands. Table 5.1 summarizes the type of polymer grade and their molecular weight. All data were provided by the supplier. The calcium carbonate filler particle used was Super-Pflex 200, supplied by Specialty Minerals Inc., USA. This precipitated calcium carbonate has a density of 2.7 \( g/cm^2 \), an average particle diameter of 0.7 \( \mu m \), a very narrow particle size distribution and a 2 wt% calcium stearic acid surface coating to improve dispersion.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>( M_w [g \text{ mol}^{-1}] )</th>
<th>( M_n [g \text{ mol}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Stamylan HD 9089S</td>
<td>70,000</td>
<td>11,000</td>
</tr>
<tr>
<td>PP</td>
<td>Stamylan P 15M10</td>
<td>350,000</td>
<td>64,000</td>
</tr>
</tbody>
</table>

**Table 5.1:** Characteristics of polymer grades used in this study.

#### Extrusion mixing

Different volume fractions of calcium carbonate (CaCO\(_3\)) particles were added to PE: 5%, 10%, 15%, 20% and 25%, and to PP: 15% and 20%. Mixing was done with a 25 mm Werner and Pfleiderer corotating twin-screw extruder, ZSK 25. The temperature of the extruder was in the range of respectively 175-180\(^\circ\)C and 185-200\(^\circ\)C for the PE and PP, the rotation speed of the screws was 150 rpm and the length of the extruder was 1050 mm. The calcium carbonate powder was fed to the polymer melt by a side feeder situated directly after the melting zone. The polymer pellets and the calcium carbonate powder were fed with the desired weight fractions (calculated from the volume fractions and densities of PE/PP and CaCO\(_3\)) by two K-Tron Soder gravimetric
material feeders (type K-CL-KQX2 and K-CL-KT20). The material flux was optimized to get the highest torque of the extruder in order to achieve a proper particle dispersion. The extruded blends were cooled directly at the exit of the extruder in water and subsequently the material strings were pelletized.

Sample preparation

Flexural test bars (ASTM D-790 127x12.7x3.2 mm³, Axxicon Iso Manufactured (AIM)) were injection moulded, using an Arburg 320S / Allrounder 500-150 injection moulding machine, at an injection temperature of 250°C, an injection speed of 100 cc/s and a mould temperature of 20°C. The mould has a L-shaped runner and an entrance of 6x3.2 mm². Two ‘Izod’ bars were cut out of the flexural bars, notched according to the ASTM D-256 protocol and marked as GATE and END indicating the distance from the injection gate, see figure 5.1a. Compression moulded ‘Izod’ bars with a thickness of 3 mm were prepared according the compression moulding process described in Chapter 3. Furthermore, the polyethylene blend with 15 vol% CaCO₃ was injection moulded in rectangular plates (70x70 mm²) of different thickness: 1, 2, 3 and 4 mm. This mould was specially manufactured by Axxicon Moulds B.V. (Helmond, the Netherlands) and had a V-shaped runner of 5 mm thickness and an entrance of 70x1 mm². The V-shaped runner caused the material to flow uniformly along the width of the cavity, which was proved by several short shot experiments. Izod impact specimens were machined from these plates with the loading direction in flow (FLOW) and perpendicular (PERP) to flow, see figure 5.1, and notched according to the ASTM D-256 protocol with a notching device.

Structure characterization

Microscopy

Microscopic techniques were used to characterize the particle dispersion and polymer morphology. Optical Light Microscopy (LM) was used to visualize the thickness of oriented skin layers in the injection moulded samples. Cross-sections of approximately 3-7 μm were prepared at low temperatures of approximately -130°C, using liquid nitrogen, at a Reichert Ultracut E rotary microtome, equipped with a glass knife. The cross-sections were viewed between crossed polarizers on an Axioplan imaging microscope and pictures were made with the combined Axio Cam camera. Scanning Electron Microscopy (SEM) was used to determine the dispersion of CaCO₃ particles. Samples were trimmed at room temperature, since deformation of the polymer surface is expected not to change the distribution of the particles. Images of the morphology of the blends were made on a Philips XL 30 Environmental Scanning Electron Microscope, equipped with a Field Emision Gun (FEG-ESEM). Notched samples of the 1 mm thick injection moulded plates of the filled PE were also subjected to in-situ tensile testing within the ESEM, using a controlled miniature tensile testing device. Transmission Electron Microscopy (TEM) was used to visualize the crystal lamellae structure between the CaCO₃ particles in the 15 vol% filled PE and PP samples. Samples were trimmed at low temperature (-130°C) and subsequently treated during 20 hours with a rutheniumtetraoxide (RuO₄) solution [23]. Ultra thin sections were obtained at room temperature using the microtome, equipped with a diamond knife.
TEM was performed on a Jeol JEM 2000 FX microscope, operated at 80 kV. Figure 5.2a shows the direction of viewing and microtoming with respect to flow direction, where applicable.

**X-ray diffraction**

Flow induced oriented structures in the moulded samples were analyzed by recording 2D wide-angle X-ray diffraction (WAXD) film patterns. WAXD experiments were performed at the European Synchrotron Radiation Facilities (ESRF) in Grenoble (France) at the micro-focus beam line (ID13). Since the initial beam size was 5 μm and the collimator-to-sample distance was about 3 mm, the resulting beam size transmitting through the sample (TD direction) is less than 10 μm, enabling us to examine the different structures over the thickness of the specimens. Samples of 1 mm width were cut from the middle of the specimens at the position of the notch and WAXD patterns were recorded with a 2D-MAR CCD detector (resolution: 2048x2048), scanning the sample with a moving stage over the thickness of the specimen (ND direction). Cutting, scanning and beam direction are illustrated in figure 5.2b. The exposure time was in the order of 1-5 seconds, using a X-ray wavelength of 0.975 Å and a sample-to-detector distance of 150 mm. Scanning was done with steps of 50 μm over half the thickness of the injection moulded samples (1.6 mm).
Mechanical testing

Impact tensile test were performed on the Izod impact bars at a speed of 1 m/s, using a Zwick Rel hydraulic tensile testing machine. To assure the desired initial speed, a pick-up unit was used to allow the piston to accelerate before loading the specimen. To reduce dynamic effects, the contact area between the pick-up unit and the piston was damped by a rubber pad [24]. Piston displacement and force, using a piezo-electric force transducer, were measured at a sample rate of 2.5 MHz. The impact toughness energy was calculated by integration of the measured force-displacement curve, divided by the initial cross-sectional area behind the notch. All tests were performed at room temperature and in five-fold.

5.3 Results and discussion

Polyethylene

Particle dispersion

The morphology of particle dispersion is given in figure 5.3, for 5, 15 and 25 vol% CaCO$_3$ filled PE samples. The CaCO$_3$ particles are strongly aggregated as bulk material, have an aspect ratio of approximately unity (spherically shaped) and do not have large size differences. In the blends, the aggregates are broken up and the particles are well dispersed in the polymer matrix, showing no large agglomeration of particles.

Impact toughness

Figure 5.4 shows the impact tensile test results as a function of blend composition for the compression moulded samples (○) and for the injection moulded flexural bars
Figure 5.3: Scanning electron microscopy images of bulk CaCO$_3$ particles and their dispersion in polyethylene; 5% (b), 15% (c) and 25% (d).

Figure 5.4: Impact toughness as function of volume % calcium carbonate for different sample types: compression moulded (○), injection moulded GATE (△) and END (◇).

GATE (△) and END (◇) samples. An increase in toughness is seen at a volume concentration of approximately 5 % calcium carbonate, but the level of increase differs quite a lot for the different manufacturing conditions of the samples. The toughness enhancement of the compression moulded samples is much lower than that of the injection moulded samples, which show a much higher increase in toughness. Similar to the results reported by Bartczak et al. [5,21], a difference is observed for the GATE and END type of specimens. They reported a toughness enhancement of approximately 10
times the initial value of unfilled polyethylene in case of GATE samples and 5 times for the END samples, whereas in this study respectively ~7 and ~5 times improvement is found. From X-ray diffraction measurements they recognized an additional flow-induced micro-structure to be present in the filled polyethylene samples, and briefly argued this to be the effect of particles with a small aspect ratio orienting themselves along the flow direction and, from the idea of surface nucleation, helping to create better oriented crystallites. The difference between GATE and END measurements was subsequently explained to be the result of a fountain flow effect, and the 'true value' of impact energy of an unoriented isotropic material was suggested to be somewhere between the limits given by the GATE and END toughness levels. In figure 5.4 this is observed not to be the case.

In the previous chapter, crystal orientation in injection moulded samples of neat materials was found to be related to the impact toughness, as long as: (1) the oriented skin layer was large in relation to the sample thickness, and (2) the presence of extended chains (shish) was not to strong. Therefore, both the difference between the compression and injection moulding conditions, as well as the difference between GATE and END type of specimens, can probably be rationalized by the presence of flow-induced crystalline orientation. However, no influence of the distance to the injection gate is observed for the unfilled flexural bars, which is in accordance with the results of Chapter 4 and Appendix A, since for 3.2 mm thick flexural bars the isotropic core dominates the impact toughness.

To investigate the influence of specimen thickness and the expected anisotropic behaviour of flow-induced structures in filled polyethylene, rectangular injection moulded plates of different thickness were tested in flow and perpendicular to flow direction. Since an optimum in impact toughness enhancement was found for the 15 vol% filled blend, this was the only composition that was used for this part of the study. Figure 5.5 shows the impact toughness results in flow and perpendicular to flow direction as a function of specimen thickness. In the previous Chapter 4 and Appendix A it was shown that a flow induced oriented structure in neat polyethylene only gave an increase in impact toughness in injection moulded samples of 1 mm thickness when loaded in flow direction. In figure 5.5 no abrupt drop in impact toughness is observed above a specimen thickness of 1 mm and an approximately linear relation is found between impact toughness and sample thickness for the flow direction. The effect of anisotropy on impact behaviour is again present, since loading perpendicular to flow direction gives impact values in the order of the unoriented compression moulded sample.

The decrease in toughness for increasing thickness is suggested to be a result of a decreasing shear rate, since the volumetric injection feed rate is kept constant, whereas the cross section of the mould cavity increases, resulting in a lower shear stress. The impact toughness of the 15 vol% GATE sample, with a thickness of 3.2 mm, is largest (see △) and has no relation with the plate samples. It seems plausible to attribute this to the fact that the cross section of the flexural bar mould cavity is significantly smaller than that of the plate mould cavity, resulting in a larger shear stress. Furthermore, the complete flow history of the different samples should be considered with respect to the strength of orientation, as e.g. the shape of the runner is different\(^1\). Apparently, the

\(^1\) This also explains why reproduction of the results reported by Bartczak et al. [5, 21] was only reached after selection of the mould and processing conditions used here.
Impact behaviour for filled polyethylene is related to the shear stress during flow, but this is still in contradiction with the observations that thick samples (> 1 mm) of neat polyethylene never show an increase in toughness, no matter how large the shear stress is. Therefore, the thickness of the oriented skin layer in the CaCO₃ filled polyethylene blends will be investigated in the next section.

Structure characterization

As discussed in the previous section, changes in impact toughness are expected to be related to flow-induced orientation in a similar manner as found in neat injection moulded polyethylene in Chapter 4. Since optimal results are found in the 15 vol% CaCO₃ filled polyethylene GATE sample, this sample is used to investigate orientation. Figure 5.6 shows an optical micrograph of half of the cross-section of this sample. Although the CaCO₃ particles absorb most of the transmitted light, an oriented skin layer can be observed (see layer A). Remarkable, however, is the extra oriented layer which can be observed near the center of the sample (see layer B), which seems to be less oriented, but more pronounced in size.

In order to obtain more information on crystal orientation, WAXD images were recorded every 50 μm along half the thickness of the samples. Intensity variations in the Debye rings of (110) and (200) reflection, giving the level of orientation, were visualized using the method as described in the previous chapter, consisting of isolating both reflections and plotting the normalized intensity as a function of the azimuth angle. This technique is preferred over the calculation of Hermans’ orientation functions, since it is capable to distinguish not only between the level of orientation but also between the type of orientation (e.g. twisted vs. non-twisted lamellae). Figure 5.7 shows the normalized intensity of the (110) and (200) reflections as a function of full azimuthal angle (0°-360°) and distance from the edge (0-1.6 mm) of the injection moulded: unfilled PE GATE sample (a,b), 15 vol% CaCO₃ filled PE GATE sample (d,e) and 15 vol% CaCO₃ PE END sample (e,f). The ‘skin-core’ effect of injection moulding is clearly present in the neat polyethylene sample, showing a thin, highly oriented, shish-kebab like ‘skin layer’ and a ‘shear layer’ of twisted oriented lamellae (row structure). The total thickness of these oriented layers (A) is approximately 300 μm, which is relatively small compared to the thickness of the sample (3.2 mm). The impact behaviour is therefore
dominated by the isotropic core and toughness is found to be in the order of the values found in Chapter 3.

If we look at the orientation plots of the 15 vol% CaCO\textsubscript{3} filled polyethylene GATE sample, the orientation in the skin layer shows a less twisted lamellae structure (see intensity spots at equator(0 and 180°) for both (110) and (200) reflections), but the thickness of the layer is similar. However, a second oriented layer is observed in the core of the sample (B), which shows a less pronounced structure development (see also figure 5.6), but covers a large part of the specimen thickness. Apparently the presence of the CaCO\textsubscript{3} particles causes an additional flow-induced oriented structure in the polymer matrix. This extra orientation is also observed in the filled END sample, but to a lesser extent. Interesting is that the level of orientation is low (normalized intensity values of \(\approx 1.5\)) in this additional layer, but shows a non-twisted lamellae structure (observed from the clear (200) intensity at the equator) instead of a twisted row structure, which is generally observed in low oriented polyethylene samples (see Chapter 4).

The existence of a non-twisted lamellae row structure is visualized with the transmission electron micrograph of figure 5.8a. In this image the flow direction is horizontal and the lamellae are found to be oriented perpendicular to flow direction as a result of flow-induced orientation (see Chapter 4). However, it is anticipated that the lamellae are nucleated on some of the surfaces of the CaCO\textsubscript{3} particles and show ‘edge-on’ growth. This nucleating ability of a CaCO\textsubscript{3} crystal face showing lamellae growth of polyethylene normal to the particle surface was also shown by Chacko et al. [25] and used as a possible explanation for toughness enhancement by Bartczak et al. [5, 21]. The kinetics of secondary nucleation on a substrate surface allows for crystal lamellar growth in b-axis direction along the particle surface and thus lamellae growth in a-axis direction away from the surface [22]. This causes a reduction of lamellae twisting and explains the non-twisted lamellae structure, even at low levels of orientation. If this lamellae orientation is merely a result of surface induced nucleation, than it is also expected to be present in filled systems which were not subjected to flow. Fig-

**Figure 5.6:** Optical micrograph of 15 vol% calcium carbonate filled polyethylene injection moulded GATE sample.
Figure 5.7: Normalized intensity at azimuthal angle of WAXD patterns scanned over half the thickness of: GATE sample of unfilled PE (a,b), GATE sample of 15 vol% CaCO$_3$ filled PE (c,d) and END sample of 15 vol% CaCO$_3$ filled PE (e,f). A normalized intensity of 1 over the complete azimuthal scan represents an unoriented structure, intensity variations indicate the presence of a flow-induced structure.
Figure 5.8b shows a TEM image of the 15 vol% CaCO$_3$ filled polyethylene compression moulded sample. Preferential lamellae orientation is indeed observed on the surfaces of the particles, but ‘edge-on’ growth is only present at two opposite surfaces of the particle. This was actually seen on all particles where lamellae orientation was found. This indicates that the crystal lattice structure within CaCO$_3$ particles are in a preferred direction (single crystal type of structure) and that at least one of the calcite crystal lattices causes epitaxial growth of polyethylene crystals. The absence of flow causes an overall random arrangement of lamellae (compare region A and B), resulting in an isotropic structure.

At the present time, the origin of the extra orientation found in the injection moulded bars is not completely clear. Bartczak et al. [5,21,22] discussed the possibility of CaCO$_3$ particles with a non-uniform aspect ratio to orient in flow and thus creating an anisotropic structure. Such effects are known to be present in talc filled polyethylene [26] and polypropylene [27,28], where the plate like talc particles were not only found to orient themselves, but also change the crystal orientation of the polymer. The differences in properties along the flow path (GATE vs. END) were suggested to be a result of a fountain flow [5]. To investigate the validity of this hypothesis, we carefully remelted the 15 vol% GATE sample for about 15 minutes at 160°C confined in a mould. Within this remelting step, flow is considered to be negligible and particle orientation thus to be retained. From the vision of particle surface induced lamellar growth, properties should be the same. In contrast with this, the impact toughness of the remelted
sample was measured to be in the order of 25 kJ/m$^2$, which is considerable smaller than the value of 67 kJ/m$^2$ measured for the original injection moulded sample. This clearly demonstrates the importance of flow-induced orientation on impact improvement, since orientation of the polymer chains is relaxed upon these remelting conditions. However, there appears to be some contribution of particle orientation, as the impact toughness of 25 kJ/m$^2$ of the remelted sample is still considerably higher than that observed in the compression moulded blend ($\sim$17 kJ/m$^2$).

In conclusion, the relation between flow-induced orientation and impact toughness behaviour reported here is similar to that of the previous chapter, where unfilled oriented polyethylene was studied. The increase in impact toughness in CaCO$_3$ filled polyethylene can therefore be explained by the presence of lamellae oriented perpendicular to the loading direction. Such a preferred lamellae orientation was found to increase the level of strain hardening in flow direction, whereas a decrease of yield stress was not observed. In Chapter 4 the importance of molecular weight on both mechanical behaviour and flow-induced structures was recognized. Differences in the results presented here (toughness improvement: $\sim$7x) and those of Bartczak et al. (toughness improvement: $\sim$10x) [5,21] are probably a result of material selection, e.g. their polyethylene was Dowlex IP-10 ($M_w \approx 75,000$ g mol$^{-1}$, $M_n \approx 16,000$ g mol$^{-1}$), and processing conditions. For better understanding the origin of extra orientation in the presence of CaCO$_3$ particles, the effect of (extensional) flow-induced orientation between hard filler particles in a shear flow can be considered and should be investigated.

Fracture mechanism

In this section a brief investigation will be done on the anisotropic fracture behaviour of these filled systems. The micro-mechanical deformation processes in particle filled semi-crystalline polymer systems has been studied extensively by Kim and Michler [19, 20] using electron microscopic and in-situ tensile techniques. For toughness enhancement, as much energy as possible has to be dissipated. Cavitation or debonding, followed by void formation, is responsible for some energy dissipation, and is also known to be of primary importance to release stress concentrations and thus reduce craze formation. With continuous growth of the voids, the matrix ligaments between the particles will start to shear yield. Energy dissipation increases further when this plastic deformation of the polymer matrix enables the surrounding material to yield, delocalizing deformation. A reduction of local yield stress is expected to promote yielding over a larger volume, but an important condition for this is that the yielded ligaments have to be capable to transfer the load to the surrounding material. Since orientation of semi-crystalline polymers increases strain hardening in flow direction (Chapter 4), localization is suppressed in this direction.

The effect of flow-induced lamellae orientation in CaCO$_3$ filled HDPE is illustrated in figure 5.9. Here scanning electron images are presented of in-situ tensile testing of the 15 vol% CaCO$_3$ filled HDPE FLOW and PERP samples of 1 mm thickness. Additional to the original notch, a razor blade notch is applied, and stretching is stopped at the moment of image recording. Both an overview as well as a detailed image are given at a representative draw ratio were deformation at micro and macro scale are well developed. The detailed images are made at a distance of approximately 300 $\mu$m from the notch, see figure 5.9a. In the overview image of the FLOW sample, no
Figure 5.9: Scanning electron microscopy images of fracture micro mechanism in front of notch of 15 vol% filled FLOW (a,b) and PERP sample (c,d): overview (a,c) and detail (b,d).

Figure 5.10: Schematic illustration of fracture micro mechanism in front of notch for FLOW and PERP samples. Loading direction in detailed images is vertical; open arrows indicate main direction of plastic deformation.
macroscopic cracks can be observed. At higher magnifications, however, debonding and void formation in the direction of loading is observed. In flow direction, the ligaments do not show a pronounced localization, due to the increased strain hardening. The ligaments are capable to transfer the load to the surrounding material, which consequently yields. Plastic deformation grows along the loading direction dissipating a lot of energy. This is schematically illustrated in figure 5.10, where the open arrows indicate the most pronounced growing direction of deformation. On the other hand, when testing perpendicular to flow direction, pronounced strain hardening is absent and the ligaments localize the strain. Plastic deformation grows faster perpendicular to the loading direction and macroscopically a localized crack line is observed, see figure 5.9c and 5.10.

Polypropylene

Particle dispersion

Since the optimal results in impact toughness were found at filler contents of 10-20 vol% in polyethylene, polypropylene was only filled with 15 and 20 vol% CaCO$_3$. Larger filler contents are expected to decrease impact properties as a result of small ligament thickness or reduced particle dispersion. The morphology of the two filled polypropylene blends are shown in figure 5.11 and the particles are again found to be well dispersed in the polymer matrix.

![Figure 5.11: Scanning electron microscopy images of 15 vol% (a) and 20 vol% (b) CaCO$_3$ particle dispersions in polypropylene.](image)

Impact toughness

The impact energy for both GATE and END samples of all polypropylene samples tested are shown in figure 5.12. The impact toughness is found to increase with CaCO$_3$ filler content, showing highest values for the GATE samples. The toughness improvement is, however, significantly lower compared to the filled polyethylene injection moulded samples. Therefore, it can be questioned whether any additional flow-induced orientation is present in these polypropylene samples.
Figure 5.12: Impact toughness for different vol% CaCO$_3$ filled polypropylene blends.

Structure characterization

The orientation in the 20 vol% filled GATE sample of polypropylene is characterized by the wide angle X-ray diffraction technique presented in a previous section. The normalized intensities of the (110) and (040) reflections as a function of full azimuthal angle (0°-360°) and distance from the edge (0-1.6 mm) are plotted in figure 5.13. A highly oriented ‘skin layer’ is observed at the edge (A) and a less oriented structure covers most of the specimen core (B). Although not shown here, the unfilled injection moulded sample only showed a clear oriented ‘skin layer’ and no pronounced orientation in the core. This indicates that the presence of CaCO$_3$ particles induces an additional flow oriented structure, similar to what was observed in polyethylene. Next, transmission electron microscopy is used to check the oriented structure between the particles.

Figure 5.13: Normalized (110) (a) and (040) (b) azimuthal scan curves plotted along the thickness of a filled polypropylene GATE sample with 20 vol% CaCO$_3$. A normalized intensity of 1 over the complete azimuthal scan represents an unoriented structure, intensity variations indicate the presence of a flow-induced structure.
Figure 5.14 shows preferential lamellae orientation on the particle surface, but, as flow is in perpendicular to this lamellar orientation, it is unclear whether this orientation is a result of surfaces or flow induced nucleation and growth. The ‘edge-on’ growth is again only observed at two opposite surfaces of the particle. This is either a direct result of flow-induced orientation, or of epitaxial crystallization on a preferred calcite crystal lattice. Toughness enhancement in polypropylene is commonly found to be modest [14–16] upon addition of hard filler particles. The fact that an ultimate increase, like observed in polyethylene, is absent, is not in contradiction with the postulated relation between flow-induced orientation and impact behaviour, since in the previous chapter orientation of unfilled polypropylene was already found not to give a large increase in impact toughness. However, recent reports [16] on toughening polypropylene with similar CaCO$_3$ particles as used in this study, show an increase in toughness by a factor of $\sim$3 at filler fractions above 20 vol\%, indicating the necessary use of higher filler contents.

Figure 5.14: Transmission electron micrographs of lamellae growth on preferred calcium carbonate particle surface in injection moulded polypropylene GATE sample with 20 vol\% CaCO$_3$. Flow is in horizontal direction.

5.4 Conclusions

Modification of polyethylene and polypropylene with CaCO$_3$ particles showed an increase in impact toughness at filler contents of 10 to 20 volume percentage. The level of toughness improvement was related to the processing conditions applied. Injection
moulding of filled polyethylene samples gave a toughness enhancement of approximately 3 to 7 times the value of unfilled samples, when tested in flow direction. Furthermore, the level of absorbed impact energy depended on flow conditions and position of the notch along the flow path. Ultimate impact values were found for specimens obtained from flexural bars tested close to the injection gate. The importance of flow-induced orientation on impact behaviour was recognized, since compression moulded samples and injection moulded samples loaded perpendicular to flow direction did not increase the impact toughness significantly as compared to unfilled polyethylene. Flow-induced oriented structures in injection moulded samples were characterized by wide angle X-ray diffraction techniques and transmission electron microscopy. Besides the usual oriented ‘skin layer’, an additional oriented structure in the specimen core was observed. These oriented structures are known (Chapter 4) to increase the strain hardening in flow direction, increasing the capability of interparticle ligaments to transfer load and deformation in the direction of loading, and thus increasing the toughness by a energy dissipation over a larger volume. Loading perpendicular to flow direction, causes localization of the strain in the ligaments, resulting in deformation development ahead of the notch, with in less energy dissipation. The filled polypropylene samples were much less sensitive to impact improvement by lamellae orientation, which is in agreement with the behaviour found in unfilled polypropylene (Chapter 4).

Acknowledgments

The authors wish to acknowledge Christian Riekel for the availability of the X-ray facilities at the Micro-focus beam-line (ID13) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and the financial support provided by the Dutch Polymer Institute (DPI) (project #164).

References

Chapter 6

Conclusions and recommendations

Main conclusions

In this thesis the deformation and failure of semi-crystalline polymer systems is studied. The intrinsic and macroscopic deformation behaviour is investigated by uniaxial compression and tensile testing, and failure by tensile testing and notched impact toughness measurements. The macroscopic response of polymers is related to their micro and molecular structure, which is much more complex for semi-crystalline polymers compared to the amorphous class. Determination of morphological structure, like e.g. degree of crystallinity, lamellar thickness and (flow-induced) oriented crystallites, is therefore the leading theme through most of the chapters. To rationalize the macroscopic behaviour, the relation between intrinsic mechanical properties and their micro-structure is necessary.

In Chapter 2 the intrinsic properties, like yield stress, strain softening and strain hardening are determined from uniaxial compression tests. Within the processing conditions and polymers used, yield stress is found to be proportional to crystallinity or lamellar thickness, which are both equally changed by the crystallization techniques applied here. Strain softening is merely a property of the glassy amorphous phase and, thus, decreases with increasing crystallinity and disappears upon testing above the glass transition temperature (e.g. polyethylene at room temperature). Similar to the behaviour known for amorphous polymers, the strain hardening modulus is postulated to be proportional to network density. The observation that crystallinity does not influence the strain hardening modulus appears to be related to the fact that, in the polymers investigated, the crystals yield at large deformation, allowing chain transfer and slip without giving a network contribution. Without the presence of chemical cross-links, physical chain entanglements are, therefore, the only interactions contributing to network density and, thus strain hardening. Strain hardening is, however, found to be related to molecular weight and crystallization rate from the melt. A decrease in strain
hardening is found with decreasing molecular weight or cooling rate from the melt. Lowering the cooling rate from the melt, results in a crystallization condition with less nucleation and pronounced growth of the crystals. This slower crystallization, with respect to number of nuclei, allows reeling in of the polymer chains upon growth of the crystals, decreasing the number of trapped entanglements in the solidified polymer. A higher molecular weight polymer shows more pronounced strain hardening and its decrease upon slower crystallization conditions is less. This is explained by the accompanying higher chain entanglement density and, furthermore, higher viscosity at the crystallization temperature, resulting in less mobility of the chains to disentangle.

In Chapter 3 the influence of intrinsic deformation behaviour on the macroscopic tensile and impact response is demonstrated. Stability of deformation is qualitatively predicted using a straight-forward analytical modeling approach. Brittle failure can either be introduced by an increase in yield stress, a decrease in strain hardening, or a decrease in tensile strength. If the type of failure (brittle or tough) in impact loading is unchanged, impact toughness increases with yield stress, strain hardening and tensile strength. Since processing conditions (e.g. cooling rate) influence the intrinsic behaviour, the macroscopic response is also strongly dependent on them.

The processing conditions used to investigate the intrinsic and macroscopic behaviour in Chapter 2 and 3 are all quiescent. Chapter 4 deals with the influence of flow and the resulting flow-induced structures and how they influence the deformation behaviour. Injection moulding and extrusion processes are used to introduce crystalline and molecular orientations. Wide and small angle X-ray scattering techniques give sufficient results on degree and structure of molecular and crystalline orientation. Different oriented structures are found along thickness and flow path, depending on the strength of the polymer flow, which was varied by a selection of material properties (e.g. molecular weight) and processing conditions (e.g. temperature and flow rate). The relation between crystalline structure and macroscopic behaviour was qualified, using the knowledge of the relationship between morphology, intrinsic properties and macroscopic behaviour obtained in the first chapters. Highly oriented structures contain a lot of oriented extended crystals (shish), which increase the yield stress, whereas lower oriented structures mainly consist of oriented lamellae. Molecular orientation in these oriented lamellae row structures increase the strain hardening modulus in flow direction. If the yield stress is high compared to strain hardening, localization is pronounced, resulting in more brittle behaviour. A lower oriented (oriented lamellae) structure, however, shows less localization when loaded in flow direction as a result of the increased strain hardening, which can even led to homogeneous deformation for e.g. extruded polyethylene. Ultimate impact toughness is found for structures exhibiting a low yield stress and large strain hardening. Due to these competing effects in level of orientation, complex structures along the specimen thickness and flow path (e.g. from injection moulding) hamper a quantitative explanation of these samples.

To conclude, in Chapter 5, the ultimate impact toughness behaviour of injection moulded calcium carbonate filled polyethylene blends is explained by the presence of an additional flow-induced oriented structure along the sample thickness. Impact toughness of the blends strongly depends on processing conditions applied, and the anisotropic
Conclusions and recommendations

strain hardening behaviour in flow directions is found to be similar to that of unfilled polymers. Although the origin of this extra orientation is not completely clear, the fact that flow history, and the resulting oriented structure, dominates the impact toughness enhancement of hard particle filled semi-crystalline polymer systems is easily recognized.

**Recommendations**

Although the title of this thesis concerns the behaviour of semi-crystalline polymers in general, only three different polymers were studied. Polyethylene and polypropylene were chosen from the fact that it is known that they can be toughened with calcium carbonate filler particles, as described in Chapter 5. Poly(ethylene terephthalate) was taken for its capability to be quenched into the amorphous phase and subsequently cold-crystallized. Besides, their glass transition temperature relative to ambient temperature was an argument for their choice. As a result, the intrinsic deformation behaviour of the PET samples, as measured with compression tests in Chapter 2, set a basis for the concepts of understanding the behaviour of semi-crystalline polymers. This slow crystallizing property of PET can probably also be used for investigation of the relation between yield stress and lamellar thickness, since controlled crystallization conditions allow a more separate variation of degree of crystallinity and lamellar thickness. An interesting polymer for future investigation, however, is polyamide, since the hydrogen bondings in this polymer will drastically affect the yield stress and maybe also the post yield behaviour.

An important aspect of the macroscopic deformation and failure behaviour not treated in Chapter 3 is the tensile strength. Determination of tensile strength can be difficult, since localization of strain often precedes failure and measurement of the true stress at failure is, therefore, not straight-forward. In samples showing homogeneous deformation, localization is suppressed. This enables true stress-strain measurements with conventional tensile testing using the assumption that there are no changes in volume (incompressible and no voiding of material). Pre-deformation of a sample by cold-rolling increases the initial level of strain hardening, resulting in homogeneous deformation of a material that will normally show localization. This is shown in figure 6.1a, where the true stress-strain curves are given for cold-rolled polypropylene samples of different molecular weight (PP-1 and PP-2 of Chapter 2 and 3). The true tensile strength at failure can directly be obtained in this way and is, as expected, related to the molecular weight of the polypropylene samples. This method of cold-rolling and subsequent tensile testing can also be used to determine the strain hardening level of the original polymer by considering the draw ratio due to pre-deformation. Figure 6.1b shows the true stress-strain curve corrected with the deformation ratio of cold-rolling. The level of strain hardening is now found to be in the same order as the one measured in the compression tests in Chapter 2.

In Chapter 4, the influence of flow-induced oriented structures on the mechanical properties was studied. A well-based relation between oriented structure and deformation behaviour was, however, difficult to establish. The reason for this was not only that the processing conditions applied (injection moulding and extrusion) contain many uncer-
tain aspects with respect to the complete thermal-mechanical flow history, but also the fact that different forms of flow-induced structures were observed. Fully controlled flow techniques should be used to create structures which can be distinguished into these different types of orientation and relate then to these flow conditions. This means that temperature, flow rate and flow history should be well defined in the experimental setup. At the present time, such a setup, existing of a flow-cell installed under a capillary rheometer, is in full operation in our group. Furthermore, a multi-pass rheometer is being modified to produce push-pull oriented samples. Although flow rate is more difficult to control as solidification occurs, the purpose of this technique is to create thick uniform oriented layers within a sample, resulting in a negligible influence of the unoriented core. Figure 6.2 shows a preliminary result of a push-pull oriented sample of polyethylene, produced with the multi-pass rheometer.

Since the boundary conditions for the flow and temperature history of both techniques are set or measured, numerical simulations of flow-induced orientation can be validated. These numerical models should, however, be able to distinguish between the
different types of orientation (shish-kebabs and twisted lamellae row structures) and, furthermore, concluding from the results of Chapter 2, they should be able to model lamellar thickness rather than sperulitical size in order to predict the materials’ yield stress. The influence of the different structures on other physical properties, such as dimensional stability, can also be studied once samples with a well defined structure are available. For example, the dimensional stability is also expected to be related to the various oriented structures, resulting in a complex and probably anisotropic behaviour. Therefore, in order to predict e.g. the final shape of a product, all orientations and their influence on shrinkage should be investigated.

The injection moulding conditions giving the toughness enhancement of CaCO₃ filled polyethylene in Chapter 5 were only found after selection of the mould and processing conditions used in this study. Complex aspects accompanied with injection moulding should not be neglected, and further investigation should be done, using controlled flow conditions like discussed above, for understanding the origin of the results. The presence of particle surface induced orientation and additional flow-induced oriented structure between particles should be further investigated. Epitaxial crystallization on a calcite crystal lattice can be studied using single calcite crystals and wide angle X-ray diffraction measurements. A method to determine the expected preferred orientation of the calcite crystal lattices within the particles, is to use electron diffraction. Numerical simulations can be used to study the effect of enhanced flow gradients between particles in a flow field, resulting in an additional flow-induced structure.
Appendix A

Influence of specimen thickness

In this appendix, the influence of specimen thickness on impact toughness is studied. Two effects of reducing specimen thickness are considered: (1) changes in stress state, and (2) effect of oriented skin layer in injection moulded samples.

A.1 Effect of stress state

It is well known that in a thick samples brittle failure is promoted due to plane strain stress conditions, increasing the triaxial stress state. However the stress state also varies over the sample thickness, see figure A.1. In a thin specimen the plane strain state is less and plane stress conditions are introduced, promoting yield instead of fracture. Deformation of the material is easier and less localized under these plane stress conditions and thus more energy is dissipated. Since thin injection moulded and extrusion casted specimens are investigated in this thesis, it is important to investigate the influence of this stress state, before relating any changes in impact behaviour to orientation as done in Chapter 4.

Experimental

Polyethylene (Stamylan 9089S) samples were compression moulded between brass plates. The polymer pellets were completely melted under atmospheric pressure at 200°C and subsequently the pressure was increased stepwise to a maximum pressure of 500 kPa. The polymer was kept at the applied pressure and temperature for at least 20 minutes in order to create homogeneous samples, followed by a cooling between plates at 20°C. Sample thickness was varied from 0.75 to 4 mm and izod impact specimens were cut out of the plates and notched according to the ASTM D-256 protocol with a notching device.

Impact tensile test were performed on the Izod impact bars at a speed of 1 m/s, using
Figure A.1: Plane strain and plane stress distribution over specimen thickness.

a Zwick Rel hydraulic tensile testing machine. To assure the desired initial speed, a pick-up unit was used to allow the piston to accelerate before loading the specimen. To reduce dynamic effects, the contact area between the pick-up unit and the piston was damped by a rubber pad. Piston displacement and force, using a piezo-electric force transducer, were measured at a sample rate of 2.5 MHz. The impact toughness energy was calculated by integration of the measured force-displacement curve, divided by the initial cross-sectional area behind the notch. All tests were performed at room temperature and in five-fold.

Results

Figure A.2 gives the impact toughness as function of specimen thickness. An increase in impact toughness is observed for a specimen thickness lower than 1 mm, where the stress state is expected to be changed. Therefore, investigation of additional parameters, e.g. orientation in Chapter 4, is only relevant when using samples with a thickness of at least 1 mm.

Figure A.2: Impact toughness as function of specimen thickness in compression moulded (isotropic) samples of PE.
A.2 Effect of oriented layer

In Chapter 4 it was found that flow induced orientation increases impact toughness in flow direction. This increase was found to be dependent on the type of oriented texture and oriented layer thickness. Maximum oriented layer thickness was found to be in the order of $150 - 350\mu m$, which was observed to be enough to change impact behaviour in injection moulded samples of 1 mm thickness. Here, we will investigate the influence of such oriented layers on the impact toughness of injection moulded samples of different thickness.

Experimental

Polyethylene (Stamylan HD9089S) and polypropylene (Stamylan P15M10) plates with a thickness of 1, 2, 3 and 4 mm were injection moulded on an Arburg 320S / Allrounder 500-150 injection moulding machine at respectively 150°C and 200°C. The injection speed was equivalent to a feed rate of 10 cc/sec and holding pressure was 450/35/200 bar for 6/4/2 sec. Sample preparation and impact testing was done as described in section A.1. testing in flow direction.

Results

![Figure A.3](image)

**Figure A.3:** Impact toughness as function of specimen thickness in injection moulded samples of PE (a) and PP (b).

Figure A.3 gives the impact toughness as function of specimen thickness. A significant increase in impact toughness is observed for a specimen thickness of 1 mm, whereas the level of toughness is approximately the same above a sample thickness of 1 mm ($\sim 8kJ/m^2$, for PE and $\sim 11kJ/m^2$, for PP). Using a fixed melt and mould temperature the thickness of the oriented skin layer is related to the injection flow rate. Although the initial feed rate was kept constant at 10 cc/sec, the speed of the flow front decreases for increasing sample thickness, due to the increase in cross-sectional area. Optical microscopy showed that the oriented layer was indeed largest in the samples of 4 mm thickness. However, the increase in oriented layer thickness is small relative to the increase in sample thickness. For example: the thickness of oriented skin layer in the 1
mm thick PP sample was $\sim 400\mu m$ and in the 2 mm sample $\sim 500\mu m$, covering respectively 80% and 50% of the total sample thickness. Apparently, the volume of oriented material in a sample needs to be larger than 50% in order to give toughness enhancement.
Samenvatting

Toepassing van polymeren, die zich kenmerken door lage prijs gekoppeld aan goede verwerkbaarheid, hangt voornamelijk af van hun mechanische eigenschappen. Ten opzichte van amorfe polymeren, behouden semi-kristallijne polymeren hun stijfheid in het temperatuursgebied tot aan hun smelttemperatuur. Hun eigenschappen hangen enerzijds af van de moleculaire parameters en anderzijds van de kristallijne microstructuur in het eindproduct. Deze structuur wordt sterk beïnvloed door de verwerkingscondities toegepast tijdens het vormgevingsproces. Het doel van dit proefschrift is het identificeren van de relatie tussen de mechanische eigenschappen en de aanwezige microstructuur. Hiertoe worden drie belangrijke experimentele technieken toegepast: (1) röntgenverstrooiingstechnieken, waarmee parameters als kristalliniteit, kristalgrootte en -oriëntatie kunnen worden gemeten; (2) drukproeven, waarin breuk van het materiaal wordt onderdrukt, zodat aanzienlijke rekken kunnen worden bereikt; en (3) trekproeven en slagvastheidsmetingen ter bepaling van het macroscopische deformatie en faalgedrag.

In hoofdstuk 2 wordt de invloed van kristalliniteit, lameldikte en molecuulgewicht op intrinsieke eigenschappen, zoals vloeispanning en rekversteviging onderzocht, voor een drietal semi-kristallijne polymeren die verschillende glastransitie temperaturen hebben ten opzichte van kamertemperatuur: polyetheen (PE), polypropyleen (PP) en polyetheentereftalaat (PET). De vloeispanning blijkt proportioneel toe te nemen met de lameldikte. Hoewel het aantal ketenverstrengelingen in vaste polymeren niet meetbaar is, lijkt de rekversteviging gerelateerd aan de netwerk dichtheid van deze verstrengelingen. Indicaties hiervoor komen voort uit de gemeten invloed van afkoelsnelheid op rekversteviging. Minder versteviging van het materiaal wordt gemeten wanneer de smelt op hogere temperaturen wordt gekristalliseerd, waardoor ketens zich beter kunnen ordenen en meer ontwarren (‘reeling in’). De gevonden versteviging in de verschillende semi-kristallijne PET monsters, die gelijk is aan die in amorf PET, impliceert een identieke relatie als geldig voor amorphe polymeren waarin versteviging proportioneel toeneemt met een toenemende netwerk dichtheid van het polymer. De observatie dat kristalliniteit geen invloed heeft op rekversteviging duidt erop dat in de onderzochte polymeren de kristallen plastisch zijn, waardoor ketens door deze kristallen kunnen bewegen en deze zodoende niet bijdragen aan het netwerk. Molecuulgewicht en procescondities, die ‘reeling in’ bepalen, zijn daardoor de voornaamste aspecten die het gedrag na vloei bepalen.
Waarom dit intrinsieke gedrag belangrijk is voor het macroscopische deformatie- en faalgedrag, wordt duidelijk gemaakt in hoofdstuk 3, waar trekproeven en slagvastheidsmetingen worden verricht aan dezelfde materialen gekarakteriseerd in hoofdstuk 2. De stabiliteit van deformatie kan kwalitatief voorspeld worden met behulp van een eenvoudig analytisch model, waarin gebruik gemaakt wordt van de intrinsieke eigenschappen. Bros-taai overgangen ontstaan enerzijds door een verhoging van de vloeispanning (voortkomend uit grotere lameldiktes) en anderzijds door verlaging van de rekversteviging (als gevolg van minder ketenverstrengelingen). In slagvastheid wordt geen bros-taai overgang gemeten, maar enkel kleine variaties in energie-opname als gevolg van veranderingen in vloeispanning en rekversteviging.


Gebruikmakend van de relatie tussen structuur en deformatie- en faalgedrag, zoals gevonden in de voorafgaande hoofdstukken, wordt in hoofdstuk 5 het slagvastheidsgeraad van krijt gevuld PE en PP onderzocht. Wederom duiden de resultaten op een effect van vloeigeschiedenis op het ontstaan van georiënteerde structuren en de daarmee gepaard gaande veranderingen in mechanische eigenschappen. De hoogste waarde in slagvastheid, in dit onderzoek gevonden, wordt waargenomen bij spuitgegoten staven met een gemiddeld percentage krijt, getest in de spuitgietrichting en waarbij het proefstuk zich zo dicht mogelijk bij de inspuiting bevond. Dit gedrag wordt verklaard door de aanwezigheid van een extra vloeigeïnduceerde oriëntatie over bijna de gehele dikte van het proefstuk. Deze oriëntatie verhoogt de rekversteviging in de testrichting (spuitgietrichting), waardoor er minder rek-lokalisatie plaats vindt in het polymeer. Hierdoor verdeelt de deformatie zich over een groter gebied, waardoor er meer energie wordt geabsorbeerd. Dat PP t.o.v. PE minder gevoelig is voor verbetering in slagvastheid door oriëntatie, zoals gevonden in hoofdstuk 4, is in overeenstemming met de mindere mate van verhoging in slagvastheid in anisotroop krijt-gevuld PP.
Dankwoord

Na een korte discussie met mijn begeleiders, over het wel of niet moeten bedanken van hen, wil ik Leon Govaert, Gerrit Peters en Han Meijer uiteindelijk toch bedanken voor de vrijheid en het vertrouwen dat ze me over de afgelopen 4,5 jaar hebben gegeven, ondanks dat zij dit alles gewoon als verplichting zien. Daarnaast wil ik Leon toch nog even extra bedanken, omdat het best nog wel eens benadrukt mag worden dat zijn enthousiasme en de tijd die hij altijd weer voor me had zeker voor een positief resultaat heeft gezorgd.

Gezien de experimentele achtergrond van dit onderzoek, was ik sterk aangewezen op opstellingen in het lab. De mannen van de werkplaats hebben het mij hierbij makkelijker gemaakt met hun snelle hulp en dat stukje gezelligheid dat ik op vloer -1 kon verwachten. Sjef Garenfeld verdient hier misschien toch wat extra lof voor zijn enthousiaste hulp bij het ontwikkelen, opbouwen, verbeteren en vooral repareren van allerlei experimentele opstellingen. Harold van Melick, Edwin Klompen en Frank Swartjes waren vooral de collega's die me geregeld bij konden staan in het oplossen van overige experimentele problemen. Verder wil ik Ab Knoppers en Peter Koets bedanken voor hun hulp bij het extruderen en spuitgieten, Anne Spoelstra en Pauline Schmit voor het TEM en lichtmicroscopisch onderzoek en Gyeong-Man Kim en Alexander Sarkissov voor hun hulp met de ESEM. De experimentele omgeving van het ESRF in Grenoble is toch beduidend anders dan een normaal mens gewend is; een combinatie van serieus en hard werken afgewisseld met de nodige ontspanning is daar gewenst. Afgezien van de directe collega’s en studenten uit onze groep, die geregeld mee zijn gegaan, wil ik de personen van SKT die daar zeker aan meegeholpen hebben bedanken. Sanjay Rastogi bedank ik in het bijzonder voor al zijn leierzame discussies, waar hij vooral in Grenoble tijd voor had. Verder is de uitwisseling van ideeën, hoewel niet van experimentele aard, met Hans van Dommelen ook zeer nuttig gebleken.

Tijdens mijn onderzoek heb ik ook een aantal studenten enthousiast kunnen maken en ik wil Roel Janssen, Jan-Willem Housmans, Hans Duijf en Lambert van Breemen bedanken voor hun inzet en medewerking tijdens hun studie, en verder alle overige studenten, die in kleinere opdrachten toch heel nuttige metingen hebben verricht.

Tot slot zijn er natuurlijk ook een aantal mensen die mij indirect hebben bijgestaan door middel van de benodigde afwisseling, ontspanning en gezelligheid en dan doel ik met name op mijn kamergenoten, vrienden en niet op de minste plaats natuurlijk Wilma, die mij vooral in de laatste weken elke dag weer opnieuw achter mijn beeldscherm zag kruipen.
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