Toughness enhancement of thin layers of polystyrene by a transition in deformation mechanism

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Summary

In this project the possibility of toughness enhancement of glassy amorphous polymers by changing sample dimensions or structure has been explored. The main goal was to find brittle-to-tough transitions in thin layers of polystyrene, and visualize the related shift in deformation mechanism. The results can be used to design material structures with controlled or ultimate toughness.

Multilayered tapes were manufactured, consisting of a large number of alternating layers of polystyrene (PS) or a polystyrene-polyphenylene ether (PS-PPE) blend, and polyethylene (PE). The PS(-PPE) layer thickness varied between 0.04 and 50 µm. Furthermore, similar tapes were made with a layer of diblock copolymer (BC) inserted between the PS(-PPE) and PE layers. These extra layers enhanced the interlayer adhesion.

The interlayer adhesion has been determined with a peel test. The adhesion appears to be very low compared to other polymeric systems: the fracture toughness for PS(-PPE)/PE tapes is around 5 J/m², and increases to 23 J/m² when BC layers are inserted. There is a dependence on layer thickness, originating from non-ideal layer tearing. These values correspond to values found by others.

The deformation behaviour of the tapes has been analyzed with a tensile tester, and the deformation mechanisms have been visualized by optical microscopy. When the PS(-PPE) layer thickness d is decreased, two types of brittle-to-tough transitions can be observed. All tapes show such a transition around \( d = 1 \) µm, the strain at break can be as high as 125%. Microscopy, the shape of the stress-strain curve and of the deforming sample reveal that this is a transition from crazing to multiple crazing; it is caused by stress transfer between PS(-PPE) and PE layers enabled by adhesion. Therefore the tapes with BC layers inserted reach an even higher strain at break (230%).

The second type of transition is associated with a shift in deformation mechanism from crazing to shearing. This transition occurs at layer thicknesses below 0.5 µm, the so-called critical thickness. It has only been observed for the PS-PPE 60-40 blend. The transition to shearing has been visualized by microscopy, and indicated by further evidence.

The occurrence of a critical thickness can be explained by an energy-based model, or by a micromechanical analysis of craze growth. The value found here is in reasonable agreement with both theories, and with experimental results obtained in similar experiments on core-shell rubber-modified blends. Also the strain at break (70%) agrees with those data.

Furthermore, some additional experiments have been performed with Cyclopore (©) sheets. These are polycarbonate sheets with micropores. Tensile tests with microscopy show that the sheets match their specification well, but that their mechanical properties are non-isotropic because of the tendency of the pores to be arranged in lines. The Cyclopore can be seen as an excellent illustration of ductile deformation in shear bands.
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Chapter 1

Introduction

In the past three decades the role of polymers in everyday and industrial applications has increased enormously. To a large extent this is due to the effort that has been put into the development of these materials. Polymers are chosen because of their specific material properties such as strength, toughness, permeability, transparency, and so on, and because of their low cost, light weight, and ease of processing. Their use is very versatile: from packaging and clothing to containers and construction materials. Their mechanical properties, however, were generally considered inferior to those of traditional materials as metals, wood or textile fibres. Thanks to a large amount of scientific research in this field some of these objections have been eliminated because of a better understanding of the macroscopic and microscopic nature of polymers. Nowadays high-performance polymer fibres such as Twaron (©) or Dyneema (©) can compete with any other fibres, and the use of polymeric foams and films as packaging material is common practice. Nevertheless, there is still a desire for improving the qualities of polymeric materials.

For instance, many glassy polymers have been used as structural components over the last decades, but there is a limitation to such applications because of the tendency of these materials to fail in a macroscopically brittle manner, i.e. with no large-scale plastic deformation before cracking. In the fracture mechanism of a glassy polymer, cracking is frequently preceded by a crazing process. These crazes usually grow in an uncontrolled manner, transform easily into cracks and cause brittle behaviour. Hence the study of control of crazing is of considerable technological interest.

Improving polymer qualities in this or other areas can be achieved by developing new kinds of polymers, or by adapting or combining existing materials.

Polymers can be combined via different techniques, such as coextrusion, blending, and surface coating.

With surface coating, thin layers of polymer are applied on top of an other (‘thick’) material. Of course this does not influence the bulk properties, but for instance the impermeability for gases and fluids, the resistance to chemical reactions, or the surface smoothness can be enhanced.
Blending of two or more polymers in a mixer is a rather simple technique. In this way several microstructures can be obtained, such as layers, spheres, or fibres in a matrix, depending on the blending conditions and the properties of the polymers.

Coextrusion is a very suitable technique for the manufacturing of complex products. The polymers may be extruded on top of each other, resulting in a multilayered structure. For instance, such films are used as packaging materials, in which each layer provides a specific property of the film, so that a complex set of requirements can be met easily. Another application of multilayered films is membranes for separation of gases. There is a lot of experience with coextrusion of films and sheets, and scientific research is now mainly focused on other, more complex layered shapes as containers.

In spite of the amount of practical experience with thin and multilayered films [38,39], there is still a need for understanding the background of the basic properties of polymeric structures like these, such as strength and toughness. The mechanical properties of a ‘thin’ sample are not necessarily the same as those of a ‘thick’ one. There may exist an unexpected change. The value of the boundary between ‘thin’ and ‘thick’ depends on the material and on the external conditions, but may be very small (nanoscale). Therefore, those thin layers are usually difficult to manufacture and examine.

There is only a limited amount of published literature about the effects of lamination on crazing and the toughness of a glassy polymer. The aim of this project was to investigate the mechanical properties of thin glassy amorphous polymeric layers, their deformation mechanisms and the possibility to enhance their toughness by lamination with ductile polymer layers. This knowledge can be used to design materials or material structures with a controlled or ultimate toughness.

As a model system was chosen polystyrene (PS), a very brittle, well-studied polymer, and polyethylene (PE) as a representative ductile polymer. For this purpose mainly multilayered films and tapes were used, made by a so-called Multiflux mixer with which structures with even thousands of layers can be obtained. The most important experiments were tensile tests, peel tests, and microscopic investigation of the materials under deformation. The work was done at the Centre for Polymers and Composites at the Eindhoven University of Technology, and at the Center for Applied Polymer Research at Case Western Reserve University in Cleveland (USA).

The next chapter will introduce some theoretical background of the mechanical properties of polymers containing thin layers. The experimental apparatus, methods, and materials will be described in chapter 3. In chapter 4, the experiments will be presented together with a discussion of their results. In the fifth chapter the conclusions will be drawn, and a few recommendations will be given.
Chapter 2

Theoretical background

The spectre of polymers shows a wide variety of mechanical properties. Some polymers are strong and tough, while others are stiff and brittle. Much effort has been established to relate macroscopic properties to properties of the polymeric chains and the polymer network.

The focus of attention in this study will be the toughness of polymers, and the possibility to enhance it by changing sample dimensions or structure. Toughness can be defined as the amount of energy a material can absorb before it fractures. The area below a stress-strain curve represents in fact the toughness per unit volume. For all polymers the maximum (yield) stress is roughly equal: 50 to 80 MPa. The macroscopic strain at break is therefore a simple measure for toughness.

In the first section attention will be focused on the molecular and microscale backgrounds of deformation of a polymeric material. In the next section two types of deformation mechanisms, crazing and shear yielding, will be reviewed. Then we will compare the theoretical maximum draw ratio to experimentally determined maximum strains. The subject of the fourth section of this chapter will be transitions from brittle to tough material behaviour when sample dimensions or sample structures are changed. We will introduce a 'critical thickness', at which this transition takes place as a result of a shift in deformation mechanism. This effect will be used in this study to enhance the toughness of a brittle polymer.

2.1 Molecular background: the maximum draw ratio

A glassy amorphous polymeric material can be considered as a complex physical network of long chain macromolecules. While the atoms within the chains are mutually bonded by a strong chemical bond, there are usually only weak Van der Waals interactions between the chains.

Above a certain molecular length, the chains are forming entanglements, which act as physical crosslinks. These entanglements are responsible for a number of properties which do not follow from the properties of the individual chains (e.g., the rubber plateau of the storage modulus).
Using the idea of entanglements one can calculate a theoretical maximum draw ratio of a single chain in a network, assuming that there is no chain slippage or breaking \[1,2,3\]. This means that the entanglements are acting like permanent crosslinks. The maximum draw ratio (also called \textit{natural draw ratio}) \( \lambda_{\text{max}} \) is defined by:

\[
\lambda_{\text{max}} = \frac{l_e}{d_e}
\]  

(2.1)

where \( l_e \) is the chain contour length, and \( d_e \) the end-to-end distance between two junctions in the network (see figure 2.1). The chain contour length is given by:

\[
l_e = \frac{l_0 M_e}{M_0}
\]  

(2.2)

in which equation \( l_0 \) is the average length of a chain (or chain segment), \( M_0 \) its weight, and \( M_e \) the molecular weight between two entanglements. Now \( d_e \) is related to the network via

\[
d_e = k \sqrt{M_e}
\]  

(2.3)

where \( k \) is a constant that can be measured in neutron scattering experiments of the radius of gyration of molecular coils in the glassy state. These equations can be combined to

\[
\lambda_{\text{max}} = \frac{l_0}{k M_0 \sqrt{M_e}}
\]  

(2.4)

Together with the network density (i.e. the entanglement density)

\[
v_e = \frac{\rho N_A}{M_e}
\]  

(2.5)

\((N_A \) is Avogadro's number, \( \rho \) is the density\), it follows that

\[
\lambda_{\text{max}} = \frac{l_0}{k M_0 \sqrt{\frac{\rho N_A}{v_e}}} = k_2 v_e^{-1/2}
\]  

(2.6)

Now we have derived an equation for the theoretical maximum draw ratio for amorphous glassy polymers. It can also be used in case of crosslinked thermosetting polymers, provided that \( M_e \) and \( v_e \) are replaced by \( M_c \) (molecular weight between crosslinks) and \( v_c \) (crosslink density).

This theory appears to be correct in a number of cases, but predicts a \( \lambda_{\text{max}} \) for PS of approximately 4.2, which means a strain to break of 320\%. However, PS is well-known for its brittleness: its experimental strain to break is only a few percent. The reason for this contradiction is that the actual deformation is not occurring throughout the
whole material, but only locally in deformation zones. In the next section the two types of localized deformation in polymers will be discussed.

2.2 Deformation mechanisms

Deformation in glassy amorphous polymeric materials can occur by two entirely different mechanisms: crazing and shear yielding. Crazing is often associated with a brittle fracture behaviour, while shearing materials are tough. According to which mechanism deformation takes place depends on the intrinsic properties of the specific polymer, but also on external circumstances such as the temperature and the strain rate. In this report, a dependence of toughness (or strain to break) on sample dimensions and sample structure will be explored. First we will look at the two mechanisms.

2.2.1 Crazing

Crazes can be described as micro-cracks which are bridged by numerous nanoscale fibrils running across from one craze interface to the other. These fibrils are connected by thinner cross-tie fibrils [4]. The fibrils consist of oriented chains which are drawn out of the craze interface. Thanks to the network of fibrils, crazes can bear a loading. This is a main difference between a crack and a craze. Craze formation itself will therefore not necessary lead to a fracture of the material. The deformation, however, is localized in a very small volume.

In the craze formation process, numerous microvoids will develop. This results in a macroscopic increase of the volume of the material [5].

Crazes are initiated at inhomogeneities, such as surface or interface damage, trapped bubbles or encapsulated particles. This kind of initiation points are always existent in practice. The crazes develop in a plane perpendicular to the direction of the maximal applied stress.
At a certain stress the fibrils can no longer bear the load. Voids will coalesce and the craze becomes a crack, which will eventually grow and reach other cracks, so that a fatal fracture can result. In practice this process will occur as good as always. Although the fibrils themselves are drawn to the maximum, the macroscopic strain to break is generally small, due to the very localized deformation. The material shows therefore a brittle fracture.

2.2.2 Shear yielding

The other important mechanism that can take place during glassy amorphous polymer deformation is shear yielding. This involves a plastic deformation, either locally or homogeneously. The volume of the material does not change while shearing, which implies an easily detectable difference with the crazing mechanism.

Shearing preferentially occurs in relatively densely entangled or crosslinked polymers, or in circumstances in which the competing crazing process is suppressed, such as under hydrostatic pressure. The polymeric chains are not broken, and often the material will regain its original shape upon annealing, due to the relaxation of the entanglement network.

Shear yielding takes place in so-called shearbands, in a direction approximately 45° to the plane of maximum applied stress (direction of maximum shear stress). There exist different types of shearbands, mainly as a result of the growth speed: microshearbands and diffuse shear zones [6]. The diffuse shear zones can extent through the whole material, until it is drawn maximally. Only then cracks originate and the material

![Figure 2.2 Shear bands in a uniaxially deformed polycarbonate sample [7].](image-url)
fractures. It will show a large strain to break: shearing leads to a tough fracture behaviour.

Figure 2.2 shows an optical micrograph of a shear yielding polycarbonate sample. The molecular chain orientation caused by the stress in the material is made visible with the help of a polarisation filter, showing distinct shear bands.

2.3 Maximum strain in a deformation zone

In section 2.1 a formula for the maximum draw ratio $\lambda_{\text{max}}$ was found. Kramer et al. compared this theoretical value with the local maximum extension ratios of a large group of amorphous polymers [3,8,9,10]. Both crazing and shear yielding materials were examined. The extension ratios inside craze fibrils ($\lambda_{\text{craze}}$) or within shear deformation zones ($\lambda_{\text{DZ}}$) were determined with optical densitometry of transmission electron micrographs.

One might expect that these local maximum strains would be equal to the theoretical values, since the whole considered volume is deforming. However, it appears from their study that this is not the case, probably as a result of the naive character of the model for the maximum draw ratio, which looks at only one extended entanglement instead of at the whole entanglement network [1,11]. It appears that there is still a clear correlation between $\lambda_{\text{max}}$ on one hand, and $\lambda_{\text{craze}}$ and $\lambda_{\text{DZ}}$ on the other hand. For craze fibrils as well as shearing zones the actual maximum strain is roughly 60% of the expected maximum draw ratio.

2.4 Transitions from brittle to tough

The deformation behaviour of a polymeric material changes under certain circumstances, and is depending on both extrinsic as intrinsic variables. It’s a well-known fact that a brittle material may become tougher when it is tested at high temperatures or low strain rates [12], or when its entanglement density is increased (see equation (2.6)).

A brittle material may also deform tougher if the volume in which the actual deformation takes place is enlarged, eventually as a result of a shift in the deformation mechanism from crazing to shearing. Adapting a material’s structure in order to enlarge the deforming volume should therefore be an effective way of toughening [13].

2.4.1 Transition from crazing to multiple crazing

The best-known example of toughness enhancement by modification of the structure is the addition of dispersed rubbery particles [14,15]. The added particles generate stress concentrations throughout the polymeric matrix. Each particle will therefore act as a craze...
initiator, so that the amount of crazes in the matrix rises considerably. The result of this is
that, at the same macroscopic stress, the average stress per craze is less than the stress per
craze in unmodified material. Therefore, the development of crazes into fatal cracks is
delayed. The material as a whole can resist a larger stress before it fractures. For obvious
reasons this toughening mechanism is called multiple crazing.

This principle is used in industrial practice since 1948 with the manufacturing of
High Impact Polystyrene (HIPS). The influence of various physical and chemical
parameters has been the subject of much research. In the optimized case the elongation to
break of polystyrene can be increased up to about 30%.

Another example of multiple crazing occurs in the case of multilayered structures,
provided that there is some adhesion between the layers. A brittle layer may break easily,
but when the adhesion between it and its neighbouring (tougher) layers is strong enough to
keep the layers parts together, the crack will not be fatal. Stress will be transferred to and
from the next layers, so that the broken layer keeps contributing to the overall strength of
the sample. A layer may in fact break up in several parts without fracture of the material
as a whole (see figure 2.3) [16]. The toughness may be even more enhanced, since craze
tips in the brittle layers initiate extra shear bands in the ductile layers, which are effective
energy absorbers. Due to the adhesion the broken layers can transfer enough energy
without being overloaded themselves. This process is also known from fibre reinforced
composites.

The transferred stress can build up as long as it is lower than the strength of the
brittle layers ($F_{\text{max}}$). A force balance results in an equation which correlates that force and
the adhesion force, which is expressed by the interfacial shear strength $\tau_m$:

$$\frac{F_{\text{max}}}{2\tau_m} = \frac{l_c}{d}$$

(2.7)

where $l_c$ is the minimum possible length of a part of a broken layer part which is able to
transfer the stress (this minimum length is called the critical transfer length) and $d$ is the
layer thickness of the brittle component [16]. Ideally, a layer slightly longer than $l_c$ will
experience one more break, whereas the one slightly shorter than $l_c$ will remain unbroken.

![Figure 2.3](image)

*Figure 2.3* Repeatedly cracked brittle layers in a multilayered sample keep contributing
to the overall strength, which is due to adhesion to ductile neighbour
layers.
Equation (2.7) implies that a decrease of \( d \) by a factor two (after addition of an extra Multiflux element) results in a decrease of \( l_e \) by a factor two. If we assume that the macroscopic strain to break of the multilayered tape is directly correlating with the number of breakages along the length of the samples, then consequently there will be a proportional two-fold increase of the macroscopic strain to break.

When the interlayer adhesion (and therefore the interfacial shear strength \( \tau_m \)) is increasing, it follows from equation (2.7) that at a constant layer thickness \( d \) the critical transfer length \( l_e \) will decrease. A layer can then undergo even more fractures before it breaks macroscopically, so that the strain to break will increase. In case of a very strong adhesion, the multilayered tape would even have the strain to break of its ductile component.

2.4.2 Transition from crazing to shearing

In the previous section the enlargement of the deforming volume by forming more crazes was discussed. It is also possible to enlarge that volume as a result of a shift in deformation mechanism from crazing to shear yielding. This will be an even better strategy, since the deformation takes places in shear zones instead of in very localized fibrils.

An indication for this scheme is the fact that in shear zones (as in craze fibrils) the maximum strain equals the maximum draw ratio \( \lambda_{DZ} = 0.6 \cdot \lambda_{\text{max}} \), so on a microscale even a brittle polymeric material is tough. Simply stated it would be sufficient to give the material such a structure that the microscopical toughness would be expanded over the whole macroscopic volume, i.e. the material must have a ‘thin’ structure.

The desired structure must prevent the development of crazes and enhance shear yielding. To suppress uncontrolled craze growing there should be a reduction of tensile stress concentrations at craze tips. In fact the process of deformation can only be sustained if the stress in the oriented (deformed) parts is below the breaking stress, while at the same time the stress in the undeformed parts is higher than the yield stress \( \sigma_y \). There are several ways to accomplish such a structure.

It may seem strange that a crazing (brittle) polymer undergoes a shift to shear yielding as a result of a reduction of sample dimensions. To clarify this point the next example: consider a network of thin ligaments between holes in a polymeric matrix. Brittle fracture can only occur if the stored elastic energy per ligament is larger than the energy required to create a brittle fracture of that ligament. The available stored elastic energy in a ligament \( (U_w) \) is proportional to its volume \( (U_w) \) and the cross-section \( (U_w) \). The energy which is required for a fracture \( (U_f) \) is proportional to its cross-section \( \cdot [17] \).

If the thickness of a ligament is large, the stored elastic energy is larger than the energy necessary for a fracture \( (U_w > U_f) \), and therefore a ligament break will occur.
When the ligament gets thinner, its volume decreases relatively faster than its cross-section. Therefore the available elastic energy is more reduced than the energy needed for a brittle fracture. Below a certain thickness, the stored elastic energy gets lower than the energy needed for brittle fracture \( U_{av} < U_{re} \), so that it cannot cause such a fracture, and a complete deformation of the ligament can take place. This may eventually lead to a fully ductile macroscopic fracture.

That certain ligament thickness, at which \( U_{av} \) equals \( U_{re} \), is called the ‘critical interparticle distance’ \( (ID_e) \). By elaborating the energy criterion mentioned above, a quantitative equation for \( ID_e \) can be found:

\[
ID_e = \frac{6(\gamma + k_1 v_e^{1/2})E}{\lambda_{max} \sigma^2_y}
\]

(2.8)

with the parameter

\[
k_1 = \frac{1}{4} UK\sqrt{\frac{\rho N_A}{\gamma}}
\]

(2.9)

where \( \gamma \) is the Van der Waals surface energy, \( E \) is the Young’s modulus, and \( U \) is the polymer backbone bond energy. Combining equation (2.8) with equation (2.6) gives:

\[
ID_e = \frac{6(\gamma + k_1 v_e^{1/2})E}{k_2 v_e^{-1/2} \sigma^2_y}
\]

(2.10)

This equation gives surprisingly correct results when compared to experimentally determined values [18]. Taking for the polystyrene which was used in this study: \( v_e = 3.2 \times 10^{25} \text{ chains m}^{-3} \), \( \gamma = 40 \times 10^{-3} \text{ Jm}^{-2} \), \( k_1 = 7.13 \times 10^{-15} \text{ J chains}^{-1/2} \text{ m}^{-1/2} \), \( k_2 = 2.36 \times 10^{13} \text{ chains}^{-1/2} \text{ m}^{3/2} \), \( E = 3.28 \text{ GPa} \) (assumed independent of \( v_e \)), and \( \sigma_y = 82.8 \text{ MPa} \) [1,19], equation (2.10) gives a value of 55nm for \( ID_e \).

The concept of a critical thickness, below which a brittle polymer becomes ductile, is also valid in the case of a stratified structure, such as a Multiflux tape. A comparable, but less straightforward, reasoning leads to a similar energy based model [12,17].

An alternative explanation for this thickness-depending transition is proposed by Kramer [1,2,20]. This theory postulates that a craze structure should contain at least two fibrils. The minimum thickness \( (L_{min}, \text{ analogous to } ID_e) \) in which the craze can fit is calculated from the fastest growing fibril spacing. This results in:
\[ L_{\text{min}} = \frac{16\Gamma}{\sigma_y(1-\lambda_{\text{max}}^{1/2})} + 2h \]  

(2.11)

where \( \Gamma \) is the surface energy involving the breakage of chains, and \( h \) is the thickness of the active zone layer at the craze-bulk interface. Taking for PS: \( \Gamma = 0.08 \text{ Jm}^{-2} \), and \( h = 25\text{nm} \) [1,21], this equation results in \( L_{\text{min}} = 80\text{nm} \), which is close to the value based on the energy balance model (55nm).

A better approximation has been suggested by Kramer, in which not the fastest growing fibril is considered, but the fibril spacing less than the fastest growing one to widen at a reduced rate [20]. The transition from crazing to shearing takes place when the craze widening velocity is equal to the velocity of widening of a shear zone. This leads to a somewhat different expression for \( L_{\text{min}} \):

\[ L_{\text{min}} = 4h - h \sqrt{4 - \frac{32\Gamma}{\sigma_y h(1-\lambda_{\text{max}}^{1/2})}} \]  

(2.12)

Using the same data for PS, equation (2.12) gives \( L_{\text{min}} = 69\text{nm} \). The dependence of \( L_{\text{min}} \) and \( ID_e \) on the entanglement density are given in figure 4.9, which shows that that influence is rather limited.

The mechanisms in the previous sections are not the only possible. A similar size effect in multilayered structures has been investigated by Ma, Sung, and others [22-25]. In that case the deformation behaviour of multilayered composites having alternating layers of polycarbonate (PC, tough) and polystyrene-acrylonitrile (SAN, brittle) was studied. Below a certain SAN layer thickness the brittle SAN could be drawn in a ductile fashion while crazing was suppressed. There was a considerable level of adhesion between the layers, which plays an important role in their micromechanical explanation. Therefore it is not directly applicable to the case of PS-PE structures.
Chapter 3

Materials and Methods

In this project some mechanical properties of thin polymeric layers have been studied in their relation to microscopic structure. The goal was to find a brittle-to-tough transition depending on sample dimensions as is described in the previous chapter, and relate it to the deformation mechanism. Polystyrene (PS) was used as a model system, and has also been studied in blends with poly(2,6-dimethyl-1,4-phenylene ether) (PPE). This was done to vary the entanglement density, which influences the critical layer thickness (see equations (2.10)-(2.12)). With the help of a Multiflux mixer tapes were manufactured consisting of alternating layers of different polymers. In particular the strain at break of these tapes has been examined by means of tensile tests. Both in-situ as post-mortem optical and scanning electron microscopy were applied to study deformation mechanisms. Peel tests provided information about interlayer adhesion. This chapter describes the materials, methods, and apparatus that were used for this purpose.

3.1 Materials

The materials which were used to make the multilayered tapes are listed in table 3.1, together with their glass transition temperature $T_g$.

<table>
<thead>
<tr>
<th>material</th>
<th>trade name</th>
<th>manufacturer</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Styron 638</td>
<td>DOW</td>
<td>88</td>
</tr>
<tr>
<td>PS</td>
<td>N7000</td>
<td>Shell</td>
<td>100</td>
</tr>
<tr>
<td>PE</td>
<td>Stamylan HDPE 7058</td>
<td>DSM</td>
<td>-110</td>
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<tr>
<td>PPE</td>
<td>PPE-803</td>
<td>GE Plastics</td>
<td>215</td>
</tr>
<tr>
<td>PMMA</td>
<td>Oroglas V052</td>
<td>Röhm &amp; Haas</td>
<td>96</td>
</tr>
<tr>
<td>P(S-EP)</td>
<td>Kraton G1701 X</td>
<td>Shell</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Sample preparation

3.2.1 Blend preparation

In order to enlarge the entanglement density of PS, (which influences the critical thickness (see equation 2.10-2.12)), it has been blended with polyphenylene ether (PPE). PPE is very suitable for this purpose, since PS and PPE are fully miscible over the total range of compositions. As a side effect, the viscosity of the blends varied, which affected the ease of processing and the minimum attainable layer thickness (section 3.2.2).

PS (Dow Styron 638) and PPE (GE Plastics PPE-803) were compounded in various weight fractions (PS-PPE 80-20, 60-40, 40-60, and 20-80) in order to obtain blends with various entanglement densities. This was done in a co-rotating twin screw extruder (Werner and Pfleiderer ZSK 25). First a master batch of PS-PPE 50-50 was produced at 290°C, which then was extruded again with extra PS or PPE to obtain the various blends. In this second extrusion process the temperature was lowered to respectively 250°C for the PS-PPE 80-20 blend, 270°C for the 60-40 blend, and 290°C for the 40-60 and 20-80 blends. The temperature was kept as low as possible to avoid degradation of the PPE. The extruded blends were pelletized.

Figure 3.1  Principle of the Multiflux mixer:
(a) A Multiflux element. The arrow indicates the flow direction.
(b) Stages of mixing (with 2 and 3 streams).
In order to check the homogeneity of each blend, and to determine their glass transition temperature \( (T_g) \), some Differential Scanning Calorimetry experiments were performed, using a Perkin-Elmer DSC-7. Blend samples were heated to 250°C, quenched to ambient temperature, and then scanned at a heating rate of 20°C/min. The entanglement densities of the blends were measured in a standard DMTA experiment on a Rheometrics RDS II spectrometer.

3.2.2 The Multiflux mixer

The multilayered tapes that were used in this project were made using a Multiflux static mixer [26-28]. This mixer can produce laminated tapes of indefinite length with a total thickness of about 0.1 to 2mm, and a width of 5 to 25mm.

The principle of the Multiflux mixer is explained in figure 3.1. The mixer consists of a square flow channel, in which an arbitrary number of specially designed elements (see figure 3.1a) are placed. The polymers that have to be mixed enter the first element in parallel horizontal layers (stage 1 in figure 3.1b). The flow is then divided in two parts (stage 2), which are compressed in vertical direction (stage 3). Next both flows are extended in horizontal direction (stage 4), and stacked again (stage 5). As a result of all these actions, the number of layers has doubled. The laminated flow may now enter a second element, which will double the number of layers again. By adding more elements the number of layers in the tapes can be set. For example, when 11 elements are placed in

![Figure 3.2 Schematic view of the Multiflux mixer.](image-url)
the mixer, and two incoming polymer flows have to be mixed, the resulting number of layers will be \(2^{12} = 4096\). This provides a simple way to make tapes consisting of many thin layers. When the number of elements is too large, the layers break up into very small droplets; this explains the use of this apparatus as a mixer. This way of mixing-by-stretching-and-folding is also known as the baker’s transformation. It is the most effective way of mixing two or more materials.

The ultimate number of layers (i.e. the ultimate thinness of layers) can be very high, but is limited by the rheological properties of the components, such as viscosity, density, and surface tension. To obtain the thinnest possible layers these properties must differ as little as possible. Of course the components may not diffuse into each other during their stay in the mixer (timescale: tens of seconds). In an experiment we investigated the possibilities of the Multiflux mixer. The materials PS (Shell N7000) and the PMMA (Röhm & Haas Orogas V052) were selected for their matching flow curves (viscosity as a function of shear rate). The minimum attainable layer thickness for this system appeared to be under 40nm!

There has been an extensive research to the effects of differing viscosities, densities, etc. on layer stability (e.g. [29-32]), and it appears that this stability is continually better understood. However, the local circumstances in a Multiflux mixer are far more difficult to model, so that in this project the minimum layer thickness has only been traced by experiment.

The Multiflux mixer that has been used was kindly provided by DSM, and is shown in figure 3.2. It can be fed by three single-screw extruders at the same time. In a coupling device the incoming polymer flows are neatly stacked as shown in figure 3.1b. In this way it is possible to insert a third component between the two others, which can be useful as a compatibilizer (a 'polymeric glue'). The stacked flows pass through the Multiflux elements, leave the mixer by a tape-die head, and are quenched in a water bath. If needed, the tape can be drawn before it reaches the water level. The extruders, the coupler and the mixing elements can be heated independently to assure optimal processing conditions. The square flow channel of the mixer is 1cm × 1cm, each element is 1cm long, the tape die has an opening of 1mm × 30mm. The extruders operate around 10-20 g/min, which makes the remaining time in the mixer 60-30s.

3.2.3 Preparation of multilayered tapes.

Thin multilayered tapes consisting of alternating layers of PE (DSM HDPE 7058) and the blends described in section 3.2.1 were manufactured with the Multiflux mixer. With all blends, tapes were made using 6 to 11 Multiflux elements, resulting in tapes with 128, 256, ..., 4096 layers. Furthermore, in every case PE and PS-PPE were applied in three different proportions: 75/25, 50/50, and 25/75 (ratio of weight fractions). For a short reference we use the following notation: each tape has a code xx-yy/zz, where xx-yy is the composition of the PS-PPE blend, and zz is the PE weight ratio of the tape. For
instance, a 60-40/75 tape has been made with the PS-PPE 60-40 blend in a ratio to PE of 25/75. The PE layers will be (about) three times as thick as the PS-PPE layers. Each kind of tape was checked for layer continuity (see section 4.2). Layer break-up resulting from the influence of viscosity provided a lower limit to the thickness of layers (see section 3.2.2). Tapes with discontinuous layers were, of course, excluded from further testing.

In order to enhance adhesion between PS-PPE and PE layers, multilayered tapes containing the Kraton diblock copolymer (BC) as a third component were prepared. (Attempts to enhance adhesion by pre-mixing 5 or 15% of BC in the PE component failed, probably because the BC concentration at the interface was too low.) Tapes were manufactured for the PS/PE/BC system only, at three different weight ratios: 25/75/1, 50/50/1, and 72/25/1. The incoming flows were stacked as shown in figure 3.1b, so that there is a layer of BC between every PS and PE layer. The BC serves as an adhesive, since its blocks are compatible with PE or PS.

An overview of usable samples is shown in table 3.2, together with their processing temperatures. Since the purpose of this project was to investigate the behaviour of PS, only the range of thicknesses of PS and PS-PPE layers is stated in the table. The total thickness of the tapes was always approximately 0.3mm, and their width 10mm. As a reminder: the layer thickness of a certain component in a tape can be varied as a result of:

- changing the number of mixing elements in the mixer,
- varying the ratio of the incoming flows, and
- drawing the tape after it has left the mixer.

Prior to any testing, the samples were annealed at 80°C for at least 24 hours, to diminish possible internal stresses as a result of molecular orientation. These stresses would otherwise influence the mechanical properties. Some samples from each category were heated to 10°C above their PS(-PPE) glass temperature. If any molecular orientation is left over, the heated samples will show shrinkage.

3.2.4 Cyclopore samples

In order to visualize deformation of a thin polymer system, some Cyclopore sheets were obtained from Cyclopore S.A. at the University of Louvain (UCL) in Belgium. Cyclopore sheets are polycarbonate (PC) sheets with a thickness of a few microns. These sheets have been bombarded perpendicularly with an heavy ion beam (Xe) in a cyclotron. Each incoming ion leaves a track of damage in the polymer. The damaged polymer chains are then etched away, so that a very small pore results, which is perpendicular to the surface. By varying the ion beam radiation time and the etching time, the pore density and pore diameter can be set. In this case the pore density was so high, that the average distance between pores was a few microns. So this is a system that is thin on microscale in two dimensions: the sheet thickness and the ligaments between the pores are on microscale. This system is an interesting step between the cases of multilayered samples (thin in one dimension) and rubber-modified blends (in 3 dimensions). The pores are not distrib-
Table 3.2  PS/PE, (PS-PPE)/PE and PS/PE/BC multilayered samples.

<table>
<thead>
<tr>
<th>PS-PPE blend composition</th>
<th>Processing temperature (°C)</th>
<th>Maximum number of Multiflux elements</th>
<th>Range of PS-PPE layer thicknesses (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-0</td>
<td>200</td>
<td>8</td>
<td>0.4 - 100</td>
</tr>
<tr>
<td>100-0 (with BC)</td>
<td>200</td>
<td>7</td>
<td>0.7 - 20</td>
</tr>
<tr>
<td>80-20</td>
<td>220</td>
<td>7</td>
<td>0.5 - 50</td>
</tr>
<tr>
<td>60-40</td>
<td>225</td>
<td>11</td>
<td>0.04 - 10</td>
</tr>
<tr>
<td>40-60</td>
<td>230</td>
<td>10</td>
<td>0.1 - 10</td>
</tr>
</tbody>
</table>

uted quite randomly, there appears to be a (slight) tendency to form arrays of pores in a preferential direction. Therefore, the sheets don’t have isotropic mechanical properties. For the purpose of this study this is not a great objection. In Table 3.3 an overview of the obtained Cyclopore sheets is shown. The average pore distance is calculated assuming that the pores are arranged in a square lattice. This (edge-to-edge) distance is comparable to the ligament thickness or interparticle distance defined in section 2.4.2.

3.3 Optical microscopy

Optical microscopy was applied to investigate the structure of multilayered samples (both before as after tensile testing and interlayer adhesion measurements), in order to check the

Table 3.3  Overview of Cyclopore (©) samples.

<table>
<thead>
<tr>
<th>Sheet #</th>
<th>Sheet thickness (µm)</th>
<th>Pore diameter (µm)</th>
<th>Pore density (cm²)</th>
<th>Average pore distance (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.01</td>
<td>6 \cdot 10⁸</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.1</td>
<td>6 \cdot 10⁸</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1</td>
<td>2 \cdot 10⁷</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>2</td>
<td>2 \cdot 10⁶</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>3</td>
<td>2 \cdot 10⁶</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>5</td>
<td>4 \cdot 10⁵</td>
<td>11</td>
</tr>
</tbody>
</table>
fracture surfaces and the crack propagation path (Carl Zeiss and Olympus BH microscope).

In order to investigate deformation behaviour during mechanical testing, another series of tensile tests were performed with a Polymer Laboratories Minimat tensile machine. This apparatus is combined with an Olympus BH2 optical microscope, and equipped with an Olympus C-35 AD-2 camera. The dumb-bell shaped specimens were viewed in transmission in a direction perpendicular to the sample’s surface. Before testing, some top and bottom layers of the samples were removed to avoid any disturbances by those outer layers, and to give all specimens the same thickness (0.3mm) The clamp distance \( l_0 \) was 15mm, and the strain rate 5mm/min. During the tensile test photographs were taken of the deforming samples. A polarizing filter was added to gain color contrast and to visualize plastic flow in the material i.e. to indicate shear deformation.

Cyclopore sheets were investigated in the same way during tensile tests, but at a strain rate of 1mm/min. Rectangular specimens were cut out of the sheets, both parallel as perpendicular to the preferential direction of the pores.

### 3.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was applied to check the continuity of the layers in the stratified tapes, and to investigate the morphology of fractured surfaces. These analyses were performed with a Cambridge Stereo Scan 200 and a JEOL 804A.

Specimens were cut from the centre of the tapes, parallel to the direction of extrusion, and perpendicular to the layers. They were then cut with a glass microtome at liquid nitrogen temperature to obtain sharp, undeformed surfaces. Next the samples were etched with an oxygen plasma during 10 minutes, in order to remove some polyethylene and gain contrast between PS (or PS-PPE) and PE layers. Finally, the samples were covered with a gold-palladium layer. Cyclopore samples were not etched, but only provided with a Au-Pd layer.

### 3.5 Mechanical testing

In order to perform tensile tests on the tapes, dumb-bell shaped specimens were machined \( l_0 = 20 \text{mm} \), parallel to the direction of extrusion), according to ASTM D 1708. The samples were strained uniaxially on a Frank 81565 IV tensile machine. The cross-head speed was 5 mm/min for all tests, at room temperature. Each tensile experiment was carried out at least in five-fold, in order to obtain reliable data.

Cyclopore samples for tensile tests were cut out of the sheets (rectangular), both parallel and perpendicular to the preferential direction of the pores.
The adhesion between PS (or PS-PPE) layers and PE layers (enhanced, if applied, by block copolymer layers) was determined by a Double Cantilever Beam (DCB) peel test as described by Bazhenov et al. [33]. In this test two adhering layers are peeled apart. Adhesion is characterized by the fracture toughness $G_{lc}$. This is the amount of energy needed for the formation of a unit new surface:

$$G_{lc} = \frac{F (\sin \theta_1 + \sin \theta_2)}{W}$$

where $F$ is the peel force, $W$ is the width of the sample and $\theta_1$ and $\theta_2$ are the angles between the beam ends (see figure 3.3).

Tapes that were used for interlayer adhesion measurements were manufactured as described in the previous section. After annealing specimens were cut out of the tapes with a Isomat diamond saw. A small strip was removed from each side of the specimens, so that any possible influence of the edges was eliminated. This resulted in samples of about 90mm × 10mm × 0.3mm. With a sharp razor blade an initial crack (with a depth of approximately 10mm) was made in each sample as accurately as possible to split the middle layers from each other. Finally, tabs were glued to the split ends of the samples. They were attached to the clamps of an Instron tensile machine (provided with a 5N load cell) with strings or paperclips. The strain rate was 10 mm/min. During a tensile experiment photographs were taken periodically, so that the peel force $F$ and the beam angles $\theta_1$ and $\theta_2$ could be determined. For each type of sample this test was carried out at least three times in order to obtain a reliable value of $G_{lc}$. With the available equipment, fracture toughnesses as low as a few J/m$^2$ could be measured.
Results and discussion

In this chapter we present the results of the experiments performed, and we give a related discussion. As a guideline we repeat the aims of this project:

- to study the influence of structure (viz. layer thickness) on the toughness of amorphous glassy polymeric materials. More specific: to investigate the possibility to enhance toughness as a result of a shift in deformation mechanism from crazing to shearing at very thin layer thicknesses.
- to visualize the deformation mechanisms in such a transition.
- to study the influence of entanglement density and interlayer adhesion on the process mentioned above.

For this purpose the following experiments have been performed with polystyrene (PS) and polyethylene (PE) as model systems:

- to obtain a varying entanglement density, blends of PS and PPE were made. The homogeneity of the blends was checked with DSC experiments; entanglement densities were determined by DMTA.
- multilayered tapes were manufactured on a Multiflux mixer, with stacked layers of PS (or PS-PPE blends) and PE. Also tapes with a thin adhesive layer (of diblock copolymer) between the PS(-PPE) and PE layers were made. The morphology of the tapes was studied using optical and Scanning Electron Microscopy.
- peel tests were carried out to measure the adhesion between layers.
- tensile tests were performed to determine the strain at break (i.e. the toughness) of the tapes. Some of these tests were done under an optical microscope, in order to study the occurring deformation mechanisms.

Furthermore the deformation of Cyclopore sheets was studied in tensile tests under an optical microscope and in a Scanning Electron Microscope.

Whenever possible the results obtained will be compared with theoretical values and with work done by others.

4.1 Characterization of PS-PPE blends

Four PS-PPE blends were extruded as described in section 3.2.1. The DSC tests revealed that all blends have only one single glass transition temperature ($T_g$) value, which confirms
Table 4.1 Glass transition temperature and entanglement density of PS-PPE blends. The values in parentheses are not determined experimentally, but estimated by linear interpolation.

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Glass transition temperature (°C)</th>
<th>Entanglement density (chains/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-0</td>
<td>88</td>
<td>2.6 \cdot 10^{25}</td>
</tr>
<tr>
<td>80-20</td>
<td>105</td>
<td>4.3 \cdot 10^{25}</td>
</tr>
<tr>
<td>60-40</td>
<td>123</td>
<td>6.2 \cdot 10^{25}</td>
</tr>
<tr>
<td>40-60</td>
<td>144</td>
<td>(9.1 \cdot 10^{25})</td>
</tr>
<tr>
<td>20-80</td>
<td>174</td>
<td>(11.1 \cdot 10^{25})</td>
</tr>
<tr>
<td>0-100</td>
<td>215</td>
<td>13.2 \cdot 10^{25}</td>
</tr>
</tbody>
</table>

The molecular mixing of PS and PPE. The $T_g$ values are shown in table 4.1. Also in that table are the entanglement densities of the blends, measured by DMTA [7]. The values of $v_e$ for the 40-60 and 20-80 blends could not be determined because these blends showed void formation during the experiment, indicating thermal degradation of the material. The remaining values show a linear dependence of the entanglement density between the values of pure PS and pure PPE. Interpolation of these data gives an estimation for the entanglement densities the 40-60 and 20-80 blends, which are stated in parentheses in table 4.1. These DMTA results are confirmed by work by Prest and Porter, who found a similar linear dependence [34].

4.2 Characterization of multilayered tapes

The morphology of the multilayered tapes made with the Multiflux mixer, were examined with Scanning Electron Microscopy. In figure 4.1 some characteristic SEM micrographs of PS-PPE/PE tapes are shown. The continuity of the layers in figure 4.1a and b is clear. In general, the variation in layer thickness is small (about 10%, figure 4.1a), however with decreasing layer thickness the variation becomes larger (see figure 4.1b).

Figure 4.1c is an example of a tape in which the layers have been broken up. The minimum possible layer thickness (or: the maximum possible number of Multiflux elements) is different for each blend (see table 3.2). This is due to the enlarged blend viscosity when the PPE content is increased. (By changing the viscosity of the PE layers, or by choosing another type of PE with a better-matching viscosity, better results could be obtained, but this was not done in order to keep this experiments comparable to other work.) All kinds of tape were checked for discontinuities several times, in order to be
Figure 4.1  
SEM micrographs of multilayered PS-PPE/PE tapes (PS-PPE 60-40): a) 5 mixing elements, PS-PPE layer thickness 5 μm; b) 9 elements, PS-PPE layer thickness 0.2 μm; c) 15 mixing elements.
sure of their layered structure. Tapes with discontinuous layers were, of course, excluded from further testing. Tapes with the block copolymer as adhesive were examined in the same way.

To avoid any unwanted effects of molecular orientation on mechanical properties, all tapes were annealed. Some samples from each category were checked for this after annealing by heating them up to $10^5^\circ \text{C}$ above the PS(-PPE) glass temperature. This revealed a shrinkage of the tapes of maximally 4%. This small value (compared to e.g. unannealed samples with a (low) typical value of 10%) indicates that there is no significant influence of orientation. Other experiments, measuring birefringence on comparable Multiflux tapes, never showed any substantial orientation [28].

4.3 Interlayer adhesion

The adhesion between two layers (measured with the fracture toughness $G_{lc}$) in a Multiflux tape was determined using the modified DCB test described in section 3.6. These tests were performed for several PS(-PPE)/PE as well as PS(-PPE)/PE/BC tapes. The results are summarized in figure 4.2. This figure shows that the value of $G_{lc}$ is very low for all layer thicknesses and tapes: maximally 28 J/m$^2$ for tapes without and 39 J/m$^2$ for tapes with adhesive layers. As a comparison: the fracture toughness for the (adhering) layered system PC/SAN is 100-1200 J/m$^2$ [33], and that of a PE/rubber system can be as high as 3200 J/m$^2$ [35]. $G_{lc}$ appears to be independent of the PS-PPE blend composition in the case of the PS(-PPE)/PE tapes. For the tapes with BC layers, there exists an influence of the composition on the adhesion. Apparently the BC is not only interacting with the PS, but also with the PPE component, which introduces extra adhesion.

![Figure 4.2 Fracture toughness of multilayered tapes versus PS(-PPE) layer thickness.](image-url)
There is a surprising influence of the layer thickness on the fracture toughness: $G_{lc}$ increases considerably when the layer thickness decreases. Examination of the delaminated fracture surfaces with an optical microscope proved that this increase is due to the tearing of layers, or to plastic PE deformation. Hence, the seemingly increased fracture toughness is caused by a multiple crack propagation path, since these processes absorb more energy than is strictly needed for the formation of the new surfaces. The tapes with thicker layers ($d>1\, \mu m$) show smooth fracture surfaces, and give therefore the most reliable value for $G_{lc}$: 5 J/m$^2$ and 23 J/m$^2$ respectively.

Furthermore, samples with thinner layers also contain more layers, since the total sample thickness is constant. So they have more interfaces which offer extra resistance to the deformation of the sample in the peel test. This also wrongly enlarges the measured $G_{lc}$ values.

As stated above, these are very low values, which make explanations assuming a significant adhesion not valid here (see e.g. [16]).

4.4 Mechanical testing

Since we are mainly interested in the toughness of multilayered tapes, we will concentrate on the strain at break as its simple measure in the tensile tests. Other mechanical properties, such as the Young's modulus or maximum strength, don't show such large differences when changing from thick to thin layers.

Figure 4.3 contains the stress-strain curves of pure PS and pure PE tape samples with the same geometry as the multilayered samples. PS (curve A) demonstrates its typical brittle behaviour, while PE (curve B) is obviously very ductile under the same testing.
In figure 4.4 the stress-strain curve of some multilayered PS/PE tapes are shown. Curve A corresponds to the ordinary PS stress-strain behaviour. The curves B, C, and D have a sharp decrease in stress at a certain strain. This appears to be a result of the rupture of PS layers, while the PE layers stay intact. The strain at break of these PS layers has increased enormously compared to macroscopically thick PS (curve A in figure 4.3).

When we assume that the behaviour of PE is not influenced by the small layer thickness [36], we can subtract the contribution of PE (see figure 4.3) from the total stress-strain curve of the composite. The result is the stress-strain behaviour of the PS component. However, for a determination of the strain at break of the PS in the tape, this is not necessary. The pure PE stress-strain curve is smooth up to 225%, so that the sudden stress drop cannot originate from PE.

Similar tensile tests for various PS-PPE/PE and PS/PE/BC tapes give the data shown in figure 4.5. In figure 4.5a the strain at break of PS/PE tapes is less than 10% for PS layer thicknesses larger than 1 μm. However, it increases strongly around a layer thickness of 1 μm. A strain of 100% occurs at a layer thickness of 0.4 μm. Thinner layers couldn’t be manufactured for this system, so the eventually reachable strain at break may even be larger.

Experiments with the PS-PPE 80-20 blend give roughly the same result (see figure 4.5b). The onset of the strain upswing is at a comparable layer thickness. Now the maximum observed strain at break is 130% at a PS-PPE layer thickness of 0.5 μm. For this blend too, it is uncertain how large the strain at break can possibly get.

The data for the PS-PPE 60-40 blend (figure 4.5c) show a different pattern. The composition of this blend appears to be appropriate for attaining smaller layer thicknesses,
Figure 4.5  Strain at break versus PS(-PPE) layer thickness for PS(-PPE)/PE tapes made with various blends: a) PS; b) PS-PPE 80-20; c) PS-PPE 60-40; d) PS-PPE 40-60; e) PS (with BC layers).
probably thanks to a good match between the viscosities of this blend and PE. The number of Multiflux elements could even be raised to eleven, without loss of layer continuity. The minimum layer thickness that could be reached is 0.05 μm. There is a clear difference in the deformation behaviour of the PS-PPE/PE 25/75 weight ratio tape and the 75/25 and 50/50 ratio tapes. The 25/75 tapes demonstrate initially the same results as the already described blends. Between 10 and 0.5 μm there is an upswing in the strain at break, to a maximum of 125%. Below this layer thickness, the strain at break decreases again to a value of about 70%. The curve of the PS-PPE/PE 75/25 and 50/50 tapes, however, shows a more gradual increase of the strain at break, which starts at a layer thickness of 0.1 μm.

This difference in deformation behaviour follows from the apparent fact that the samples undergo a different brittle-to-ductile transition. The transition around 1 μm (to a strain at break of 125%) is from crazing to multiple crazing (see section 2.4.1). All PS-PPE 100-0 and 80-20 tapes also show this type of transition. The transition to 70% at lower layers thicknesses is related to a shift from crazing to shear yielding (section 2.4.2). Proof of this difference in transitions will be discussed in the next section.

For the PS-PPE 40-60 blend, there is only one transition found for all PS-PPE/PE ratios. (see figure 4.5d). This is also a transition from crazing to shearing. The critical thickness in this case is about 0.23 μm, and the eventual strain at break is again 70%.

Finally, the results of the tensile tests with the PS/PE/BC tapes are shown in figure 4.5e. There is a clear transition from crazing to multiple crazing. As expected, the enhanced adhesion doesn’t have influence on the value of the critical layer thickness: around 1 μm, which is the same as for the PS/PE tapes. The maximum strain at break, however, is much higher: 230%. In fact there are so many non-fatal cracks possible in the PS layers, that it is the PE component which fractures first now. This is an example of the influence of adhesion on multiple crazing as described in section 2.4.1.

4.5 Visualization of the brittle-to-tough transitions

Now we will have a closer look at the deforming samples of which the strain at break curves were shown in the previous section. This is done by means of optical microscopy during mechanical testing as described in section 3.3. Since all phenomena of interest (both types of transitions) appear in the case of the PS-PPE 60-40 blend at a PS-PPE/PE ratio of 25/75, those tapes will be discussed here. The strain data are given in the curve of figure 4.5c.

In figure 4.6 polarized optical transmission micrographs of tape samples under uniaxial strain are shown. The loading direction in this figure is vertical. Figures 4.6a to c contain photos of tapes with a PS-PPE layer thickness of 1.5 μm, which were taken at several strain levels: 0%, 4%, and 8% respectively.
Figure 4.6  Polarized optical micrographs of strained PS-PPE/PE tapes, for several PS-PPE layer thicknesses and strain levels. Blend: PS-PPE 60-40; PS-PPE/PE ratio 25/75; a) 1.5 μm, 0%; b) 1.5 μm, 4%; c) 1.5 μm, 8%; d) 0.5 μm, 0%; e) 0.5 μm, 4%; f) 0.5 μm, 8%; g) 0.04 μm, 0%; h) 0.04 μm, 4%; i) 0.04 μm, 13%.
At a strain of 4% (figure 4.6b) thin lines are visible which are running perpendicularly to the direction of load. These lines correspond to small cracks, since the scale of magnification is too small to visualize real crazes directly. However, the cracks must necessarily be preceded by crazes. As expected, increasing the strain results in a clear increase of the number of cracks (see figure 4.6c). For this PS-PPE layer thickness, no transition takes place; the number of cracks keeps increasing until the sample breaks at a strain of 30%.

In the second row of pictures (figures 4.6d to f) the PS-PPE layer thickness has been reduced to 0.5 μm. This tape has a strain at break of 125%. Again, the cracks appear, and their number is larger than in thicker layers. The toughness enhancement is due to the process of multiple crazing. Attempts to quantify this process by counting cracks didn’t give clear results, probably because there is still a considerable number of crazes that aren’t visible. They are too small, or blurred because they are in layers on the bottom side of the sample.

This process takes also place in all PS-PPE 100-0 and 80-20 tapes. There is no colouring, although the strain at break is very large for PS-PPE (>100%, while the macroscopic value is 2.7%). The actual number of cracks/crazes is again difficult to determine, but the shape of the curve is another indication of the occurrence of this kind of transition.

It follows from equation 2.7 that the critical transfer length \( l_c \) diminishes proportionally to the layer thickness \( d \). When the layer thickness decreased by a factor two, so is \( l_c \). In other words: the number of crazes doubles, and so does the strain at break. (Assuming that the strain at break is proportional to the number of crazes.) Indeed we see this relation in the case of these tapes (figure 4.5a to c, e). This gives also an indication for multiple crazing.

The last row of micrographs is taken from tapes with a PS-PPE layer thickness of 0.04 μm (figures 4.6g to i). This thickness is below the critical layer thickness: the deformation mechanism has been changed drastically here. Even at a strain of 13% (and much higher, see figure 4.6i) there are no visible cracks, but the bright colours indicate the occurrence of shear yielding in the whole volume observed, including the PS-PPE. The PS-PPE layers are still unbroken. The colours don’t originate (only) from the yielding of the PE in the tape, since in that case figures 4.6c and f would show equally bright colours. All this indicates a deformation mechanism transition in PS-PPE from crazing to shearing, as described in section 2.4.2.

Further evidence for this type of transition follows from the shape of the stress-strain curves. In figure 4.7 such curves of two tapes from figure 4.6 are shown. Curve A belongs to a tape with a PS-PPE layer thickness of 0.5 μm (figure 4.6d to f). This curve corresponds to the typical behaviour of a craze deforming polymer [5]. Curve B (PS-PPE layer thickness 0.04 μm, figure 4.6g to i) is clearly showing strain hardening, which is characteristic for shear yielding [14]. The sample also shows stable neck formation during straining, and the layers are still adhering after the tensile test (which has been checked

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A parameter which is of importance for the transition from crazing to shear yielding is the craze initiation stress $\sigma_c$. One would expect that if the layer thickness decreases, the craze initiation stress increases, so that at the critical layer thickness the yield stress would be smaller than $\sigma_c$. In that case it would be energetically favourable for the material to yield. The craze initiation stress is difficult to determine, however, since emerging crazes are very hard to observe, even under a microscope.
Figure 4.9 Critical thickness versus entanglement density for PS-PPE blends.

An attempt to measure the engineering stress at which the cracks appear gives the results shown in figure 4.8. This stress is easy to determine, but it is clear that the data don't give much support for the assumption, although there is a stress rise for thinner layers. Only one sample shows a substantial increase (to 64 MPa), but even that is too low to come near the yield stress of PS (82.8 MPa). Looking at cracks instead of at crazes, and using the engineering stress, makes this approach obviously too simple.

The conclusions from these tests and micrographs are that we have found transitions to multiple crazing in all PS-PPE 100-0/..., 80-20/..., and 60-40/75 tapes with a PS(PPE) layer thickness below 1 μm, and that there is a transition to shear yielding in the 60-40/... and 40-60/... tapes, for layer thicknesses below 0.04 and below 0.23 μm respectively.

It is remarkable that the 60-40/75 tapes show both types of transition, while the other 60-40/... and 40-60/... tapes only show a transition to shearing. Apparently these tapes skip the multiple crazing stage. This can be subscribed to the fact that upon decreasing the PE content of the tape, fracture of a PS-PPE layer will result in a relatively much higher stress level in the neighbouring PE layers. Hence, a fracture of the PE layers is more likely to occur immediately after the first fracture of a PS-PPE layer. This results in a fatal macroscopic rupture of the tape, which then shows brittle behaviour. If the PE content is large enough (60-40/75 tape), this process doesn't occur and the tape can undergo multiple crazing without premature failure. In the case of the 40-60/... tapes the stress transfer mechanism is obviously not present, or both types of transition may coincide, so that only one upswing is obtained. At this point further research must give more clarity.
In figure 4.9 the experimental critical thicknesses are compared to the values for \( L_{\text{min}} \) calculated as a function of the entanglement density from theory (equations (2.10)-(2.12)). In addition, this figure contains results from others [17], obtained in the earlier-mentioned investigations of \( ID_e \) in core-shell rubber-modified blends. It is clear that theory and experimental data correspond well. Notwithstanding the simplicity of some assumptions, all three models offer a satisfying prediction of the order of magnitude of the critical thickness. It should be noted that the models from equation 2.11 and 2.12 are only valid when the occurrence of a brittle-to-tough transition is due to a shift in deformation mechanism to shear yielding. The strain at break for layer thicknesses below the critical thickness (70\%) is also in excellent agreement with data from [17].

4.6 Cyclopore experiments

Cyclopore sheets can serve as an illustrative example of the complexity which has to be dealt with when studying three-dimensional deformation on a microscopic scale. A description of the sheets studied can be found in section 3.2.4.

In figure 4.10 a SEM micrograph of a Cyclopore sample is shown (with a sheet thickness of 8 \( \mu \text{m} \), pore diameter 5 \( \mu \text{m} \), a pore density of \( 4 \cdot 10^5 \text{ cm}^{-2} \), and a average pore distance of 11 \( \mu \text{m} \)). The pores are clearly to be seen and have a well-defined
diameter. Their distribution over the sheet is random, but on a micro-scale certainly not homogeneous. This hinders the determination and usefulness of an average pore distance, but the calculated value of 11 \( \mu \text{m} \) appears to be fairly satisfying. Furthermore there is a slight tendency to form arrays of pores. This is a result of the sheet production process, in which an ion beam swaps up and down over the PC sheet. (Of course this makes the mechanical properties of the sheets non-isotropic. Since Cyclopore is generally applied as a membrane, this has never been considered a problem.) The pores are perpendicular to the surface. We can conclude from this micrograph that the sheet specifications are met well and that Cyclopore is a system between the one-dimensional ‘thinness’ of the multilayered tapes and the three-dimensional ‘thinness’ of rubber-modified structures with small holes described in [17].

To study their deformation on a microscopic scale, the Cyclopore samples were subjected to tensile tests with the Minimat. Although we are not interested in the macroscopic stress-strain behaviour, the microscopic developments during deformation are worthwhile studying. Cyclopore is standard grade PC, so it is very ductile and it deforms via shear yielding. However, brittle behaviour can occur in notched samples tested at high speed. In rubber-modified PC examined under such circumstances a brittle-to-tough transition has been observed at a critical interparticle distance \( ID_e \) around 0.2 to 0.7 \( \mu \text{m} \) [7].

In figure 4.11a a few polarized optical micrographs are shown of the same Cyclopore sheet as in figure 4.10. Again we see that the actual sheet meets its specification, and that the pores tend to be arranged in lines. The bright yellow spots in the figures originate from light that shines directly through the holes into the microscope’s objective.

When the Cyclopore is strained (figure 4.11b), the pores are deforming to elliptical shapes. Upon further straining, neighbouring pores are coalescing, which accounts for the lines of light in figure 4.11c. These lines have a preferential direction which is 45° to the direction of applied stress. The pores elongate in that direction, because that is the direction of maximum stress in shear yielding (see section 2.2.2).

Furthermore, the initiation of these deformation bands is clearly correlated with inhomogeneities in the pore distribution: a higher pore density results in a higher probability for deformation band initiation.

Considering these aspects, the Cyclopore system gives a really nice visualization of plastic deformation in shear bands.
Figure 4.11  Polarized optical micrographs of Cyclopore samples (sheet thickness 8 μm, pore diameter 5 μm, pore density $4 \cdot 10^7$ cm$^2$, average pore distance 11 μm) at various strains. a) 0% strain; b) 4% strain; c) 10% strain.
Chapter 5

Conclusions

In this chapter the conclusions which can be drawn from this project will be enumerated. The main goal was to find brittle-to-tough transitions in thin layers of polystyrene, and visualize the relating shift in deformation mechanism. Multilayered tapes were manufactured with a Multiflux mixer, consisting of alternating layers of polyethylene (PE) and a polystyrene-polyphenylene ether (PS-PPE) blend. They were tested in a tensile machine, and studied with microscopy under straining.

Blends with a different percentage of PPE (0%, 20%, 40%, 60%, 80%) were made. This was done to vary the entanglement density, which should influence the occurrence of a brittle-to-tough transition. As a side effect, the viscosity of the blends changed, which affected the ease of processing and the minimum attainable layer thickness. No attempts were made, however, to match the viscosities of both phases by changing the PE viscosity. Especially the PS-PPE 40-60 and 20-80 blends appeared to be too difficult to process. Multilayered tapes were made with the other blends in various layer thicknesses, and with varying PS-PPE/PE composition. The minimum attainable PS-PPE layer thickness depends on the blend composition; for the PS-PPE 60-40 blend layers with a thickness of 0.04 μm appeared continuous. Furthermore, similar multilayered tapes were manufactured with a thin layer of a diblock copolymer (BC) between the PS-PPE and PE layers, by which the interlayer adhesion was enhanced. Attempts to enhance adhesion by mixing BC in the PE component failed.

The adhesion between PS and PE layers, and between PS-PPE 60-40 and PE layers was determined using a DCB test. This determination was hampered by the tearing of thin layers and plastic deformation of the PE. Tapes without adhering BC interlayers which didn’t show tearing gave a value of 5 J/m² for the fracture toughness, which is very low. Insertion of the BC layers increased the fracture toughness to 23 J/m², still low when compared to systems as PC/SAN. Therefore, mechanisms that emanate from a strong interlayer adhesion to explain a brittle-to-tough transition do not apply in this case.

The results of the tensile tests show a sharp increase in strain at break around a (so-called critical) PS-PPE layer thickness of approximately 1 μm for each kind of tape. These brittle-to-tough transitions are connected with a shift of deformation mechanism from crazing to multiple crazing. Due to the (even extremely small) adhesion to ductile PE layers, more than one crack can exist in the brittle PS(-PPE) layers without causing
catastrophic failure leading to macroscopic fracture of the sample. This mechanism has been verified by extensive micrography. The strain at break can get as high as 125%.

Only in the case of tapes made with the PS-PPE 60-40 blend in a 25/75 ratio to PE another kind of transition was found that enhances toughness; it is connected to a shift in deformation mechanism from crazing to shear yielding. This phenomena has also been visualized by microscopy. It occurs at PS-PPE layer thicknesses below 0.5 μm. This critical thickness is in the same order of magnitude predicted by theory. The deforming samples show stable neck formation, and eventually reached a strain at break around 70%. Attempts to measure the craze initiation stress, hoping to determine the layer thickness at which it would be equal to the yield stress, failed.

Finally, Cyclopore sheets give a nice visualization of plastic deformation in shear zones. The sheets match their specifications, but it should be noted that their mechanical properties are not isotropic. This is due to the existence of arrays of pores in the sheets.

Recommendations for future projects can be given. Modelling the polymer flow in the Multiflux mixer can give insight in the influence of material parameters and process variables on the final product. This know-how is needed to optimize its operation, when producing layered structures as well as when mixing two or more components. Further understanding of the brittle-to-tough transitions can be obtained when they are subjected to a careful micromechanical investigation (as has been done in the case of the PC/SAN system [22-25]). The research should not be limited to PS, nor to multilayered structures. This knowledge will be very useful to design a polymeric material (or material structure) with ultimate toughness.
References

27. Schilo, D. and K. Ostertag, Verfahrenstechnik 6 (1972) 45.
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