Stellingen
Behorende bij het proefschrift

FORMATION AND STABILITY OF BLENDS WITH A CO-CONTINUOUS MORPHOLOGY
van Remco Willemse

1. Bij de vorming van een co-continue morfologie in een polymeer mengsel spelen vanzelfsprekend de parameters, die de vorming van druppels en vezels bepalen, een rol. Dit proefschrift: hoofdstuk 3 en 4.

2. Het verband tussen fase-inversie en viscositeitsverhouding gegeven door Ho e.a. is het resultaat van een fit door hun ongelukkig gekozen experimenten.
Dit proefschrift: hoofdstuk 3.

3. De kritische waarden 2 en 5 voor Ca/Ca_en in respectievelijk afschuif- of rekstroming *, waarboven een druppel affien kan deformeren, zijn niet toevallig en kunnen vervangen worden door Ca=1 ongeacht het type stroming.
* P.H.M. Elemans; PhD-thesis, TU Eindhoven (1986);

4. De hoge temperatuursoëfficiënt van de grensvlakspanning in blends van polypropyleen en polystyreen zoals gemeten door Escudie is het resultaat van degradiatie van polypropyleen.

5. De grensvlakkracht, die tijdens het mengen op een druppel/vezel werkt, kan naast een kracht ten gevolge van de 'echte' grensvlakspanning ook bepaald worden door een elastische kracht, waardoor er een schijnbare andere grensvlakspanning heerst.
Afstudeerverslag van Annemieke Langenaa, TU Delft, juli 1997
H. Vanoene, *J.Colloid and Interface Science*, 40, 448 (1972)
6. Een juiste bepaling van de morfologie van een polymeer blend tijdens stroming met on-line dielektrische spectroscopie vereist een juiste kennis van de waarden van zowel de vormfactor, $A_v$, als de ‘size’ factor, $\beta$, in plaats van aannamen daarover. A. Boersma; PhD-thesis; TU-Delft (1998); hoofdstuk 7.

7. Om het verspreiden van virussen te voorkomen moet het ‘gedownload’ software in quarantaine geplaatst worden.

8. Kennis van eerder gepubliceerde ideeën en resultaten (literatuur) is vaak een drempel voor verder onderzoek. Marcel Crok; Kunst als wetenschap; Chemisch Magazine juli/augustus 1998.

9. Het uitvoeren van alleen ‘nuttig’ wetenschappelijk onderzoek mag wel gestimuleerd worden (tweede of derde geldstroom) maar niet verplicht worden.

10. In Artikel 22.2 en in de toelichting (deel II, paragraaf j) van het promotiereglement moet ook een kledingvoorschrift gegeven worden voor de persoon die na de promotiezitting de deur opent voor de comissie, die voor en na nader beraad de senaatszaal respectievelijk verlaat en weer betreedt.

Delft, 23 november 1998
FORMATION AND STABILITY OF BLENDS
WITH A
CO-CONTINUOUS MORPHOLOGY
Front and back cover: color of a product of ‘HDPE-zeepflesjes’ waste after mixing in an extruder. Fortunately the smell of the cover does not correspond to that of the processed waste.
FORMATION AND STABILITY OF BLENDS

WITH A

CO-CONTINUOUS MORPHOLOGY

PROEFSCHRIFT

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Het onderzoek beschreven in dit proefschrift is gefinancierd door Senter in het kader van het IOP recycling.
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Introduction

1. INTRODUCTION

Blending of polymers is an effective way to obtain 'tailor-made' materials for specific application. It enables generating rapidly and economically, a desired set of properties, e.g. mechanical, barrier or chemical properties, or better processability in order to fulfill the customers' requirements. For that reason the polymer blending industry is still growing. Some examples of commercial blends are [1]:

- Blends of polypropylene (PP) and ethylene-propylene rubber, e.g. Keltan (DSM), Hostalen PP (Hoechst) and Vestolen EM (Hüls AG), have excellent impact properties and are suitable for inexpensive bumpers for automobiles.
- Blends of PP and polyamide (PA), with PA being the matrix phase, e.g. Akuloy RM (DSM) or Ultramid KR (BASF AG), have excellent impact resistance making them suitable for automotive, garden and power tool applications.
- Blends of polyethylene (PE) / PA with a lamellar morphology, e.g. Durethan C (Bayer AG/Miles), offer better oxygen barrier properties for consumer packaging.
- Blends of PA and acrylonitril-butadiene-styrene (ABS) with a co-continuous morphology, e.g. Stapron N (DSM), have good dimensional stability and excellent mechanical properties. The impact strength of this blend exceeds that of either ABS or PA.
- Blends of PA and polyphenylene ether (PPE) with particles of PPE, e.g. Noryl GTX (GE Plastics), show a combination of excellent chemical resistance in many hostile environments, excellent mechanical properties, high heat resistance and dimensional stability making them suitable for furniture, automotive and other consumer applications.

Most polymers are immiscible, and blending usually leads to heterogeneous morphologies. Several morphologies can be distinguished such as: droplets or fibres in a matrix and co-continuous morphologies as shown in Fig.1 a, b and c, respectively. The droplets/matrix type of morphology, e.g. small dispersed rubber particles, may improve the impact strength of the blend (e.g.[2-6]). This improvement depends both on volume fraction and phase dimensions [5,6]. The fibre/matrix
morphology may improve the tensile properties of the blend (modulus, strength) if the fibrous component is the stiff and strong one, e.g. fibres of a thermotropic liquid crystalline polymer [7-12]. This improvement depends on volume fraction, aspect ratio and orientation of the rods [13]. The dependence on orientation angle of the rods results in an anisotropic material with an improvement of the tensile properties of the blend parallel to the fibre direction, whereas no improvement of these properties is found perpendicular to the fibre direction [7,13]. Blends which exhibit a co-continuous morphology are expected to give an isotropic blend. Furthermore, these blends may combine the properties of both blend components [14-19]. Besides these types of morphologies also lamellar morphologies can be formed. Blends of the latter type are used to improve the barrier properties to solvents and gasses [20-22], e.g. the improved barrier property with respect to organic solvents of polyethylene due to the incorporation of nylon 6. However, some improvement can also be obtained in a dispersed morphology due to an increased path length (tortuosity), which the gas or solvent has to follow through the blend [23].

![Figure 1.1](image)

Figure 1.1: Several morphologies found in immiscible polymer blends: a. droplets in a matrix, b. fibres in a matrix and c. co-continuous morphology.

It can be concluded that the type of the morphology [2-23] and its phase dimensions [5,6,19] determine the properties of a blend. In order to control these properties the morphology development during the mixing process should be fully understood. These morphologies are non-equilibrium structures that are generated during the mixing of the polymers. As such, they are unstable and they start changing as soon as the fluid comes out of the mixer or even during the mixing process. A desired morphology in a blend obtained by a proper choice of the mixing process, may remain unchanged if frozen in rapidly. During further processing (e.g. injection or compression molding) the blend has to be remelted and the frozen-in morphology is apt to start changing again.
Introduction

The main issues of this thesis are the formation, stability and properties of blends with a co-
continuous morphology. In this chapter a short review of the development and stability of a
morphology in general and the co-continuous morphology in particular is given. At the end of this
chapter the scope of this thesis is given.

1.1 Morphology development

In the initial stage of a mixing process the components are brought together as pellets or
powder. The components are melted and in the molten state they are subjected to mechanical
deformation. In general, two main modes of mixing can be distinguished: distributive and dispersive
mixing. In distributive mixing (large dispersed domains; passive interfaces) phase size reduction is
the result of the affine deformation of the distributed phases. The total amount of shear is the
determining factor. In dispersive mixing (small dispersed domains; active interfaces) phase size
reduction is the result of breakup of phase domains. Here, shear stress and interfacial tension are the
determining factors. Several theories have been developed in order to describe this mixing process
[24-31].

1.1.1 Deformation and breakup

Mixing of polymers usually leads to a dispersed phase (droplets or threads of the minor
component) in a continuous phase of the major component. An elementary process is the
deformation and breakup of droplets in a flow field, which is mainly governed by the ratio of the
deforming stress, \( \tau = \eta_m \dot{\gamma} \) (with \( \eta_m \) the viscosity of the matrix phase and \( \dot{\gamma} \) the shear rate), and
the interfacial stress, \( \sigma/R \) (with \( \sigma \) the interfacial tension and \( R \) the droplet radius), expressed in the
capillary number:

\[
Ca = \frac{\tau R}{\sigma} = \frac{\eta_m \dot{\gamma} R}{\sigma}
\]  \hspace{1cm} (1.1)

Above a critical value, \( Ca_{\text{crit}} \), the shear stress overrules the interfacial stress and the droplet is
stretched until breakup occurs. Grace [24] showed that for breakup of Newtonian droplets in
stationary flow, \( Ca_{\text{crit}} \) depends on the type of flow and the viscosity ratio, \( p = \eta_1 / \eta_m \) (with \( \eta_1 \) the
viscosity of the dispersed phase). The concept of the critical capillary number can be used to predict the phase dimensions in a polymer blend. If $Ca = Ca_{\text{crit}}$ is inserted in Eq. (1.1), then a minimum droplet size, $B_{\text{min}}$, can be calculated with:

$$B_{\text{min}} = \frac{2 Ca_{\text{crit}} \sigma}{\eta_m \dot{\gamma}}$$  \hspace{1cm} (1.2)

The phase dimensions found in real mixing processes are usually larger than this minimum droplet size. Grace's observations are only valid for a single droplet in a matrix, whereas during mixing a large number of droplets are present, which can coalesce. Furthermore, Grace studied the break-up behaviour of droplets in stationary flow. The values for $Ca_{\text{crit}}$ give the condition at which a single droplet remains stable. Wu [25] gave a similar equation for calculating the phase dimensions, which should be valid for more concentrated dispersions in the case of the mixing of polymers:

$$B_{\text{av}} = \frac{\sigma}{\eta_m \dot{\gamma}} A_p^{0.84}$$  \hspace{1cm} (1.3)

where the (+) or (-) sign in the exponent applies for $p > 1$ or for $p < 1$, respectively. However, Eq. (1.3) is not universal, too, because all blends used had a dispersed phase concentration of 15 wt% [25].

In polymer blending the droplets usually stretch into long threads and break up into a line of smaller droplets [26,27]. For the elementary process of breakup of highly deformed droplets (threads) into a line of droplets the critical value is $Ca_{\text{crit}} = 1$. With this value of the critical capillary number the mixing process can be divided into two modes [27]:

- Distributive mixing, where deformation of the droplets of the dispersed component occurs if locally $Ca >> 1$. It is generally assumed that the droplets deform then into threads.
- Dispersive mixing, where breakup of the deformed droplets occurs if locally $Ca < 1$. The interfacial stress will favour breakup of the threads, and droplets are formed.

Several mixing models can be found in literature [28-31], which take into account multiple particle interactions, in particular coalescence, in order to describe the phase dimensions found during mixing. Some of these models [29,30] take this coalescence for granted. These models
describe the phase dimensions without considering the mixing parameters such as flow type, viscosities and the process time. Other models [27,31] consider 'strong' and 'weak' zones in a mixer, where different mixing mechanisms occur. The strong zone represents the region in a mixer, where high deformation rates are present. The droplets can deform into long threads until Ca=1. Coalescence does not occur in this region due to the short collision time of droplets. The 'weak' zone represents the more or less quiescent region of the mixer. The droplets will not deform into threads, because the deforming shear stress is now much smaller than the interfacial stress. Threads, which enter this region, will break up if the breakup time of this thread is smaller than the residence time within this region. Coalescence of droplets can occur.

![Graph](image)

**Figure 1.2:** Volume fraction, $\phi_1$, at which phase inversion occurs as a function of the viscosity ratio, $p=\eta_d/\eta_m$ according to several relations found in literature [36-39] (solid lines). • are results discussed in this thesis.

### 1.1.2 Co-continuous morphology

It is usually assumed that this type of morphology can exist at the point of phase inversion. Several relations found in literature relate this point to the viscosity ratio, e.g. [36-39], shown in Fig.1.2. However, no agreement between experimental results described in this thesis, and the relations is obtained (Fig.1.2). The viscosity ratio alone is apparently not a suitable parameter for the
calculation of the phase inversion point. In Fig.1.3 a typical SEM picture of a co-continuous morphology is shown, where elongated structures can be seen after extraction of one of the components. It is to be expected that several other parameters, e.g. the viscosities, the phase dimensions, the interfacial tension, the process conditions and the process times, determine the stability of these elongated structures. The influence of these parameters is not taken into account in the models for co-continuous morphologies given in literature so far.

![Typical SEM picture of a co-continuous morphology](image)

**Figure 1.3:** Typical SEM picture of a co-continuous morphology in a blend of 50% PP and 50% PE after extraction of the PE phase. Elongated structured can be seen.

Furthermore, it is not clear how these morphologies are formed during the mixing of two polymers. By considering an equilibrium of breakup and coalescence of droplets as described in section 1.1.1 these co-continuous morphologies can only be formed if the coalescence of droplets and/or fibres leads to a network-like structure [26]. Consequently, the phase dimensions of such a co-continuous morphology are usually coarser than those of a dispersion [34,35], as illustrated in Fig. 1.4.

These coarse co-continuous morphologies, however, were not found in our blends [40-42], where the phase dimensions of the co-continuous morphology and those of a dispersed structure are similar as shown in Fig.1.5. The formation of a co-continuous morphology may not be the result of coalescence of droplets and fibres only and another mechanism is expected to play a role, too. The
mixing theories as described above neglect the initial stage of mixing in which sheets are formed [43-48]. These sheets will break up and a network may be formed [47]. The degree of progress of the mixing process and the lifetime of the formed network, before it breaks up, can explain the limited applicability of the relations for phase inversion. From this point of view the co-continuous morphology is just an intermediate stage of mixing [49,50].

Figure 1.4: Dependence of the phase dimensions on the composition of a blend of PP and Polycarbonate (PC) [34].

Figure 1.5: Some typical SEM pictures of PE/PS blends with 40% PS, after [40].
a. a co-continuous morphology; b. A dispersed type of morphology both after extraction of the PS phase.
1.2 Stability

1.2.1 General

The blend morphologies are non-equilibrium structures that are generated during the mixing of the polymers. As such, they are unstable and they start changing as soon as the fluid comes out of the mixer. A desired morphology in a blend only stays unchanged if frozen in rapidly. During further processing (e.g. injection or compression molding) the blend has to be remelted and the frozen-in morphology starts changing again and a coarsening of the phase dimensions usually occurs. The interfacial-tension driven changes in morphology can occur via different mechanism, viz. coalescence, breakup, retraction and end-pinching. Which one of these mechanism will be operative depends on the initial morphology of the blend [51]. Coarsening of the phase dimensions and a change of the morphology can occur simultaneously.

1.2.2 Co-continuous morphology

The effect of the interfacial tension driven change of the morphology is rather straightforward in the case of fibres and droplets, its effect in the case of a co-continuous morphology, however, is not clear at all [19,52]. Verhoogt [52] found that blends of 20 % SEBS (a styrene-ethylene/butylene block copolymer) in PEE (a polyetherester) which showed a co-continuous morphology, broke up leading to a dispersion whereas blends with 30 and 50 % SEBS in PEE which also showed a co-continuous morphology, did not break up and the co-continuous morphology was preserved. The phase dimensions, however, increased. Similar results were found by Quintens [19] in blends of PC (polycarbonate) and SAN (styrene acrylonitrile). A transition from a co-continuous structure to a dispersed phase structure occurred in the 70/30 PC/SAN blend after long annealing times. In the 60/40 PC/SAN blends coarsening of the phase dimensions was found, whereas the co-continuous morphology was preserved.

1.3 Mechanical properties

The properties of a polymer blend depend on several factors such as: the properties of the blend components, the blend composition, the morphology and the interface. There are several mixing rules which are used to estimate the mechanical properties of a blend: such as modulus,
Introduction

tensile strength, strain at break and toughness [53]. Some of these rules take into account the type of morphology and its geometrical background, whereas others only give a composition dependence based on some mathematical considerations. This is illustrated by considering the modulus of a blend in case of a fibrillar and a co-continuous morphology. Halpin [13] developed a model describing the modulus of a blend as a function of the aspect ratio, L/D, of the fibres and the composition of the blend. The modulus of a fibrillar morphology in the case of stiff fibres with L/D = 1 and 100, both parallel and perpendicular to the fibre, is shown in Fig. 1.6. It appears that the modulus parallel to the fibres increases with increasing aspect ratio. The modulus perpendicular to the fibres, however, is considerably lower and does not depend on the value of L/D.

The modulus of a blend with a co-continuous morphology has been considered to follow the model of Davies [54], which is also shown in Fig. 1.6. This model is the result of a mathematical consideration and does not take into account any geometrical conditions, and for that reason it usually fails in real systems [16,55].

![Figure 1.6: Calculated tensile modulus versus composition](image)

**Figure 1.6:** Calculated tensile modulus versus composition: (—) is the modulus of a blend with a co-continuous morphology [54]; (---) and (....) are the moduli of a fibrillar morphology parallel and perpendicular to the fibres, respectively, with a. L/D=1 and b. L/D=100 [13]. The modulus of the blend components are 200 and 2500 MPa, respectively.
The mixing rules for moduli do not take into account the interface of the blend. In practice, the blend components shows a poor interfacial adhesion. This poor interfacial adhesion, however, hardly influence the stiffness of a blend, e.g. the incorporation of a stiff component will lead to a stiffer blend, and for that reason these relatively simple mixing rules for moduli can be used. By contrast, the poor interfacial adhesion between the blend components usually causes a lower tensile strength and a lower maximum strain at break, e.g.[56,57].

A model describing toughness is difficult to formulate. Besides the influence of morphology, phase dimensions, adhesion, and the properties of the blend components, the toughness of a blend depends to a great extent on the mechanism of energy dissipation in the blend, e.g. multiple crazing or shear yielding. A proper choice of the blend components, composition and mixing conditions will enforce a certain toughening mechanism leading to high synergy [4,5,6,58,59].

As discussed above, predictions of the complete set of properties of a blend is not yet possible. Only some general statements with respect to structure and property can be made. In case of co-continuity the best balance of properties is expected [1], e.g. high toughness [1,60,61], high stiffness [14,15,17,19] and a large deformability [19].

1.4 Recycling

The first commercial plastics were developed over one hundred years ago, but the growth of the petrochemical industry was the catalyst behind plastics becoming major consumer materials. Nowadays, the plastics have not only replaced many wood, leather, paper, metal and glass products in many applications, but they have facilitated the development of entirely new types of products, too. The enormous growth of the plastic industry eventually contributes to the solid waste stream. The possibilities of dealing with this stream are landfilling, burning to regain energy and recycling to new products. In the future landfilling will be limited [62] and recycling of the plastics should be enhanced.

The major part of the total plastic consumption lies in the packaging sector (42%) and the main types of plastic are: low density polyethylene, high density polyethylene, polypropylene, polystryrene, polyvinylchloride and polyethylene terephtalate. A plastic waste stream from this sector contains all these types of plastic which are immiscible leading to a heterogeneous blend. By
controlling the morphology of this blend the properties may also be controlled, as was discussed above. In some cases a compatibilizer may be used to improve some properties. However, in practice no constant distribution of the different types of plastics is found and no constant set of properties can be achieved. The properties of a product which contains this multicomponent waste, are for that reason unsatisfactory and preferably the different types should be separated, which is up to now economically unattractive. The recycling of this commingled waste stream is therefore often limited to the production of low-value products, e.g. timber replacement.

Renfree [63] studied a stream of post-consumer plastics which was mixed with another common waste plastic, polystyrene, to improve the mechanical properties of the materials. The polystyrene was found to improve the mechanical properties, especially at those volume fractions of the polystyrene where a co-continuous morphology was found.

1.5 Motivation

This research project was part of a so-called IOP project (IOP-recycling) financed by the Dutch Department of Economic Affairs which was carried out in co-operation with the Twente University of Technology and TNO. The goal of the project was to find a good and cheap method for recycling of multi-component plastic waste without the use of a compatibilizer. The composition of this waste stream is expected to vary and it is difficult to obtain a constant set of properties. The idea was to blend this multi-component waste stream with at most 30 wt% of another waste stream, which contains mainly polystyrene or another relatively stiff plastic, in such a way that a co-continuous morphology is formed leading to better tensile properties. From Fig 1.2 it might be concluded that the formation of a co-continuous morphology at lower volume fractions (<50%) is only possible within a certain range of viscosity ratios [36-39]. The points in this figure indicate that no reliable prediction of the composition at which a co-continuous morphology may exist, can be made. For that reason several model blend series of PE/PP, PP/PS, PE/PS and PA6/PE are made to trace the process parameters which determine the formation and stability of a blend with a co-continuous morphology.
1.6 Scope of this thesis

In chapter 2 of this thesis the initial morphology of the blend as it is processed in the mixer and its effect on the final morphology is studied. The initial morphology consists of sheets [42-49] which may contribute to the formation of the co-continuous morphology. In chapter 3 a model for co-continuity is introduced which takes into account the geometrical requirements of a co-continuous morphology. The co-continuous morphology is depicted as an assembly of randomly oriented rods and the stability of these morphologies is studied. The effect of the matrix viscosity and the interfacial tension on the composition range, where co-continuity is possible, is discussed in chapter 3 and chapter 4. In chapter 5 the stability of polymer blends during compression molding and injection molding is discussed. The mechanical properties of blends with a co-continuous morphology are compared with a dispersed type of morphology in chapter 6. The morphology development of blends of PP and PE and their properties are studied in chapter 7. Some of these blends, which act as a model system for plastic waste, are mixed with PS to improve the stiffness of the blend. Finally, in chapter 8 some general conclusions drawn made with respect to the development of a co-continuous morphology, the effect of some mixing parameters on the stability of this morphology and the properties of this morphology.

1.7 References

42. Willemsen, R.C. and Posthumo de Boer, A., Co-continuous morphologies in polymer blends: the effect of mixing time, submitted to Polymer Communication (1998)
47. Willemsen, R.C., Ramaker, E.J.J., Van Dam, J. and Posthumo de Boer, A., Morphology development in immiscible polymer blends: initial morphology and phase dimensions, submitted to Polymer (1997)
2. MORPHOLOGY DEVELOPMENT IN IMMISCIBLE POLYMER BLENDS;*

The initial morphology

2.1 Introduction

Most studies on polymer blending have been focussed on elementary processes such as drop (de)formation, thread breakup and coalescence [1-12]. Less work has been done on the morphology development starting from the initial pellets [13-17]. Generally it is observed that a quick morphology change and a rapid decrease of phase dimensions occur in the initial stages of mixing [18]. Scott and Macosko [15] found that the initial morphology obtained by blending in a batch mixer consisted of 'sheets' of the dispersed phase. Lindt [13] and Sundararaj et al. [14] showed that this 'sheeting' mechanism also occurred in a single screw and twin screw extruder. The sheets break up due to interfacial disturbances, eventually leading to a morphology of dispersed droplets or threads.

It will be shown in this chapter that the morphology formation and phase size reduction in single-screw extrusion proceeds through the formation of sheets which eventually break up into threads, droplets or a network (co-continuous structure). The measured phase dimensions can quantitatively be described by deformation of sheets rather than by deformation of droplets. It will be shown furthermore that independently of the capillary number the phase dimensions do not significantly decrease any further after sheet breakup, whether or not the blend is passed through a static mixer or just through neutral elements. The type of morphology obtained, however, does depend on the capillary number which governs the stability of the structures formed after sheet breakup. A fibrillar or co-continuous morphology breaks up into droplets at lower values of the capillary number. These structures are then intermediate structures, which exist only during a certain time in the extruder. At higher capillary numbers these structures may remain stable during the total process time. The co-continuous morphology is then not an intermediate type of morphology as shown in this chapter. In literature, by contrast, this morphology is usually considered to be an intermediate type of morphology [19-20].

* based on: Willemse, R.C.; Ramaker, E.J.J.; Van Dam, J. and Posthuma de Boer, A.; Morphology development in immiscible polymer blends: initial morphology and phase dimensions; subm.to Polym.(1998)
2.2 Theory

The prediction of the morphology and the phase dimensions obtained by blending of immiscible polymers is difficult because of the complicated nature of the blending process. Several theories have been proposed for various blending mechanisms and for specific parts of the total process. So far, only few theories have appeared pertaining to a 'sheeting' mechanism. In this section the traditional approach to a prediction of phase sizes in polymer blending will be compared to a prediction of the phase sizes based on a 'sheeting' mechanism.

2.2.1 Droplets and threads

The classical approach to predicting phase sizes in heterogeneous polymer blends is based on the elementary process of breakup of isolated droplets in a flow field of a matrix phase, governed by the value of the Capillary number:

\[ Ca = \frac{\tau R}{\sigma} = \frac{\eta_m \dot{\gamma} R}{\sigma} \] (2.1)

which is the ratio of the deforming stress \( \tau = \eta_m \dot{\gamma} \) (with \( \eta_m \) the viscosity of the matrix phase and \( \dot{\gamma} \) the shear rate) and the interfacial stress \( \sigma/R \) (with \( \sigma \) the interfacial tension and \( R \) the droplet radius). Above a critical value, \( Ca_{crit} \), the shear stress overrules the interfacial stress and the droplet is stretched until it breaks. The resulting droplet diameter \( B_{min} \) is:

\[ B_{min} = \frac{2 Ca_{crit} \sigma}{\eta_m \dot{\gamma}} \] (2.2)

Grace [21] showed that for breakup of Newtonian droplets in stationary flow \( Ca_{crit} \) depends on the type of flow and the viscosity ratio, \( p = \eta_d / \eta_m \) (\( \eta_d \) being the viscosity of the dispersed phase). Grace’s observations are valid only for isolated droplets, whereas during mixing a large number of droplets are close together and can coalesce leading to larger phase sizes. Furthermore, his values for \( Ca_{crit} \) give only the conditions for stability of a droplet in stationary flow. In real mixing processes, the droplets will be subjected to non-stationary deformation, and, at sufficiently high values of \( Ca \), the droplets will be stretched into long threads which eventually will break up into a
line of smaller droplets [5,7]. As a result of the elongation the diameter of the extending droplet decreases and, consequently, the local capillary number decreases until the critical value for breakup, \( \text{Ca}_{\text{crit}} = 1 \), of the extended thread is reached [7]. The extended thread will then break up according to the Raleigh mechanism, and a line of droplets will be formed with diameters approximately twice the thickness of the breaking thread.

The phase size thus obtained depends on the total deformation of the original droplet or pellet. Assuming affine deformation, the diameter of the thread, \( B_{\text{thread}} \), depends on the total amount of imposed strain (\( \gamma = \gamma_t + \gamma_i \)) according to [1]:

\[
\frac{B_{\text{thread}}}{2R_0} = (1 + \gamma^2)^{1/4}
\]  

(2.3)

where \( R_0 \) is the radius of the original droplet. This affine deformation is possible in shear only if \( \text{Ca}/\text{Ca}_{\text{crit}} > 2 \) [6]. In elongational flow affine deformation occurs only if \( \text{Ca}/\text{Ca}_{\text{crit}} > 5 \) [7]. In most mixing devices the flows are dominated by shear since elongation is difficult to sustain for long times. For this reason and because of our experimental conditions only shear flow is considered in this chapter.

The diameter \( B_{\text{thread}} \), as a function of \( \gamma \) is shown in Fig. 2.1. This figure demonstrates that the phase dimensions of 0.1 - 10 \( \mu m \) typically found after mixing are not predicted by Equation (2.3) starting from the typical initial pellet size (3 mm). Delamare [11] used an initial droplet size of 0.53 \( \mu m \), which was found after the melting zone in order to fit his results without explaining the choice of this value. The typical phase dimensions found after blending can be explained by using the concept of reorientations [1]. By reorienting and folding the extending droplet ("bakers' transformation") the thread diameter will be given by:

\[
\frac{B_{\text{thread}}}{2R_0} = \prod_{j=1}^{n} (\gamma_j)^{-1/2}
\]  

(2.4)

in which \( n \) is the number of reorientations and \( \gamma_j \) is the amount of strain between two reorientations. If, for example \( \gamma = 2 \) between each reorientation [6], twenty reorientations are necessary to arrive at
$B_{\text{thread}} = 3 \mu m$, starting from 3 mm. The "bakers' transformation" is, however, realised only in well
designed static mixers and in certain dynamic mixers such as co-rotating twin-screw extruders.
Single-screw extruders, however, are inferior for creating these reorientations. Yet, the phase
dimensions after single-screw extrusion are usually in the range of 0.1 - 10 $\mu m$ [13,14] and a
different mechanism is required for explaining these observations.

![Graph showing B vs. \( \gamma \) for Thread and Sheet with initial pellet size indicated.]

**Figure 2.1:** The diameter of the thread and the thickness of the sheet in the case of affine
deformation of a pellet of 3 mm thickness into a thread (Eq. (2.3)) or a sheet
(Eq. (2.6)), respectively.

The phase dimensions calculated with Eq.(2.2) are droplet diameters formed during mixing.
These droplets, however, can only exist if the formed threads break up. This breakup of threads
according to the Raleigh mechanism will occur only if the residence time of the thread is larger than
the breakup time. This breakup time, $t_b$, can be estimated using Tomotika's theory [22]:

$$t_b = \frac{\eta_m B_{\text{thread}}}{\sigma \Omega_m} \ln\left(\frac{0.81 B_{\text{thread}}}{2 \alpha_0}\right) \quad (2.5)$$

where $\alpha_0$ is the amplitude of the initial disturbance, usually estimated between $10^{-7}$ and $10^9$ m
[23,24] and $\Omega_m$ is a function of the viscosity ratio [22]. Eq. (2.5) should be used with care. It is valid
only for Newtonian systems in quiescent condition, which is usually not the case in polymer blending. Stretching has a stabilizing effect against breakup of the liquid thread, leading to thinner threads [24].

The prediction of the phase sizes according to Eqs. (2.2), (2.3) and (2.4) - if applicable at all - will be invalidated even more if coalescence of the droplets occurs, leading to an increase of the average phase size. Coalescence will occur only if the concentration of droplets is sufficiently high and if the droplet diameter does not exceed a critical diameter [7].

2.2.2 Sheets

The theories briefly described above are valid for dispersed droplets and threads only and do not include the mechanism of their initial formation. In the initial stages of blending a quick morphology change occurs involving formation of striated structures [9,13-17]. Plochocki [9] postulated an ‘abrasion’ mechanism for this morphology change. The group of Macosko [14-16] showed that a ‘sheeting’ mechanism is causing this morphology change where pellets are stretched into ribbons or ‘sheets’ upon melting. Sundararaj et al. [16] presented a map showing the different conditions where either ‘sheets’ or threads may be formed using the ratio of normal stresses and the Deborah number as parameters. It was shown that sheets can easily be formed in shear flow and that threads, however, are formed only at low shear rates (< 5-10 s⁻¹). Sheets are not transformed into threads because the interfacial forces are far too low under most circumstances to change the shape of the cross-section of the sheets significantly [5,16].

In the shear flow the thickness of the sheets decreases until interfacial disturbances will initiate breakup of the sheets. The decrease in thickness of the sheets can be calculated as a striation thickness [1]. Starting from a sphere with initial radius $R_o$ a ribbon (‘sheet’) will be formed in shear flow having a width equal to the radius of the original sphere but having a much smaller thickness $B_{sheet}$. The length of the ribbon after deformation is given by $L=2R_o \left(1+\gamma^2\right)^{1/2}$ if $\gamma >> 1$ [1]. Its volume is $V=1/4\pi (2R_o) B_{sheet} L$ which should be equal to the volume of the original sphere, $V=1/6\pi(2R_o)^3$. This leads to the following expression for $B_{sheet}$ if $\gamma >> 1$: 
\[
\frac{B_{\text{sheet}}}{2R_0} = \frac{2}{3}(1+\gamma)^{\frac{1}{2}}
\]  

(2.6)

The sheet thickness, \( B_{\text{sheet}} \), as a function of overall deformation is shown in Fig.2.1. From this Figure it can be seen that the sheet thickness decreases much more rapidly with deformation than the thread diameter does.

At a certain thickness the sheets will start breaking up by hole formation, which may be caused by interfacial instabilities, which occur in layered structures during flow [25], or by impurities in the blend [14]. The holes will grow due to interfacial forces and finally the holes will coalesce leaving a network of ligaments, which may be the precursor of a co-continuous morphology. This network can break up into threads or droplets [17], depending on the blending conditions. The phase dimensions of the resulting structures are of the same order of magnitude as the final sheet thickness. Eq. (2.6) can, therefore, be used to predict the final phase sizes. From Fig.2.1 it can be seen that the typical phase sizes of 0.1 - 1 \( \mu \)m found after blending are indeed predicted by Eq. (2.6).

It can be concluded that a ‘sheeting’ mechanism can explain the quick change in phase dimensions found in different mixing methods [9, 13-17]. Shear flow is indeed an effective way of dispersing because the reduction in striation thickness is concluded by breakup of the sheets into dispersed structures. Phase size reduction by way of deformation of threads which finally break up into droplets is much less effective.

A further deformation of droplets after sheet breakup does not lead to formation of new sheets because at these small phase sizes the interfacial forces are of such a magnitude that droplets will be deformed into threads or will hardly be deformed at all. Deformation of these droplets into threads which subsequently break up is not very effective for size reduction as was shown above, so the phase dimensions are expected to stay approximately constant after sheet break up. This will be shown below.
2.3 Experimental

Blends of polyethylene (PE) and polystyrene (PS) were made using different processing methods. A single screw extruder was used to study the sheet formation in an extruder, which is inferior in achieving reorientations. So, an effective mixing was not expected. The effect of subsequent further mixing on phase dimensions and co-continuity was studied by feeding the extrudate to a static mixer. A co-extrusion setup feeding both components to a static mixer separately was used to exclude the influence of the melting process on the morphology development and to create layered structures over a large range of phase sizes. In addition to the static mixer a variable number of ‘neutral’ elements were used, which only extend the residence time and the total amount of imposed shear. With these elements the morphology development after sheet breakup was studied.

2.3.1 Processing

For the single screw extrusion a Collin Laboratory single screw extruder equipped with a transport screw (D = 20 mm, L/D = 20) was used feeding a static mixer, which contains an adjustable number (0-11) of static mixing elements. For the co-extrusion setup [26] the Collin extruder, described above, and a Händle extruder (D = 17 mm, L/D = 20) were used for feeding PE and PS separately to the same static mixer. The PS melt is injected centrally in the PE stream as a thread with a diameter of approximately 2 mm just in front of the static mixer. The composition of the PS/PE blends can be varied by changing the screw rotational speed of the Händle extruder. The static mixing elements used in both types of experiments were of the type Ross ISG (15 mm diameter), which contains 4 channels with a diameter of 2.7 mm. The average shear rate in these channels at the operating conditions used for all experiments was estimated to be about 22 s⁻¹. The polymers and their viscosities are listed in Table 2.1.

Blends of 5 wt% and 17.5 wt% PS in PE1 were used to study the sheet formation at 200°C as a function of the number of mixing elements with both processing methods described above. The extruded blends were quenched in water.
Table 2.1: Trade names and shear viscosities at $\dot{\gamma} = 22 \text{ s}^{-1}$ of the polymers used.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Grade</th>
<th>$\eta$ (Pa.s) $(T = 200^\circ\text{C})$</th>
<th>$\eta$ (Pa.s) $(T = 250^\circ\text{C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Hostyrene N2000 (SHELL)</td>
<td>780</td>
<td>160</td>
</tr>
<tr>
<td>PE1</td>
<td>StamylanLD 2100TN00 (DSM)</td>
<td>1860</td>
<td>1210</td>
</tr>
<tr>
<td>PE2</td>
<td>StamylanLD 2102TN26 (DSM)</td>
<td>960</td>
<td>540</td>
</tr>
</tbody>
</table>

The formation of a co-continuous morphology was studied by preparing blends of PS in PE1 and PS in PE2 with 10, 20-70 wt% PS using the single screw setup. Further, a blend of 30 wt% PS in PE1, which exhibits a co-continuous morphology, was made using the co-extrusion setup in order to exclude the influence of the melting process. The result of these experiments should prove the origin of a co-continuous morphology.

2.3.2 Stability experiments

Blends were made in the Collin extruder at 200°C, which fed the static mixer containing 1 Ross ISG element. The stability of these blends during further processing was studied by extending the static mixer with an adjustable number of 'neutral' elements with different lengths: 1, 2, 4, 6 and 7 cm. The elements contain 4 channels parallel to each other with the same diameter as the channels in the Ross ISG elements. The Ross ISG elements (Fig. 2.2a) enforce a "bakers’ transformation", whereas the 'neutral' elements which contain 4 parallel channels with a diameter of 2.7 mm (Fig. 2.2b) only extend the residence time at a constant shear rate. By a combination of these elements the static mixer can be extended by 1 to 27 cm. These lengths correspond to an extended residence time of about 1 to 23.4 s. Two systems were studied: system 1, which contains 17.5 wt% PS in PE1 and system 2, which contains 17.5 wt% PS in PE2. System 1 and 2 were processed at 200 and 250°C in these 'neutral' elements, respectively, with the objective of comparing the stability of the morphology at different levels of viscosities.
Morphology development

Figure 2.2: The elements used in the static mixer: a. Ross ISG and b. 'neutral' elements.

2.3.3 Characterization

The extruded strands were broken in liquid nitrogen and extraction of the PS phase was performed in a Soxhlet extraction apparatus with 2-butanone during 3 days. This was sufficient for complete removal of the soluble fraction. In the case of co-continuity 100% of the PS phase can be extracted [27], which is also possible in the case of sheets due to the continuity of the sheet phase. If the sheets break up leading to a dispersion, less PS can be extracted, because a part of this phase is entrapped within the insoluble phase. In the case of fibres more PS can be extracted than in the case of droplets as will be shown later.

A scanning electron microscope (Philips XL 20) was used to study the morphology and the phase dimensions after extraction. Samples were fractured prior to extraction. The reported droplet radii, fibre diameters and sheet thicknesses given are the results of 50 to 100 measurements of the holes resulting after extraction. In order to determine the stability of the fibres during flow the morphology parallel to the flow direction was studied. In these cases the sample surfaces were smoothed parallel to the flow direction by using a diamond knife under liquid nitrogen. These smooth surfaces enable the determination of the length of the fibres.

2.4 Results and discussion

2.4.1 Single screw extrusion

The morphology found at the end of the extruder had an ‘onion’-like structure with rather irregular ‘sheets’ of 1-4 μm thickness and also showed some fibres and droplets of the same size.
A typical example of this structure is given in Figs. 2.3a and 2.3b, showing the morphology both parallel and perpendicular to the flow direction of a blend of 17.5 wt% of PS in PE1. Extraction of these blends resulted in removal of 90-95% of the PS-phase indicating a large degree of continuity of this phase. From these experiments it appears that a 'sheeting' mechanism occurs in single-screw extrusion. The average shear rate in these experiments (22 s⁻¹) exceeded the value of critical value for sheet formation of 10 s⁻¹ given by Sundararaj [16]. The width of the sheets (10 - 100 μm) appears to be much smaller than the width of the original pellets (3 mm). Apparently, some breakup of the sheets already took place, which is not surprising considering the complex flow history of the pellets in the extruder. This may also explain the observed fibres and droplets.

**Figure 2.3:** Morphology of the blend with 17.5 wt% PS in PE1: a and b represent the morphology at the end of the extruder screw parallel and perpendicular to the original flow field, respectively; c and d represent the morphology after 10 mixing elements parallel and perpendicular to the original flow field, respectively. (after extraction of PS phase).
Morphology development

The blend leaving the extruder was fed to a static mixer, and no further decrease in phase sizes was found except for the first mixing element, as is shown in Fig.2.4. Increasing the number of mixing elements up to 10 did not result in smaller phase dimensions despite the extra shear and reorientations imposed by the static mixer. An example of the morphology of the blend after 10 mixing elements, both parallel and perpendicular to the flow direction is shown in Fig.2.3c and 2.3d. The original sheet-like morphology has broken up into a fibrillar structure in this example. Depending on the capillary number breakup into droplets can occur as well. This will be discussed below.

![Graph showing phase dimensions](image)

**Figure 2.4:** The minimum and maximum phase dimensions of the PS phase as a function of the number of mixing elements following single screw extrusion.

The thickness of the sheets of 1-4 μm found after extrusion is in agreement with Eq.(2.6). According to this equation a sheet thickness 2 μm will be formed from pellets of 3 mm at an overall deformation in the extruder of approximately $\gamma=1000$. If a mechanism of thread formation and breakup would have been occurring, fibres and droplets should have been found with a diameter of approximately 100 μm (Eq.(2.3)). This was not observed.
From the above and from Fig. 2.3 it can be concluded that the initial morphology of the blends consists of sheets which subsequently break up into a network of ligaments which will then break up into fibres and droplets. This was indeed found for blends of PS in PE2. From the SEM-pictures shown in Fig. 2.5 it appears that the morphology of a blend with 40 wt% PS in PE2 changes as the number of mixing elements increases. The phase dimensions, however, remain more or less constant. The extraction results of these PS/PE2 blends shown in Fig. 2.6 indicate that the morphology breaks up when more mixing elements are used, e.g. less PS can be extracted from the blend using 10 elements. From the blends of 40, 50, 60 and 70 wt% PS in PE2 100% of the PS phase can be extracted before these blends enter the static mixer, whereas after passing 10 mixing elements only 100% PS can be extracted from the blends with 60 and 70 wt% PS in PE2. This means that the co-continuous morphology is only stable at 60 and 70 wt% PS. The co-continuous morphology at 40 and 50 wt% PS in PE2 is an intermediate structure which breaks up into droplets and fibres.

Figure 2.5: Morphology of the blend with 40 wt% PS in PE2 prepared by single screw extrusion and static mixing (after extraction of PS): a.3 and b.10 mixing elements

The blends of PS in PE1 show a different behaviour. From the extraction experiments it appeared that a co-continuous morphology is formed in blends of 30 wt% PS in PE1 and upwards. This morphology is formed after the breakup of the sheets but no droplets and fibres were formed. The formed network of ligaments, viz. the co-continuous morphology, is in this case stable independently of the number of mixing elements, as can be seen in Fig. 2.7.
Figure 2.6: Fraction of PS extracted from blends of PS/PE2 prepared by single screw extrusion as a function of the amount of PS in the blends: •, △ and □ blends prepared with 0, 3 and 10 mixing elements, respectively.

Figure 2.7: Morphology of the blend with 40 wt% PS in PE1 prepared by single screw extrusion and with static mixing (after extraction of PS): a.3 and b. 10 mixing elements.
2.4.2 Co-extrusion

A sheet morphology was obtained by blending the molten polymers in the Ross static mixer if the number of mixing elements was smaller than 7. Using a larger number of mixing elements resulted in morphologies with dispersed threads or droplets. Sheets were obtained with a large distribution in thickness and with large disturbances on the surface. An example is shown in Fig. 2.8. The sheet thicknesses as a function of the number of mixing elements, determined from electron micrographs, are given in Table 2.2. These thicknesses decrease rapidly with the number of mixing elements until sheet breakup occurs and a dispersed morphology is obtained with a constant phase size. This is shown in Fig. 2.9. The measured sheet thickness can be compared with the striation thickness as expected in the Ross static mixer [28]:

\[ B_{\text{striation}} = \frac{0.002}{2 \cdot (4^N)} \]

(2.7)

with \( N \) the number of mixing elements and 0.002 the initial thickness of the PS phase in m. Eq. (2.7) gives a fair description of the measured phase sizes for the mixing elements 1 to 6. For larger numbers of mixing elements sheet breakup occurs and the phase sizes remain constant.

Figure 2.8: A typical example of sheets of PS in PE1 (17.5 wt% PS) prepared by coextrusion using 5 mixing elements (after extraction of the PS phase).
Morphology development

Table 2.2: Sheet thickness and particle size as a function of the number of mixing elements in case of blends with 5 wt% and 17.5 wt% PS in PE1 prepared by coextrusion.

<table>
<thead>
<tr>
<th>Number of elements</th>
<th>5 wt% PS</th>
<th>17.5 wt% PS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sheet (µm)</td>
<td>Particles (µm)</td>
</tr>
<tr>
<td>0</td>
<td>= 2000</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>88.6 ± 19.1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>23.8 ± 15.9</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>11.7 ± 10.0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>3.6 ± 3.5</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>3.4 ± 3.0</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1.0 ± 0.8</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>0.3 ± 0.2</td>
</tr>
</tbody>
</table>

The breakup of the sheets is illustrated by the results of extraction of the PS-phase. In the case of sheets 100% of the PS phase can be extracted, because the sheets form continuous structures. This continuity is destroyed if the sheets break up into a dispersion of either threads or droplets, leading to a lower fraction of the PS that can be extracted. The extraction results shown in Fig. 2.10 confirm that the sheets in the blends of 5 and 17.5 wt% PS break up after 6 mixing elements destroying the continuity of the PS phase. The phase dimensions of the resulting fibres or droplets remain remarkably constant even after a high number of mixing elements (Table 2.2 and Fig. 2.9). The type of morphology, however, can vary as will be shown in the next section. The extractable amount of PS in the blend with 30 wt% PS remains 100% after 6 elements, but the layered structure starts to disappear. No dispersion is formed, but the morphology becomes co-continuous.
Figure 2.9: Phase dimensions of the PS phase in PE1 as a function of the number of Ross ISG mixing elements after coextrusion; (full line) striaton thickness, Eq. (2.6); O, + and Δ represent 5, 17.5 and 30 wt% PS, respectively.

Figure 2.10: Fraction of PS extracted from blends prepared by coextrusion as a function of the number of mixing elements: O = 5 wt% PS; + = 17.5 wt% PS; Δ = 30 wt% PS.
2.4.3 Stability of the morphology after sheet breakup

It is generally asserted that the flow in a mixer may stabilize the morphology [6,7,26]. The co-continuous morphology in a blend of 30 and 40 wt%PS in PE1 indeed remains stable independent of the number of mixing elements, whereas the one in a blend of 30 and 40 wt% PS in PE2 breaks up. The viscosities of the PE phases differ and apparently the morphology in the blends with PE2 is unstable due to a low viscosity.

Figure 2.11: Morphology of a blend of 17.5 wt% PS in PE1 prepared by single screw extrusion parallel to the flow direction: a. after leaving the Ross ISG mixing element and b. after 23 s (γ=515) leaving the 'neutral' elements. The fibres were stable.

Figure 2.12: Morphology of the blend of 17.5 wt% PS in PE2 prepared by single screw extrusion parallel to the flow direction: a. after leaving the Ross ISG mixing element and b. after 4s (γ=100) leaving the 'neutral' elements. The fibres broke up.
Breakup of blend morphologies under conditions of flow was studied by extending the static mixer with 'neutral' elements as described in experimental. Two blends were compared: system 1, consisting of 17.5 wt% PS in PE1, and system 2 consisting of 17.5 wt% PS in PE2. Both blends exhibit a fibrillar morphology as shown in Fig.2.11a and 2.12a, but differ in the viscosity of the major component. The fibres in blend system 1 did not break up during the flow through the complete 'neutral' section (residence time is 23 s) as shown in Fig.2.11b and confirmed by the extraction results in Fig.2.13. The fibres in blend system 2, however, broke up and droplets were formed as shown in Fig.2.12b. This breakup is confirmed by the decreasing amount of extractable PS shown in Fig.2.13.

![Graph](image)

**Figure 2.13:** Fraction of PS extracted as a function of the residence time in the 'neutral elements': ■=system 1, ●=system 2. The fibres in blends of system 2 break up.

The relevant parameters, calculated capillary numbers and calculated breakup times for both systems are given in Table 2.3. It can be seen that for system 1 the capillary number in the elements is $Ca=2$ and breakup did not occur, although the process time exceeded the calculated breakup time. In system 2, on the other hand, $Ca=0.8$ and breakup of the fibres took place within 4 s. It appears that the shear stabilizes the fibre if $Ca>1$, whereas breakup occurs if $Ca<1$. 
Table 2.3: Viscosity ratio, interfacial tension, phase dimensions and the resulting capillary numbers and the breakup times (Eq.(2.5)) during processing in 'neutral' elements.

<table>
<thead>
<tr>
<th>System</th>
<th>p (-)</th>
<th>σ (mN/m)</th>
<th>B_{ave} t=0 (μm)</th>
<th>Ca (-)</th>
<th>t_b (Eq.(2.3)) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>4.5 [5]</td>
<td>0.4±0.2</td>
<td>2.0</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>3.5 (*)</td>
<td>0.5±0.2</td>
<td>0.8</td>
<td>3</td>
</tr>
</tbody>
</table>

(*) calculated using the theory described in [29].

Table 2.4: The average aspect ratio, L/B and diameter of the fibres (system 1) and fibres/droplets (system 2) as a function of the residence time (t)

<table>
<thead>
<tr>
<th>Flow time (t)</th>
<th>Average extra shear</th>
<th>System 1 Fibres: for all t</th>
<th>System 2 Fibres: t &lt; 1.8 s</th>
<th>System 2 Droplets: t &gt; 1.8 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>(-)</td>
<td>L/B</td>
<td>B (μm)</td>
<td>L/B</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>30</td>
<td>0.4 ± 0.2</td>
<td>34</td>
</tr>
<tr>
<td>0.9</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>1.8</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>4.5</td>
<td>100</td>
<td>26</td>
<td>0.7 ± 0.3</td>
<td>4</td>
</tr>
<tr>
<td>9.0</td>
<td>200</td>
<td>24</td>
<td>0.6 ± 0.3</td>
<td>2</td>
</tr>
<tr>
<td>13.5</td>
<td>300</td>
<td>39</td>
<td>0.5 ± 0.2</td>
<td>2</td>
</tr>
<tr>
<td>18.0</td>
<td>400</td>
<td>31</td>
<td>0.6 ± 0.2</td>
<td>3</td>
</tr>
<tr>
<td>23.4</td>
<td>515</td>
<td>39</td>
<td>0.6 ± 0.2</td>
<td>3</td>
</tr>
</tbody>
</table>

The phase dimensions (fibre diameter and droplet diameter) did not change significantly on passing the ‘neutral’ elements in either blend system as shown in Table 2.4. This is analogous to the behaviour in the ‘active’ mixing elements after break up of the sheets as shown in Figs. 2.4 and 2.9. The average value of L/B in system 1 remains approximately 30, whereas the value of L/B in system 2 decreased rapidly due to the breakup of the fibres as shown in Table 2.4. It was found that after breakup the droplets were a factor of 1.6 as thick as the original fibre. These droplets formed after breakup did not deform into a long thread anymore.
2.5 General discussion

Sheets are formed in the initial stage of polymer blending. This is found in processes where blending and melting proceed simultaneously, as was shown in blending of immiscible polymers in batch mixers [15], single screw [13] and twin screw extruders [14]. In these blending processes melting and mixing proceed concurrently and sheet formation can be seen as the consequence of the interaction of these process steps [17,19]. Yet, sheet formation need not necessarily be the consequence of a concurrent blending/melting process, but may well be the consequence of the geometry of shear flow. Shear flow leads to an increase in length of a fluid particle in the flow direction at sufficient large deformations, and to an associated decrease in thickness, leaving the width largely unchanged especially in the initial stage where the deforming stress largely exceeds the interfacial stress. Molten pellets are thus deformed into ribbons ('sheets') when subjected to shear flow. This view is supported by our micrographic observations and by the good agreement between the measured phase sizes and predictions based on Eq.(2.6).

As stated earlier, this mechanism of deformation of 'sheets' followed by breakup is an effective way of dispersing two polymers. It is much more effective in reducing dimensions of the dispersed phase than deformation of droplets into threads followed by formation of lines of smaller droplets. This latter mechanism involves two-dimensional reduction of lateral dimensions of the thread and implicitly requires elongational flow or large interfacial stresses in order to maintain the cylindrical shape. Of course, sheets can be formed only so long as the interfacial stresses are small compared to the deforming stresses.

As expected, sheets are formed by feeding the static mixer with separately prepared polymer melts. The measured layer thicknesses neatly follow the power law for the striation thickness (Eq. 2.7) until breakup sets in. This method of producing fairly well defined sheets leads to the same sheet thickness before breakup and the same final phase dimensions as insingle-screw extrusion.

The final phase dimensions are determined by the breakup of the sheets. It appears that a critical sheet thickness for breakup exists, which probably is determined by the growth of disturbances on the sheet surface. The growth of such interfacial disturbances depends on rheological parameters and process conditions [30,31], a phenomenon which is not yet fully understood. If the critical sheet thickness could be predicted, the phase dimensions would be known a priori. From our
Morphology development

results it appears that the critical thickness for sheet breakup is not dependent on the viscosity of the major component.

After sheet breakup the phase dimensions do not change significantly whether or not the blend is passed through a static mixer or just through neutral elements. The type of morphology obtained after breakup of the sheets depends on the stability of the fibrous structures formed after sheet breakup. At high values of the capillary number the threads are stable whereas at low values the threads break up into droplets. The lateral dimensions of the threads and droplets are approximately equal. The remarkable result is that the final dimensions obtained on blending are not dependent on the value of the capillary number, contrary to classical theories.

The phase dimensions of a co-continuous morphology are similar to the ones of a dispersion. By contrast, Fig.1.1c shows a rather coarse structure. This is misleading and the sketch of a co-continuous morphology in this Figure is probably drawn with the idea that these morphologies are formed after a coarsening process [32-34]. In this chapter it is shown that the sheets appeared to be the precursors of the co-continuous morphology and this morphology is not necessarily the result of a multiple coalescence process in a dispersion. After sheet breakup a network is formed which either breaks up leading to a dispersion or remains stable leading to a co-continuous morphology.

2.6 Conclusions

It is shown that a 'sheeting' mechanism occurs during the initial stage of mixing both in single screw extrusion and static mixing. This mechanism leads to a rapid decrease of the phase dimensions as shown both experimentally and theoretically. After the breakup of the sheets no further significant decrease of the phase dimensions is found.

The type of morphology depends on the stability of the fibres formed after the sheet breaks up. If the capillary number is higher than 1, then a fibre/matrix morphology is formed. If this capillary number is lower, breakup occurs and a droplet matrix morphology is formed. The phase sizes do not depend on the capillary number.

The sheets are shown to be the precursors of the co-continuous morphology. Depending on the stability of the network of ligaments in the mixer after sheet breakup the co-continuous morphology is either just an intermediate type of morphology or the final morphology.
2.7 References

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34. Heikens, D. and Barentsen, W., Polym., 18, 69 (1977)
3. CO-CONTINUOUS MORPHOLOGIES IN POLYMER BLENDS: a new model*

3.1 Introduction

In this chapter a new model is introduced which can predict the effect of the process conditions and polymer properties on the composition range within which co-continuous morphologies can exist. It was shown in chapter 2 that these morphologies are formed after breakup of sheets. This breakup leads to a network of ligaments surrounded by the other component, which is a mutually interpenetrating morphology, a so-called co-continuous morphology. These network ligaments should be stable during mixing, else the co-continuous morphology is just an intermediate type of morphology. The stability of these ligaments depends on several factors such as: the nature of the polymers (interfacial tension, viscosities and the ratio of these viscosities), their volume fraction and the processing conditions. Abundant literature exists concerning the effect of the factors mentioned above on the formation of dispersed morphologies (see chapter 1), but relatively little is known about the effect of these factors on the composition range within which co-continuity can be found [1-12]. Continuity of one phase within the other can occur at low volume fractions, depending on the shape of the dispersed particles [5]. In the case of spherical droplets continuity (percolation) of the minor phase is possible above 16 vol% droplets, whereas this percolation threshold value is much lower in the case of fibres. The percolation threshold value, however, is only the volume fraction limit for the onset of continuity of the minor phase. Not all the material of the minor phase belongs to the percolating structure then. At increasing volume fraction the proportion of the minor component incorporated in the percolating structure will increase until at a certain volume fraction all material of this component becomes part of the single percolating structure. In other words, by then a fully continuous phase of the minor component in the major phase is obtained, a fully co-continuous morphology. In this chapter only these fully co-continuous morphologies are considered.

Several relations have been reported giving the volume fraction at which co-continuity can be formed as a function of the viscosity ratio only [6-12]. These relations, however, give a volume fraction for phase inversion rather than a range of compositions at which co-continuity is possible. They do not take into account any requirements as to the shape of the dispersed component necessary

to obtain co-continuity. Especially at low volume fractions co-continuity can only exist if the minor blend component consists of structures with an extended shape. Only then this component is capable of forming a continuous network. This can be accomplished under appropriate blending conditions. For this reason it is to be expected that the formation of a co-continuous morphology will be strongly dependent on the processing conditions and the processing properties of the blend components. In this chapter a semi-empirical relation is derived giving the volume fraction limits for co-continuity as a function of matrix viscosity, interfacial tension and shear rate during blending. It is based on a simple picture of a co-continuous structure as a dense packing of randomly oriented rodlike particles of the minor phase and on the micro-rheological requirements for the stability of such rods. The model is shown to be in quantitative agreement with experimental results for blends of polystyrene in polyethylene of various viscosities, blended at various conditions.

3.2 Theory
3.2.1 Existing relations for co-continuity

Co-continuity occurs around the phase inversion point, where a dispersion of component 1 in a matrix of component 2 will change into a dispersion of component 2 in a matrix of component 1. In literature several empirical relations have been proposed to describe the point of phase inversion. The relation used most frequently was given by Paul [6], Jordhamo [7], and was later generalized by Miles [8]:

$$\frac{\phi_1}{\phi_2} = \frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})}$$

(3.1)

where $\eta_i(\dot{\gamma})$ is the viscosity of component i at blending conditions and $\phi_i$ is its volume fraction at which phase inversion occurs. Avgelopoulou [9] used the torque ratio instead of a viscosity ratio, thus including all stresses that act on the polymers during blending in a batch mixer, such as shearing and elongational stresses. Ho [10] also found a relation between volume fraction and torque ratio. Assuming the torque ratio and the viscosity ratio to be equal [9], Ho's [10] result can be written as:
\[
\frac{\phi_1}{\phi_2} = 1.22 \left( \frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})} \right)^{0.29}
\] (3.2)

This relation was found by a least square analysis of experimental data [10], explaining perhaps why inverting the designations, 1 and 2, does not give an identical result, as might be expected. Eqs. (3.1) and (3.2) are shown in Fig. 3.1.

![Graph](image)

**Figure 3.1:** Volume fraction at phase inversion of a binary blend as a function of the viscosity ratio, \( p \), according to the Eqs.(3.1) to (3.4).○, experimental results (A, B, C, D and E are described in this chapter; other points are described in chapter 4).

Several attempts were made to develop a theory which describes phase inversion in polymer blends. Metelkin [12] used the theory of Tomotika [13] for the instability of a liquid cylinder surrounded by another liquid. At the point of phase inversion the breakup time of a ligament of component 1 surrounded by a matrix of component 2 should equal the breakup time of a ligament of component 2 surrounded by a matrix of component 1. The result is [12]:
\[
\frac{\phi_1}{\phi_2} = \frac{\eta_1}{\eta_2} F\left(\frac{\eta_1}{\eta_2}\right)
\]

in which \(F(\eta_1/\eta_2) = 1 + 2.25\log(\eta_1/\eta_2) + 1.81[\log(\eta_1/\eta_2)]^2\).

Utracki [11] used a theory which describes the influence of dispersed particles on the viscosity of a liquid. Phase inversion is assumed to occur if the viscosity of a dispersion of component 1 in component 2 equals the viscosity of a dispersion of component 2 in component 1. The result is:

\[
\phi_2 = \frac{1}{2} \left( 1 - \frac{\log\left(\frac{\eta_1}{\eta_2}\right)}{[\eta]} \right)
\]

in which \([\eta]\) is a dimensionless intrinsic viscosity of the dispersed phase. A value of \([\eta] = 1.9\) was chosen in order to fit experimental results. The results of both theories are also shown in Fig. 3.1.

Eqs. (3.1) to (3.4) describe the phase inversion as a function of the viscosity ratio, \(p = \eta_1/\eta_2\). Given the experimental results found in literature [11] and our own results (the latter are shown in Fig. 3.1), it appears that the viscosity ratio alone is not sufficient to predict the phase inversion point in all circumstances. Apparently, other factors such as the interfacial tension, the absolute values of the viscosities rather than their ratio, the phase dimensions and the mixing conditions have an effect on the formation of co-continuous structures. These factors are not taken into account in Eqs. (3.1) to (3.4). Moreover, these relations just give a single composition for phase inversion, whereas experimentally a range of compositions is found for fully co-continuous structures. For these reasons a new model was developed, introducing the dependence of the formation of the co-continuous morphology on material properties and processing conditions via the consideration of the shape of the dispersed phase required for achieving co-continuity.

3.2.2 A simplified picture of full co-continuity

The relations described above do not take into consideration any requirements as to the shape of the dispersed phase. However, in order for the minor phase to become continuous inside the major
phase, certain requirements for its shape should be satisfied. Suppose that 10 vol% of component 1 in 90 vol% of component 2 gives a co-continuous morphology. This can never be achieved if the minor phase is present in the form of spherical droplets, because the randomly distributed droplets will not touch one another. Above 16 vol% droplets percolation will occur [5], but a fully continuous phase will be formed only when the maximum packing density of spheres is reached (=70 vol% spheres, depending on type of packing). In order to obtain a continuous phase at low volume fractions of component 1 (0-50 vol%), its particles must be elongated. In order to find the volume fraction, where a fully co-continuous morphology can exist, a practical approach is to consider the minor phase at this volume fraction as randomly oriented rodlike particles at their maximum packing density. At this density all the rods will touch, which is a prerequisite for full co-continuity. Representing co-continuous structures by a packing of rodlike particles is, admittedly, a gross simplification. In true co-continuous structures the rods have 'coalesced' at their cross-over points and they may have extremely non-circular cross-sections. However, this simple model captures the essential geometrical conditions for continuity of a minor phase. So, in our approach the dispersed minor phase will become fully continuous, as soon as the maximum packing density for its shape is reached.

The maximum packing density ($\phi_{max}$) of randomly oriented rods depends on the aspect ratio $L/B$, where $L$ is the length and $B$ is the diameter of the particle. The following empirical relation can be found in literature [14] for the maximum packing density of randomly oriented stiff rods:

$$\frac{1}{\phi_{max}} = 1.38 + 0.0376\left(\frac{L}{B}\right)^{1.4}$$  \hspace{1cm} (3.5)

For spheres (aspect ratio of 1) $\phi_{max}$ is 0.7. The maximum packing density will decrease when the aspect ratio increases: e.g. randomly oriented rods with an aspect ratio of 16 have a maximum packing density of only 0.31. The maximum packing density given by Eq. (3.5) is the minimum volume fraction of the minor component at which full co-continuity can exist for the given $L/B$. The upper bound for the composition range of full co-continuity is also given by Eq. (3.5), if it is applied to the other component. This consideration leads to a composition range for the existence of full co-continuity, as is found experimentally. This is in contrast to Eqs. (3.1) to (3.4), which only define
a phase inversion point.

With this model the volume fraction for the phase inversion point, or, more accurately, the lower limit for co-continuous morphologies, becomes a function of the parameter \(L/B\). It is not a function of the viscosity ratio, \(\rho\). It is illustrative, however, to present this volume fraction, \(\phi_{\text{max}}\), in a 3D-plot as a function of \(L/B\) and \(\rho\) in order to enable a comparison with Eqs. (3.1) to (3.4). Fig. 3.2 shows \(\phi_i\) as a function of the aspect ratio \(L/B\), derived from Eq. (3.5) with \(\phi_i = \phi_{\text{max}}\), and the viscosity ratio \((0.1 < \rho < 1)\). Although there is no dependency on \(\rho\), the Figure serves to illustrate that Eqs. (3.1) to (3.4) require different values of \(L/B\) at the phase inversion point. This can be shown by projecting the curves of Fig. 3.1 on the surface in Fig. 3.2. For example, at \(\rho=0.5\), Eq. (3.1) requires an aspect ratio for the elongated particles of at least 15, whereas Eq. (3.2) only requires a ratio of about 7.

![Figure 3.2: Volume fraction at phase inversion as a function of the viscosity ratio, \(\rho\), and the aspect ratio, \(L/B\), according to Eq. (3.9). The lines represent the projections of Eqs. (3.1) to (3.4) to illustrate that they require different values of \(L/B\).]
In the present approach the factor L/B follows from purely geometrical considerations. It results from the requirement, that particles of the minor phase should have an elongated shape in order to be continuous at low volume fractions. This shape should also be stable during processing. This stability is determined by the interfacial tension of the system, the phase dimensions, the values of the viscosities and the mixing conditions. In this way the factor L/B introduces the effects of all these factors on the limits of the composition region between which co-continuity can be found. Since Eqs. (3.1) to (3.4) and all other possible ones must obey the purely geometrical conditions for co-continuity, the effect of the above mentioned factors on L/B will also lead to finding the conditions for validity of these relations.

3.2.3 Conditions for the stability of elongated particles

During the mixing process the domains of each component are deformed by the applied flow field. The deformation results in elongated particles of the dispersed phase. It was shown above, that elongated particles are needed for the formation of a fully continuous phase below a volume fraction of 0.7. In this Section it is tried to establish the conditions for the stability of these particles.

Co-continuity is obtained when the aspect ratio of the deformed particles becomes such that their volume fraction, $\phi_d$, is equal to $\phi_{\text{max}}(L/B)$ given by Eq. (3.5). Whether such aspect ratios can exist, depends on the local capillary number, which is given by:

$$Ca = \frac{\eta_m \dot{\gamma} B}{2 \sigma}$$

(3.6)

with $\sigma$ the interfacial tension, $\eta_m$ the viscosity of the matrix phase and $\dot{\gamma}$ the shear rate.

We start by examining a domain of the minor component of equivalent sphere diameter $2R_0$ as it deforms into a long cylinder and changes its L/B in a given flow field. The diameter, B, of the cylinder is a function of the deformation, and, therefore, the aspect ratio (conservation of volume):
By using Eq. (3.7) the capillary number becomes:

\[
Ca = \frac{\left(\frac{2}{3}\right)^{\frac{1}{3}} \eta_m \dot{\gamma} R_0 \left(\frac{L}{B}\right)^{\frac{1}{3}}}{\sigma}
\]  

(3.8)

During the flow in the mixer at high values of Ca the shear stress overrules the interfacial stress and the particles are stretched. As L/B increases, Ca decreases. As was discussed in chapter 1 and 2 the mixing process can be divided into two regimes [15]:

1. Distributive mixing: Ca >> 1.

The drops are extended (affinely) into long slender threads which are stable. Consequently a co-continuous morphology can be generated over a wide range of compositions.

2. Dispersive mixing: Ca ≤ 1.

The elongating particles are not stable during flow. Co-continuous morphologies can exist only over a narrow range of compositions.

The discussion of the conditions for the formation of elongated structures has been limited so far to a single isolated particle. Neither multi-particle interactions nor the influence of coalescence have been accounted for, which must occur if a co-continuous structure is imagined to be formed from elongated droplets. By using the capillary number in the fashion described above, however, it is not implied that the mechanism of formation of the co-continuous morphology should be a deformation of droplets to threads which subsequently are closely packed and which locally coalesce. In reality the formation of co-continuous structures more likely proceeds by a sheet forming mechanism, which was already discussed in chapter 2. The condition Ca > 1 given above regards the possible stability of elongated structures, whatever their origin.

3.2.4 New relation for co-continuity

As stated above, a co-continuous morphology may be modeled by a dense packing of elongated particles. The lower limit of the volume fraction where a full co-continuous phase can be found is given as a function of the aspect ratio by Eq. (3.5). The condition for existence of such elongated particles is Ca>1, where Ca is given by Eq. (3.8). Although strictly speaking these two
Co-continuous morphologies, a new model

equations are relevant in different situations (dense packing versus isolated drops), by combining these equations for \( \text{Ca}=1 \) we obtain an approximate expression, giving the lower limit for co-continuity in terms of \( \sigma, \eta_m, \dot{\gamma}, \) and \( R_0 \):

\[
\frac{1}{\phi_{d,cc}} = 1.38 + 0.0213 \left( \frac{\eta_m \dot{\gamma}}{\sigma} R_0 \right)^{4.2}
\]  
(3.9)

In Fig. 3.3 the limit for co-continuity according to Eq. (3.9) is shown, demonstrating the strong dependence of \( \phi_{d,cc} \) on \( \eta_m, \dot{\gamma} / \sigma \) and on \( R_0 \), a size which is determined by the particulars of the blending process. From this Figure it appears that co-continuity is possible even at low volume fractions provided \( \eta_m \dot{\gamma} / \sigma \) or \( R_0 \) are high enough. As the typical phase dimensions in polymer blending are approximately \( 1 \text{ \mu m} \) (\( 2R_0=1 \text{ \mu m} \)), co-continuity will be possible at volume fractions below 0.5 provided \( \eta_m \dot{\gamma} / \sigma \) exceeds the value of \( 4.4 \times 10^6 \text{ m}^{-1} \) in order to get elongated particles (\( L/B > 8 \) in this case). This can be achieved by a proper choice of the polymers used (\( \eta_m \)) and the blending conditions (\( \dot{\gamma} \)). For example, for a blend with \( \sigma = 5 \text{ mN/m}, 2R_0=1 \text{ \mu m} \) and \( \dot{\gamma} = 20 \text{ s}^{-1} \) the viscosity of the matrix phase should exceed 1000 Pa.s for co-continuity possible below 50 vol%.

Eq. (3.9) does not include \( p \) as an independent variable, whereas Eqs. (3.1) to (3.4), used so far, show a dependency on \( p \) only. An apparent dependence of \( \phi_{d,cc} \) on \( p \) closely resembling Eq. (3.3) can be obtained only if the viscosity of the dispersed phase is kept constant and the viscosity of the matrix is varied. This is illustrated in Fig. 3.4 using values for \( \eta_m, \dot{\gamma}, \sigma \) and \( R_0 \) as experimentally found for the system PS/PE described in the next section. If the viscosity of the matrix is kept constant and the viscosity of the dispersed phase is varied, \( \phi_{d,cc} \) is independent of \( p \). This is illustrated too in Fig. 3.4. In fact, all sorts of apparent dependencies of \( \phi_{d,cc} \) on \( p \) can be obtained experimentally depending on the way \( \eta_m \) and \( \eta_d \) are varied in the experiments. This explains why some experimental results do not support any of Eqs. (3.1) to (3.4), while others do.

Eq. (3.9) gives the lower limit of the range of volume fractions within which a co-continuous structure can exist. The upper limit will be given by an analogous formula in which the two components of the blends have changed role. As stated previously in relation to Eq. (3.5) this consideration naturally leads to a composition range for existence of full co-continuity, as is found experimentally.
Figure 3.3: Composition at onset of co-continuity as a function of \( \left( \eta_m \frac{\dot{\gamma}}{\sigma} \right) \cdot R_o \) according to Eq. (3.9) and \( L/B \) according to Eq. (3.5).

Figure 3.4: Apparent dependence of the compositions at which co-continuity is possible on \( p \) according to Eq. (3.9); a. \( \eta_d = 900 \text{ Pa.s}; \eta_m = 900-9000 \text{ Pa.s} \) and b. \( \eta_m = 1800 \text{ Pa.s}; \eta_d = 180-1800 \text{ Pa.s} \); in both cases: \( \sigma = 4.5 \text{ mN/m}; \ \dot{\gamma} = 22 \text{ s}^{-1}; 2R_o = 0.7 \mu\text{m}. \)
3.3 Experimental

Two grades of polystyrene (PS) and two grades of low density polyethylene (PE) shown in Table 3.1, were used to prepare the blend series shown in Table 3.2. Nine different compositions (10 to 90 wt% PS in PE) were made by extrusion at 200°C and 250°C. The mixing equipment consisted of a 20 mm Collin laboratory extruder equipped with a transport screw, and a static mixer in series with the extruder containing 10 Ross ISG 15 mm diameter mixing elements. Each element contains 4 channels with a radius of 0.135 cm. The average shear rate in the channels was estimated to be 22 s⁻¹. The extruded strands were quenched in water.

A Rheometrics RMS-800, operating in the plate/plate configuration, was used to measure the rheological behaviour of the polymers. The measurements were carried out in the angular frequency range of 0.1-100 rad/s with a strain of 5%. The Cox-Merz rule appeared to be valid. The viscosities of the polymers at 22 s⁻¹ for temperatures of 200 and 250°C are given in Table 3.1.

### Table 3.1: Trade names and shear viscosities at $\dot{\gamma} = 22$ s⁻¹ of the polymers used.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Trade name (manufacturer)</th>
<th>Viscosity (Pa.s) at 200°C</th>
<th>Viscosity (Pa.s) at 250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>Hostyrene N2000 (Shell)</td>
<td>780</td>
<td>160</td>
</tr>
<tr>
<td>PS2</td>
<td>Styron 678E (DOW)</td>
<td>1440</td>
<td>380</td>
</tr>
<tr>
<td>PE1</td>
<td>Stamylan LD 2100TN00 (DSM)</td>
<td>1860</td>
<td>1210</td>
</tr>
<tr>
<td>PE2</td>
<td>Stamylan LD 2102TN26 (DSM)</td>
<td>960</td>
<td>540</td>
</tr>
</tbody>
</table>

The interfacial tension between PE and PS at 200°C is 4.5 mN/m, determined both experimentally [16] and theoretically [17]. The calculated value at 250°C is 3.5 mN/m [17].

Co-continuity in the blends was checked by extraction experiments. The strands were broken in liquid nitrogen and extraction of the PS phase was performed in a Soxhlet extraction apparatus with 2-butanol during 3 days. This was sufficient for complete removal of the soluble fraction. The samples were checked whether they were self supporting after extraction. Five pieces of the extruded strands were used to obtain an average value. In the case of co-continuity 100% of the PS phase can
be extracted. It was not possible to extract the LDPE phase without damaging the PS phase. For that reason the upper limit for the composition range of co-continuity could not be determined. In all reported experiments PE is the matrix phase. A scanning electron microscope (Philips XL 20) was used to study the phase dimensions after extraction. The droplet radii and ligament thicknesses given are the results of 50 to 100 measurements of the holes resulting from the extraction.

3.4 Results and discussion

The main experimental results obtained for the different blends are summarized in Table 3.2 together with the calculated compositions for the onset of full co-continuity according to Eq. (3.9) and the calculated phase inversion points according to Eqs. (3.1) and (3.2). The experimental results shown in this chapter demonstrate the influence of variations in viscosities on the composition for co-continuity, as will be discussed in detail below. Experimental results regarding the influences of the interfacial tension will be reported separately in chapter 4 of this thesis.

Table 3.2: Blends studied in this work, the viscosity ratio of the components, their expected inversion points (vol%) according to Eqs. (3.1) and (3.2), and the volume fractions for the lower limit of co-continuity according to Eq.(3.9) and measured experimentally.

<table>
<thead>
<tr>
<th>Series</th>
<th>Blend components</th>
<th>T (°C)</th>
<th>p</th>
<th>$\phi_1$ (vol %)</th>
<th>$\phi_1$ (vol %)</th>
<th>$\phi_{asc}$ (vol %)</th>
<th>$\phi_{v,PS}$ (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PS1,PE1</td>
<td>200</td>
<td>0.4</td>
<td>30</td>
<td>48</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>B</td>
<td>PS1,PE2</td>
<td>200</td>
<td>0.8</td>
<td>45</td>
<td>53</td>
<td>64</td>
<td>56</td>
</tr>
<tr>
<td>C</td>
<td>PS2,PE1</td>
<td>200</td>
<td>0.8</td>
<td>44</td>
<td>53</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>D</td>
<td>PS1,PE2</td>
<td>250</td>
<td>0.3</td>
<td>24</td>
<td>46</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>E</td>
<td>PS2,PE2</td>
<td>250</td>
<td>0.7</td>
<td>41</td>
<td>52</td>
<td>46</td>
<td>46</td>
</tr>
</tbody>
</table>
3.4.1 Constant viscosity of the dispersed phase

Increasing the matrix viscosity leads to more stable ligaments of the minor phase, and co-continuity is possible at lower volume fractions. It was shown in Fig. 3.4 that only then the composition, where co-continuity is possible, appears to depend on the viscosity ratio. This calculated trend was checked by comparing the blends of series A and B, made at 200°C. The matrix viscosity in series A is twice as high as in series B. If the phase dimensions are the same, then co-continuity in the blends of series A is expected at a lower volume fraction than in the blends of series B made under the same conditions, according to Eq. (3.9) and Fig. 3.3. SEM pictures of several compositions are shown in Fig. 3.5 and 3.6. As shown in Table 3.3 no significant difference of the phase dimensions is found between the blends of series A and B, despite the differences in viscosity ratio. Elongated structures are found from 27 vol% PS and higher in the blends of series A, whereas in the blends of series B a dispersion of droplets is found up to 46 vol% PS.

![Figure 3.5: Scanning Electron Micrographs of blends of series A; a, b, c and d contain 17, 27, 35 and 46 vol% PS, respectively.](image-url)
Table 3.3: Number average local diameter, B, and the standard deviation (in µm), of the PS phase measured in the blends.

<table>
<thead>
<tr>
<th>vol% PS</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.43 ± 0.17</td>
<td>0.52 ± 0.19</td>
<td>0.47 ± 0.24</td>
<td>0.57 ± 0.27</td>
<td>0.44 ± 0.16</td>
</tr>
<tr>
<td>17</td>
<td>0.49 ± 0.16</td>
<td>0.56 ± 0.22</td>
<td>0.51 ± 0.22</td>
<td>0.57 ± 0.25</td>
<td>0.43 ± 0.18</td>
</tr>
<tr>
<td>27</td>
<td>0.61 ± 0.33</td>
<td>0.64 ± 0.27</td>
<td>0.64 ± 0.30</td>
<td>0.68 ± 0.31</td>
<td>0.65 ± 0.22</td>
</tr>
<tr>
<td>35</td>
<td>0.84 ± 0.35</td>
<td>0.76 ± 0.35</td>
<td>0.61 ± 0.25</td>
<td>0.90 ± 0.54</td>
<td>0.71 ± 0.29</td>
</tr>
<tr>
<td>46</td>
<td>0.99 ± 0.39</td>
<td>0.84 ± 0.39</td>
<td>0.98 ± 0.40</td>
<td>1.50 ± 0.60</td>
<td>1.43 ± 0.6</td>
</tr>
</tbody>
</table>

Figure 3.6: Scanning Electron Micrographs of blends of series B; a, b, c and d as in Fig. 3.5.

The results of the extraction experiments are given in Table 3.4. The blends containing 80 and 90 wt% PS were not self-supporting after extraction and were not taken into consideration. Co-continuity was found at 27 vol% PS for series A (p=0.4) and at 56 vol% PS for series B (p=0.8).
Table 3.4: Percentage of PS extracted from the blends as a function of the volume fraction.

<table>
<thead>
<tr>
<th>vol% PS</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>22 ± 7</td>
<td>24 ± 1</td>
<td>25 ± 5</td>
<td>18 ± 1</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>17</td>
<td>86 ± 3</td>
<td>34 ± 4</td>
<td>72 ± 9</td>
<td>31 ± 4</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>27</td>
<td>99 ± 2</td>
<td>77 ± 2</td>
<td>100</td>
<td>60 ± 12</td>
<td>60 ± 10</td>
</tr>
<tr>
<td>35</td>
<td>100</td>
<td>94 ± 4</td>
<td>100</td>
<td>92 ± 2</td>
<td>86 ± 4</td>
</tr>
<tr>
<td>46</td>
<td>100</td>
<td>93 ± 2</td>
<td>100</td>
<td>99 ± 2</td>
<td>100</td>
</tr>
<tr>
<td>56</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>66</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3.5: Capillary number calculated from the local diameter of the PS phase in the blends as a function of the volume fraction.

<table>
<thead>
<tr>
<th>vol% PS</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2.0 ± 0.8</td>
<td>1.2 ± 0.4</td>
<td>2.1 ± 1.0</td>
<td>1.0 ± 0.5</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>17</td>
<td>2.2 ± 0.8</td>
<td>1.3 ± 0.5</td>
<td>2.3 ± 1.0</td>
<td>1.0 ± 0.5</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>27</td>
<td>2.8 ± 1.5</td>
<td>1.5 ± 0.7</td>
<td>2.9 ± 1.3</td>
<td>1.2 ± 0.6</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>35</td>
<td>3.8 ± 1.6</td>
<td>1.8 ± 0.9</td>
<td>2.8 ± 1.2</td>
<td>1.5 ± 0.9</td>
<td>1.2 ± 0.5</td>
</tr>
<tr>
<td>46</td>
<td>4.5 ± 1.7</td>
<td>2.0 ± 0.9</td>
<td>4.5 ± 1.9</td>
<td>2.5 ± 1.0</td>
<td>2.4 ± 1.0</td>
</tr>
</tbody>
</table>

The new model uses the value of the capillary number in the mixer to predict the type of morphology. The values of Ca based on the average size of the PS domains in the blend are given in Table 3.5. It is clear from this Table that the blends of series A have experienced distributive mixing at every composition (Ca>1). Co-continuous morphologies can be expected at all these compositions. In reality, co-continuity starts at 27 vol% PS. The capillary number in series B based on the average phase diameter is also larger than 1 in all blends. Extraction results show that co-continuity does not start until 56 vol% PS.

The results presented above demonstrate that the average diameter of the ligaments is not the
best measure of the phase dimensions to be used in the capillary number. In a real blend there is a
distribution of sizes (Fig. 3.5 and 3.6). The thinnest ligaments can experience dispersive mixing,
because their capillary number is much lower than the average value. They will break and destroy
the phase continuity. The stability of the morphology is determined by the existence of these thin
ligaments and not by the average size. So, it is the minimum diameter measured in the sample that
should be used in the capillary number to assess the conditions for full co-continuity.

Eq. (3.6) can also be used to calculate the minimum stable diameter by introducing the
condition $Ca=1$ and solving for $B$. For the blends of series A, a value of $B=0.22 \mu m$ is found. All
ligaments thinner than $0.22 \mu m$ will break up in the mixer and destroy the co-continuous
morphology. One can see from Table 3.3 that such thin ligaments hardly exist in the blends of series
A at 27 vol\% PS or more. Consequently, these blends are co-continuous. The minimum stable
ligament diameter for the blends of series B, on the other hand, is $0.44 \mu m$. In Table 3.3 we can see
that thinner ligaments are present in these blends up to 46 vol\% PS. Above this value these thin
ligaments are no longer present and co-continuity is possible. Co-continuity starts at 56 vol\% PS.

Although even the minimum capillary number is larger than 1, no co-continuity was found
at volume fractions lower than 27 vol\% for series A. SEM pictures show that no elongated structures
are found at these compositions (Fig.3.5). The measured phase dimensions at these compositions,
however, are not only ligament thicknesses, but also the diameters of the droplets formed by breakup
of the thinnest ligaments. These droplets have twice the diameter of the original ligament. This leads
to an apparently higher minimum capillary number in the blends

3.4.2 Constant viscosity of the matrix phase

The calculations for Fig. 3.4 showed that a constant matrix viscosity should give a constant
composition at which co-continuity is possible, independent of the viscosity of the dispersed phase.
In order to check this calculated trend the results of the blends of series A and C are compared. Co-
continuity in series A was found at 27 vol\% PS (Table 3.4). Table 3.3 indicates that no significant
difference of the phase dimensions is found between the series A and C, and the blends of series C
have experienced distributive mixing, too (Table 3.5). Co-continuity in series C should, therefore,
also be expected at 27 vol\% PS, something that is verified by the extraction results, given in Table
3.4. At this volume fraction elongated structures are found as shown in Fig. 3.7. These elongated structures and co-continuity, on the other hand, are not found in blends of series B, which have about the same viscosity ratio, but a lower matrix viscosity.

![Scanning Electron Micrographs](image)

**Figure 3.7:** Scanning Electron Micrographs of blends of series C; a, b, c and d as in Fig. 3.5.

The comparison of series A and C demonstrates that varying the viscosity of the dispersed phase does not affect the composition at which co-continuity is found, in agreement with Fig. 3.4. Lower matrix viscosities will shift co-continuity to higher volume fractions of the dispersed phase according to Fig. 3.3. This was investigated experimentally by making blends at 250°C with PE2 as the matrix. At this temperature the viscosity ratios of the components of series D and E are similar to the ones of the blends A and C, respectively, while the interfacial tension hardly changed. Fig. 3.8 shows the morphologies for series D at this temperature. No elongated structures were found, until the PS phase becomes continuous at 46 vol% PS. Images similar to the ones in Fig. 3.8 were obtained for series E. The phase dimensions are given in Table 3.3.
Figure 3.8: Scanning Electron Micrographs of blends of series D; a, b, c and d as in Figure 3.5.

No significant difference of the phase dimensions is found by increasing the temperature from 200 to 250°C, except for the 46 vol% PS blends (Table 3.3). The calculated capillary numbers are given in Table 3.5. At both viscosity ratios the blends D and E with less then 46 vol% PS have experienced dispersive mixing. The 46 vol% PS blends have experienced distributive mixing and co-continuous morphologies were indeed found at this composition for both blends (Table 3.4). The diameter of the thinnest stable ligament in these blends, calculated with Eq. (3.6), is $B = 0.59 \mu m$. Only at 46 vol% PS were thinner filaments absent. These results show that lower viscosities (250°C) at a constant viscosity ratio shift the co-continuity range to higher volume fractions. For example, at $\rho = 0.3-0.4$ the composition at which co-continuity is found shifts from 27 vol% PS (series A made at 200°C) to 46 vol% PS (series D made at 250°C), when the matrix viscosity is reduced by a factor of 3.5.
The volume fractions at which co-continuity was found experimentally are shown in Fig. 3.9 as a function of $\eta_m \dot{\gamma}/\sigma$ and $2R_o$. Co-continuity in the blends of series A, B and C can be described with Eq. (3.9) if $2R_o = 0.7 \mu m$. Co-continuity in the blends of series D and E can be described with Eq. (3.9) if $2R_o = 1.4 \mu m$. From the SEM pictures it can been seen that the minimum phase diameters in the blends of series D and E in the case of co-continuity were indeed twice as large as those in series A, B and C.

![Figure 3.9](https://example.com/figure39.png)

**Figure 3.9:** Comparison of the experimental results of series A, B and C ($2R_o = 0.7 \mu m$) and of series D and E ($2R_o = 1.4 \mu m$) with the curve that describes the composition at which co-continuity is possible as a function of $(\eta_m \dot{\gamma}/\sigma)\cdot R_o$ (Eq. (3.9)).

### 3.5 General Discussion

In the past, co-continuity has usually been associated with phase inversion. A number of relations have been proposed relating the composition for phase inversion to the viscosity ratio of the polymers. These relations obviously are insufficient to describe experimental results, as is illustrated in Fig. 3.1. Fully co-continuous structures may indeed be expected to occur at the composition where the matrix and the dispersed phase change role. However, this may well be the
case over a range of compositions (e.g. [5]). As co-continuity requires a certain well defined degree of distribution of the components of the blend, it is to be expected that the classical factors governing formation of dispersion, such as shear rate, viscosity and interfacial tension should determine the composition range for co-continuity.

Full co-continuity at low volume fractions of the dispersed component can exist only provided this component is dispersed in a network-like structure with ligaments of sufficiently large aspect ratio. The relation between composition and aspect ratio employed in this chapter stems from experimental results on systems which are only analogous to our systems but certainly different in geometrical detail. Clearly one can envisage a more sophisticated approach than the empirical result expressed by Eq. (3.5), for instance, a mathematical model based on a network theory using network strands of certain aspect ratios. However, the essential point that there is a dependency of the concentration for onset of full co-continuity on the aspect ratio of the ligaments is well expressed in Eq. (3.5).

In order to determine the possible stability of the extended structural elements we have used the classical approach of the local capillary number. This, again, is an approximation, since the condition expressed in the limiting capillary number holds only for isolated dispersed particles whereas the ligaments to which this condition is applied form a dense network. In the derivation of Eq. (3.9) we have not made any assumption regarding the mechanism of blending or the mechanism of formation of co-continuous structures. We have merely combined the geometrical conditions for existence of co-continuous structures with micro-rheological conditions for stability of the weakest parts of these structures, the ligaments.

This results in a relation (Eq. (3.9)) which has two essential properties, i.e.: -1- it relates the composition of existence of co-continuous structures to blending conditions and micro-rheological properties, and -2- it naturally leads to a range of compositions. Eq. (3.9) has neither the viscosity ratio nor the viscosity of the dispersed phase as an explicit variable. From the independence of $\phi_{acc}$ of $\eta_d$ one should, however, not conclude that the blending process itself is independent of $\eta_d$. Both viscosities, of course, play a role in the blending process, and $\eta_d$ seems to be a factor in determining the magnitude of $R_0$ via the process of sheet breakup, although for a given combination of polymers (e.g. PE/PS) $R_0$ does not appear to vary a great deal. The experimental results presented in this
chapter confirm that \( \phi_{acc} \) is largely independent of \( \eta_d \).

The factors \( \eta_{in} \), \( \dot{\gamma} \) and \( \sigma \) at the one hand, and \( R_b \) at the other, differ in as much that the former can be determined a priori whereas the latter has to be measured afterwards. Consequently, our model cannot be used in a predictive manner. A prediction of the phase dimensions, and in particular the minimum phase dimensions, requires detailed knowledge of the blending process. Several attempts have been made to predict the final particle size in blending processes, as was discussed in chapter 1 and 2, generally with limited success. For a reliable prediction of the phase dimensions a description of the morphology development in the mixing equipment is required. It was already shown in chapter 2 that in the early stages of polymer blending a quick morphology change occurs by a mechanism of sheet formation. A quantitative modeling of this 'sheeting' mechanism would enable a prediction of \( R_b \) and, consequently, of the critical volume fraction for full co-continuity.

3.6 Conclusion

Geometrical requirements have to be fulfilled for co-continuous structures to exist at low volume fractions of the minor component. An empirical expression originally derived for glass fibre filled systems can be used for describing the volume fraction for the onset of full co-continuity as a function of the aspect ratio. Combination of the geometrical requirements with micro-rheological conditions for stability of extended structures leads to a new relation describing the critical volume fraction of the minor phase as a function of the matrix viscosity, the interfacial tension, the shear rate and the phase dimensions. This relation implies a range of compositions within which fully co-continuous structures can exist. Experimental evidence for the system PE/PS shows that the model quantitatively predicts trends in the critical volume fraction as a function of the viscosities of the polymers. The critical volume fraction does not depend on the viscosity of the dispersed phase. A prediction a priori is not yet within reach, because the phase dimensions have to be measured afterwards.
3.7 References

4. CO-CONTINUOUS MORPHOLOGIES IN POLYMER BLENDS:

the influence of the interfacial tension

4.1 Introduction

In chapter 3 of this thesis a model is presented which gives a geometrical description of a co-continuous morphology. This leads to an equation, that describes the critical volume fraction of the minor phase for complete co-continuity as a function of the matrix viscosity, the interfacial tension, the shear rate and the phase dimensions rather than the viscosity ratio only. Experimental evidence is given in chapter 3 for the system PE/PS which shows that the new model quantitatively predicts trends in the critical volume fraction as a function of the viscosities of both phases.

In this chapter the effect of the interfacial tension on the composition range at which co-continuity is possible is examined. It is expected that the co-continuous morphology is more stable if the interfacial tension is low, which will result in a broad composition range at which co-continuity is possible. A high interfacial tension, however, is expected to give a small composition range at which co-continuity is possible. Results for the following blend systems: polyethylene/polystyrene, polyethylene/polyamide, polyethylene/polypropylene and polypropylene/polystyrene will be compared with the predictions by the model.

4.2 Co-continuous morphology: the influence of the interfacial tension

An equation was derived in chapter 3, that describes the critical volume fraction of the minor phase for complete co-continuity, \( \phi_{d,cc} \), as a function of the matrix viscosity, \( \eta_m \), the interfacial tension, \( \sigma \), the shear rate, \( \dot{\gamma} \), and the phase dimensions, \( R_0 \) as discussed in chapter 3 [1]:

\[
\frac{1}{\phi_{d,cc}} = 1.38 + 0.0213 \left( \frac{\eta_m \dot{\gamma}}{\sigma} R_0 \right)^{4.2}
\]  

(4.1)

Eq. (4.1) gives the lower limit of the range of volume fractions of the minor phase, where fully co-continuous morphologies are possible, for the specific polymer system and for the specific blending conditions. Fig. 3.9 shows the limit for co-continuity ($\phi_{\text{dec}}$) according to Eq. (4.1) as a function of ($\eta_\text{m} \dot{\gamma} /\sigma$) and $R_0$, a size which is determined by the particulars of the blending process. Eq. (4.1) gives the lower limit of the region of existence of a co-continuous structure. The upper limit will be given by an analogous formula in which the two components of the blends have changed role.

From Fig. 3.9 and Eq. (4.1) it can be seen that the volume fraction at which co-continuity is possible, decreases as the matrix viscosity ($\eta_\text{m}$) increases, and co-continuity becomes possible over a wider range of compositions for the same phase size. This was verified experimentally in chapter 3. The value of $R_0$ and the resulting diameter B calculated from Eq. (3.7) appeared to correspond to the minimum phase dimensions found in the blends during mixing. It is expected that the interfacial tension also influences the composition at which co-continuity is possible.

The influence of the interfacial tension on composition range, however, is twofold. Firstly, the interfacial tension is a deciding factor in determining the stability of the ligaments of the co-continuous structures. Since the interfacial tension is a variable in Eq. (4.1), it is to be expected that the interfacial tension has a similar, but opposite, effect as the matrix viscosity. Secondly, the interfacial tension has an indirect effect on $\phi_{\text{dec}}$ via its influence on the magnitude of $R_0$. It is to be expected that the effect of increasing the interfacial tension will be an increase in the phase dimensions, counteracting the direct effect of the interfacial tension on $\phi_{\text{dec}}$. This indirect effect can, as yet, not be quantified. It can be accounted for in Eq. (4.1) by measuring the phase dimensions separately afterwards. The direct effect is stronger than the indirect effect as will be shown below.

4.3 Experimental

4.3.1 Blends and blend components

The polymers that were used to form the experimental blends are shown in Table 4.1. Six series of blends (I, II, III, IV, V and VI as shown in Table 4.2) were made, each consisting of five blends with volume fractions of about 10 to 50 vol% of the minor component.
Table 4.1: Trade names and shear viscosities, $\eta$, at $\dot{\gamma} = 22$ and 30 s$^{-1}$ of the polymers.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Trade name (manufacturer)</th>
<th>$\eta$ (Pa.s) at 200°C and 22 s$^{-1}$</th>
<th>$\eta$ (Pa.s) at 200°C and 30 s$^{-1}$</th>
<th>$\eta$ (Pa.s) at 250°C and 22 s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>Hostyrene N2000 (Shell)</td>
<td>780</td>
<td>650</td>
<td>160</td>
</tr>
<tr>
<td>PS2</td>
<td>Hostyrene N7000 (Shell)</td>
<td>2690</td>
<td>-</td>
<td>1154</td>
</tr>
<tr>
<td>PS3</td>
<td>Styron 678E (DOW)</td>
<td>-</td>
<td>1115</td>
<td>-</td>
</tr>
<tr>
<td>PE1</td>
<td>Stamylan LD 2100TN00 (DSM)</td>
<td>1860</td>
<td>-</td>
<td>1210</td>
</tr>
<tr>
<td>PE2</td>
<td>Stamylan LD 2102TN26 (DSM)</td>
<td>960</td>
<td>-</td>
<td>540</td>
</tr>
<tr>
<td>PA6</td>
<td>Akulon K 136 (DSM)</td>
<td>-</td>
<td>-</td>
<td>1500</td>
</tr>
<tr>
<td>PP1</td>
<td>Stamylan PP 19MN10 (DSM)</td>
<td>520</td>
<td>450</td>
<td>-</td>
</tr>
<tr>
<td>PP2</td>
<td>Stamylan PP 13E10 (DSM)</td>
<td>-</td>
<td>1690</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2: Blend components, processing temperature, interfacial tension, viscosity ratio, matrix viscosity of the prepared blends, the shear rate and the lower limits of co-continuity measured experimentally.

<table>
<thead>
<tr>
<th>Series</th>
<th>Blend components</th>
<th>Temperature (°C)</th>
<th>$\sigma$ (mN/m)</th>
<th>viscosity ratio</th>
<th>$\eta_m$ (Pa.s)</th>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>$\phi_{d,cc}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>PS1 in PE1</td>
<td>200</td>
<td>4.5*</td>
<td>0.4</td>
<td>1860</td>
<td>22</td>
<td>27</td>
</tr>
<tr>
<td>II</td>
<td>PE2 in PA6</td>
<td>250</td>
<td>10.7*</td>
<td>0.4</td>
<td>1500</td>
<td>22</td>
<td>56</td>
</tr>
<tr>
<td>III</td>
<td>PS2 in PE2</td>
<td>250</td>
<td>3.5*</td>
<td>2.1</td>
<td>540</td>
<td>22</td>
<td>46</td>
</tr>
<tr>
<td>IV</td>
<td>PE1 in PP1</td>
<td>200</td>
<td>0.8*</td>
<td>2.1</td>
<td>445</td>
<td>22</td>
<td>28</td>
</tr>
<tr>
<td>V</td>
<td>PS1 in PP2</td>
<td>200</td>
<td>5°</td>
<td>0.4</td>
<td>1690</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>VI</td>
<td>PS3 in PP1</td>
<td>200</td>
<td>2.9**</td>
<td>2.5</td>
<td>445</td>
<td>30</td>
<td>34</td>
</tr>
</tbody>
</table>

* from ref. [2]; + from ref. [3]; o from ref. [4]; ** from Appendix to this chapter
A Rheometrics RMS-800, operating in the plate/plate configuration, was used to measure the rheological behaviour of the polymers. The measurements were carried out in the angular frequency range of 0.1-100 rad/s with a strain of 5%. The Cox-Merz rule appeared to be valid. The viscosities at a shear rate of 22 and 30 s\(^{-1}\) and at temperatures of 200 and 250°C (the conditions inside the mixer) are also shown in Table 4.1.

4.3.2 Processing

The mixing equipment consisted of a 20 mm Collin laboratory extruder equipped with a transport screw (D=20 mm, L/D=20), and a static mixer in series with the extruder containing 10 Ross ISG 15 mm diameter mixing elements. Each element contained 4 channels with a radius of 1.35 mm. The average shear rate in the channels was estimated to be 22 s\(^{-1}\) (series I-IV) or 30 s\(^{-1}\) (series V and VI). The extruded strands were quenched in water. PA6 was dried before mixing during 7 days in a vacuum oven at 80°C.

4.3.3 Characterizing

Co-continuity in the blends was checked by extraction experiments [5]. The strands were broken in liquid nitrogen and extraction of the PS (in PS/PE and PS/PP blends) or PE (in PE/PP and PE/PA6 blends) was performed in a Soxhlet extraction apparatus with 2-butanol (PS) or iso-octane (PE) during 3 days. This was sufficient for the complete removal of the soluble fraction. Five pieces of the extruded strands were used to obtain an average value. The samples were checked whether they were self supporting after extraction. In the case of co-continuity, 100% of the PS phase (in PS/PE and PS/PP) or the PE phase (in PE/PP or PE/PA6) could be extracted. It was not possible to extract the PE phase from the PE/PS blends, the PP phase from the PE/PP and PS/PP blends or the PA6 phase from the PA6/PE blends without damaging the remaining phase. For that reason the upper limit for the composition range of co-continuity could not be determined. A scanning electron microscope (Philips XL 20) was used to study the phase dimensions after extraction. The reported droplet radii and filament thicknesses are the number averages of 50 to 100 measurements of the holes resulting from the extraction.
4.4 Results and discussion

The main experimental results for the different series are summarized in Table 4.2. The effect of the interfacial tension on the composition range at which full co-continuity is possible can not directly be distinguished from Table 4.2, e.g. the blends of series I and IV differ in their value of the interfacial tension but co-continuity in both series is possible at 27-28 vol% of the minor phase. In order to exclude the effect of other parameters, such as the matrix viscosity and shear rate, which also determine the composition range at which co-continuity is possible, the results are presented below so that series I and II are compared in which the matrix viscosity is high and series III and IV are compared in which the matrix viscosity is low. By comparing the results in such a way the influence of variation of the interfacial tension on the lower bound at which co-continuity starts can properly be distinguished. It can then be seen that a high interfacial tension will lead to a small composition range, whereas a low interfacial tension will lead to a broad range where co-continuity is possible as will be discussed in detail below.

The blends of series V can be compared with those of series I (comparable viscosity, viscosity ratio, shear stress and interfacial tension) leading in both series to a comparable volume fraction at which co-continuity is possible. The blends of series VI should be compared with series III (comparable viscosity, viscosity ratio, shear stress and interfacial tension), however, different results were obtained. For that reason, the blends of series I to IV and the blends of series V and VI are discussed separately.

4.4.1 A high matrix viscosity

Series I and II are compared here. They both have a matrix with a relative high viscosity, but they differ in their values of the interfacial tension. Both from the SEM pictures (Fig. 4.1) and from the extraction measurements (Fig. 4.2), it can be seen that the blends of series I show a wide co-continuous range starting at 27 vol% of PS, whereas blends of series II show a narrow co-continuous range starting at 54 vol% PE.
Table 4.3: Number average local diameter, B, of the dispersed phase and the % dispersed phase extracted and the minimum capillary number in the blends of series I and II.

<table>
<thead>
<tr>
<th></th>
<th>Series I</th>
<th></th>
<th></th>
<th>Series II</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(PS/PE)</td>
<td></td>
<td></td>
<td>(PE/PA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vol%</td>
<td></td>
<td></td>
<td></td>
<td>vol%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td>PE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>% PS extracted</td>
<td></td>
<td>B</td>
<td>% PE extracted</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(µm)</td>
<td></td>
<td></td>
<td>(µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.43 ± 0.17</td>
<td>22</td>
<td>1.2</td>
<td>11</td>
<td>1.41 ± 1.01</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>0.49 ± 0.16</td>
<td>86</td>
<td>1.5</td>
<td>23</td>
<td>1.59 ± 1.31</td>
<td>3</td>
</tr>
<tr>
<td>27</td>
<td>0.61 ± 0.33</td>
<td>100</td>
<td>1.3</td>
<td>33</td>
<td>1.88 ± 1.28</td>
<td>24</td>
</tr>
<tr>
<td>35</td>
<td>0.84 ± 0.35</td>
<td>100</td>
<td>2.2</td>
<td>44</td>
<td>2.21 ± 1.32</td>
<td>75</td>
</tr>
<tr>
<td>46</td>
<td>0.99 ± 0.39</td>
<td>100</td>
<td>2.7</td>
<td>54</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt; 1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.1: Scanning Electron Micrographs of blends of: (a) Series I with 35 vol% PS in PE and (b) Series II with 33 vol% PE in PA6.

The results of series I can be described with Eq.(4.1) by using \(2R_0=0.7 \text{ µm}\) as shown in Fig. 4.3. The parameter \(R_0\) seems to be a fit parameter, but from this value the filament thickness of the PS phase, B, can be calculated which is still stable in case of co-continuity. Solving Eq.(3.5) for \(\phi=0.27\) and putting the result in Eq. (3.7) with \(2R_0=0.7\)µm gives \(B=0.23\)µm. This value appears to correspond to the minimum phase dimensions in the blend of 27 vol% PS in PE, which is 0.28 µm (calculated from Table 4.3).
Figure 4.2: %PS (○) and PE (□) extracted from the blends of series I and II, respectively, as a function of the blend composition.

Blends of series II have an interfacial tension which is at least twice as high as that of series I. An increased value for the interfacial tension (all other parameters remaining the same) has two effects. First, it is expected to increase the phase dimensions of the minor component for the same conditions in the mixer. Second, it decreases the value of the capillary number, reducing the region of distributive mixing and thus reducing the range of co-continuity. These counteracting effects on the composition at which co-continuity is possible (Eq.(4.1)) are both evident in the comparison of series I and II. Comparing the SEM pictures, shown in Fig. 4.1, it can be seen that the blends of series II do not contain elongated structures in contrast to the blends of series I. The minimum phase dimensions in series II are approximately twice as high as the ones in blends of series I (Table 4.3). By introducing \(2R_s = 1.4 \ \mu m\), which is twice the value of \(2R_s\) in series I, in Eq. (4.1) co-continuity is expected only above 50 vol\% PE in PA6. The calculated capillary numbers based on the minimum phase diameters found by SEM analysis indicate that the blends of series II experienced dispersive mixing and co-continuity is not expected up to 44 vol\% PE. The results of the extraction experiments in Fig.4.2 show that co-continuity starts at 54 vol\% PE in PA6, which is indeed above 50 vol\% PE as was expected, instead of the 27 vol\% minor phase as in series I.
In Fig. 4.3 a comparison of the experimental results with calculations using Equation (4.1) are shown (□, ○). The parameter $R_0$ (which is proportional to the minimum phase dimensions found in the two systems), differs by a factor of 2. The SEM pictures of the blends indeed show a coarser structure in the PE/PA6 blends. It is obvious that a high interfacial tension is not favourable for co-continuity at low volume fractions and although only the lower limit for co-continuity is determined it is to be expected that the same holds for the upper limit.

Figure 4.3: Composition for onset of full co-continuity as a function of $\eta_m \frac{\gamma}{\sigma}$ and $R_0$ according to Equation (4.1) Experimental results of series I (○, $2R_0=0.7$ μm), series III (□, $2R_0=1.4$ μm), series III (■, $2R_0=1.4$ μm), series IV (+, $2R_0=0.3$ μm), series V (●, $2R_0=0.7$ μm) and series VI (▼, $2R_0=1.4$ μm).

In addition the different composition at which co-continuity is possible some illustrative differences between the blends of series I and II appear from the extraction experiments. First, the amount of extracted PE from the blends of series II is much lower than the amount of extracted PS from series I at the same composition, except in the case of full co-continuity. Second, at compositions below the percolation threshold for droplets still 22% of the minor component can be extracted from the PE/PS blends whereas non of the minor component can be
extracted from the PE/PA6 blends. Lyngaae-Jørgensen and Utracki [5] indicated that, above 16 vol% spherical droplets, percolation of these droplets will occur and some of them can be extracted, whereas, below this volume fraction, extraction of the dispersed phase is not possible. Our results shown in Fig.4.2 illustrate that at these compositions a droplet/matrix structure is formed in the PE/PA6 blend (11 vol% PE in PA6) whereas a part of the minor phase in the PE/PS blend (9 vol% PS in PE) has an elongated shape.

4.4.2 A low matrix viscosity

Series III and IV are compared here. Both series have a low matrix viscosity, but they differ in their value of the interfacial tension. As a result of the low matrix viscosity, the blends of series III show co-continuity only above 46 vol% PS. This is found both from the extraction measurements (Table 4.4) and from the SEM pictures (e.g. Fig. 4.4a). From the minimum capillary number it appears that all the blends of series III with less than 46 vol% PS have experienced dispersive mixing, which results in a droplet/matrix morphology (Fig.4.4a). The 46 vol% PS blend has experienced distributive mixing and a co-continuous morphology is indeed found at this composition.

Table 4.4: Number average local diameter, B, of the dispersed phase, percentage dispersed phase extracted and minimum capillary number in the blends of series III and IV.

<table>
<thead>
<tr>
<th>Series III</th>
<th>(PS1/PE)</th>
<th></th>
<th>Series IV</th>
<th>(PE/PP1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol% PS</td>
<td>B (µm)</td>
<td>%PS extracted</td>
<td>Cₐₘᵢₙ</td>
<td>vol% PE</td>
</tr>
<tr>
<td>9</td>
<td>0.51 ± 0.21</td>
<td>16</td>
<td>0.5</td>
<td>9</td>
</tr>
<tr>
<td>17</td>
<td>0.63 ± 0.27</td>
<td>16</td>
<td>0.6</td>
<td>18</td>
</tr>
<tr>
<td>27</td>
<td>0.59 ± 0.22</td>
<td>62</td>
<td>0.6</td>
<td>28</td>
</tr>
<tr>
<td>35</td>
<td>0.80 ± 0.36</td>
<td>86</td>
<td>0.7</td>
<td>37</td>
</tr>
<tr>
<td>46</td>
<td>1.48 ± 0.67</td>
<td>100</td>
<td>1.4</td>
<td>47</td>
</tr>
</tbody>
</table>
Figure 4.4: Scanning Electron Micrographs of blends of: (a) Series III with 35 vol% PS in PE and (b) Series IV with 37 vol% PE in PP.

A lower value of the interfacial tension in series IV (1/4 of the value in series III) is expected to decrease the phase dimensions and to increase the value of the capillary number, leading to a broader region of compositions at which co-continuity is possible. Both effects are evident when series III and IV are compared. In Fig. 4.4a it can be seen that the blends of series III do not contain elongated structures in contrast to the blends of series IV as shown in Fig. 4.4b. The minimum phase dimensions found in series IV in case of co-continuity are smaller than those found in series III, see Table 4.4. The calculated minimum capillary numbers are also shown in Table 4.4. The blends of series III experienced dispersive mixing up to 46 vol% PS, whereas series IV experienced distributive mixing in the whole composition range. Thus, co-continuity in series IV is expected to begin at a volume fraction less than 46 vol% PE. From the extraction experiments, shown in Table 4.4, it appears that co-continuity in series IV starts at 28 vol% PE. This verifies the trend that a low interfacial tension will result in blends with co-continuity in a broad composition range.

Although the minimum capillary number is larger than 1, no co-continuity is found at volume fractions lower than 28 vol% PE in PP. Droplets formed by breakup of the thinnest filaments during mixing have twice the diameter of the original filament. This leads to an apparently higher minimum capillary number as was already discussed above. Calculations using Eq. (4.1) are shown in Figure 4.4. The blends of series III are described with a value of $2R_0=1.4\mu m$, while series IV are described using a value of $2R_0=0.5\mu m(\blacksquare, \oplus)$.
4.4.3 PP/PS blends

Series V and VI are discussed here. Both blends contain PP and PS and it should be expected that these blends are comparable with PE/PS blends with equal viscosities and under more or less equal process conditions, because the interfacial tension of PP/PS and PE/PS is approximately 5 mN/m. This is indeed the case for blends of series V which can be compared with the PE/PS1 blends of series I. Co-continuity starts around 25 vol% PS1 in PP2 as shown in Table 4.5. The comparison of the PP1/PS3 blends of series VI with the PE/PS blends of series III show a divergent behaviour. Despite of a low matrix viscosity co-continuity starts already at 34 vol% PS in series VI as shown in Table 4.5, whereas co-continuity starts at 46 vol% PS in series III. This deviation, however, does not indicate a failure of the model, but is the result of the lower value of the interfacial tension of the PP1/PS3 system (lower than the expected value of 5 mN/m) due to the low molecular weight of PP1. This is discussed in the Appendix.

Table 4.5: Number average local diameter, B, of the dispersed phase, percentage dispersed phase extracted and minimum capillary number in the blends of series V and VI. Corrected values for \( C_{a_{min}} \) in blends of series VI are given.

<table>
<thead>
<tr>
<th>Series V</th>
<th>PS1/PP2</th>
<th>Series VI</th>
<th>PS3/PP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol% PS</td>
<td>B (μm)</td>
<td>%PS extracted</td>
<td>( C_{a_{min}} )*</td>
</tr>
<tr>
<td>8</td>
<td>0.48 ± 0.16</td>
<td>45</td>
<td>1.6</td>
</tr>
<tr>
<td>16</td>
<td>0.55 ± 0.23</td>
<td>66</td>
<td>1.7</td>
</tr>
<tr>
<td>25</td>
<td>0.51 ± 0.18</td>
<td>100</td>
<td>1.7</td>
</tr>
<tr>
<td>34</td>
<td>0.56 ± 0.17</td>
<td>100</td>
<td>2.0</td>
</tr>
<tr>
<td>44</td>
<td>1.53 ± 0.18</td>
<td>100</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* \( \sigma = 5 \text{ mN/m}; + \sigma = 2.9 \text{ mN/m} \)

By taking this lower value of the interfacial tension into account it appears that the minimum capillary numbers exceed the value of 1 leading to a co-continuous morphology at around \( \Phi_{ps} = 0.34 \) as shown in Table 4.5. The SEM pictures of the PP2/PS1 blends are compara-
ble to those of series I. The SEM picture of the PP1/PS3 are somewhat different. Fig 4.5a clearly shows a co-continuous morphology, whereas Fig 4.5b shows a structure with some elongated structures. The extraction experiments in Table 4.5, however, indicated that this structure in the blend of 34% PS3 in PP1 is co-continuous.

The minimum phase dimensions of the blends of series V and VI in the case of co-continuity are comparable to the ones of series I and III and the results of series V and VI can be described with $2R_0 = 0.7$ and 1.4 $\mu$m, respectively, as shown in Fig. 4.3.

![Figure 4.5: Scanning Electron Micrographs of blends of: (a) Series V with 34 vol% PS in PP and (b) Series VI with 34 vol% PS in PP.](image)

4.5 General discussion

The experiments described in this chapter demonstrate the pronounced effect of the interfacial tension on the composition range at which full co-continuity is possible. This effect is to be expected because full co-continuity can exist only if the two blend components are distributed in a well-defined way, which is determined by the parameters governing formation of dispersions: shear rate, viscosity and interfacial tension. Obviously, the classical relations for phase inversion, summarized in chapter 3, in which the viscosity ratio is the only parameter cannot account for this effect. This effect is, however, predicted correctly by the model described in chapter 3 and as can be seen in Fig. 4.3.

The interfacial tension plays a twofold role in this model. First, it determines the stability of the extended structures required for obtaining full co-continuity, together with the matrix
viscosity and shear rate. It enters directly into the model via the capillary number: an increasing value of $\sigma$ will decrease the value of $\phi_{d\infty}$ in Eq. (4.1) if other parameters are kept constant. Second, $\sigma$ is one of the parameters that determine the phase dimensions. These phase dimensions are determined by the particular blending process. At present they cannot be predicted a priori [6,7]. There is growing evidence that blend morphologies are usually generated via the mechanism of sheet formation, as discussed in chapter 2. The final phase dimensions appear to be determined by the process of sheet breakup.

The effects of the phase dimensions and interfacial tension on $\phi_{d\infty}$ are counteracting and can even cancel each other. From the results presented in this chapter it appears that the direct effect of the interfacial tension on the limits of the range of co-continuity is stronger than its indirect effect via the phase size. Consequently, a lower interfacial tension leads to a broader range of co-continuity despite the smaller phase dimensions. If these dimensions could be kept constant, the effect would be even more pronounced. A high interfacial tension leads to a narrow region where full co-continuity is possible. This does not mean, however, that co-continuity in these cases is never possible at lower volume fractions. If one generates larger phase dimensions than those produced in our mixer, then co-continuity will be possible at lower volume fractions. The model is able to describe the influence of the matrix viscosity and the interfacial tension on the range of co-continuity, although a prediction of the morphology under any mixing conditions is not yet within reach because no reliable method exists up to now for predicting the phase dimensions during the mixing process.

4.6 Conclusion

The composition range for full co-continuity is dependent on the interfacial tension. Increasing the interfacial tension shifts the limiting composition for onset of co-continuity to higher concentrations, narrowing the composition range.

The interfacial tension influences the stability of the co-continuous morphology as well as the phase dimensions. The latter effect appears to be smaller than the former.

The experimental results can quantitatively be predicted by the model described in chapter 3 provided the phase dimensions are measured separately.
4.7 Appendix to Chapter 4

The interfacial tension: general

The interfacial tension ($\sigma_{AB}$) of a polymer pair A and B is determined by the increase of the free energy due to the formation of an interface. Two contributions can be distinguished: the increase of energy due to the interaction at the interface and the decrease of the entropy due to the turning back of the chains at the interface, e.g. [9]. Most calculated values for the interfacial tension poorly agree with the ones obtained experimentally [10]. The influence of the molecular weight is often neglected, i.e. the theories are only valid for polymers with infinite molecular weight. Normally the interfacial tension decreases with decreasing molecular weight as a result of a smaller loss of entropy due to the shorter chains at the interface [11]. Kamal et al. [12] found a strong influence of $M_o$ of PS on $\sigma_{PP/PS}$ at a $M_{nPS}$ lower than $\pm$ 70,000. According to various experimental data published in literature [3] the interfacial tension of polymer pairs decreases linearly with increasing temperature. The temperature coefficient is of the order $10^{-2}$ mN/mK. If these effects of the molecular weigh and temperature are neglected then the experimental values for the interfacial tension may differ considerably from the theoretical ones.

The differences between theoretical and experimental values show that the interfacial tension of polymer blends depends on the molecular weight of the components. This can be a problem if one of the components starts to degrade leading to smaller molecules, which is indeed found in the case of PP [8,13]. This degradation of PP will result in a strong decrease of the interfacial tension [8], which is indeed found in literature [12,14,15].

Interfacial tension PP/PS blends

It was shown in this chapter that the results of the PP/PS blends could not be described as straightforward as the results of the PE/PS, PE/PP and PE/PA6 blends using theoretical values of the interfacial tension, and it appeared that the determination of the interfacial tension was necessary. Several methods can be used [16-20]. We used the spinning drop method, which is described elsewhere [18]. In this method the interfacial tension was calculated with the following relationship [18]:

$$\sigma = \frac{\omega^2 d^3 \Delta \rho}{32}$$
where $\omega$ is the rotational speed in rad/s, $d$ is the diameter of the cylindrical PP droplet and $\Delta \rho$ the density difference between PP and PS which is approximately 200 kg/m$^3$. A slice of PP (thickness $\pm$ 0.1 mm), which was first cleaned with alcohol, was placed between two PS cylinders (diameter $\pm$ 5 mm). A glass tube, which contains the PP slice and the PS cylinders, was rotated at 13000 RPM at a temperature of 200°C and the slice of PP will deform into a droplet in the PS matrix. The dimensions of the droplet were measured with an optical Jenapol-microscope.

The molecular weight and its distribution (MWD) of PP1 and PP2 were determined by GPC analysis. The analysis was done on a standard high temperature GPC column at 140°C. PP2 was first dissolved in 1,2,4 trichlorobenzene at 170°C.

**Table 4.6:** Interfacial tension of PP2/PS1 and PP1/PS3 at 200°C.

<table>
<thead>
<tr>
<th>Polymer pair</th>
<th>$\sigma_{PP/PS}$ at 200°C (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP2/PS1</td>
<td>4.9</td>
</tr>
<tr>
<td>PP1/PS3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The results of the spinning drop experiments for the two PP/PS-systems are presented in Table 4.6. A remarkable difference between the interfacial tension of both PP/PS-systems is found at 200°C. An interfacial tension of 4.9 mN/m for PP2/PS1 is more or less expected for PP/PS [4]. A value of 2.9 mN/m for the pair PP1/PS3, however, is rather low. This may be the result of the low molecular weight of PP1 compared to the one of PP2. Theoretically, the interfacial tension should decrease with decreasing molecular weight. Kamal et al. [15] found a strong influence of $M_n$ of PS on $\sigma_{PP/PS}$ at a $M_{b,PS}$ lower than ± 70,000. If we compare this with PP1 with a $M_n$ of 64,900, it is to be expected that PP1 will give a lower interfacial tension than PP2 with a $M_n$ of 87,900. This was indeed measured.

The results of the PP/PS blends showed that a theoretical value for the interfacial tension can lead to a wrong interpretation of the results. Due to a lower molecular weight of one of the components the interfacial tension is lower than the theoretical value.
4.8 References

5. STABILITY OF THE POLYMER BLEND MORPHOLOGY:
   the role of the initial morphology*

5.1 Introduction

Mixing of polymers leads to blends with a heterogeneous morphology due to the immiscibility of these polymers. These morphologies are non-equilibrium structures that are generated during the mixing process. As such, they are unstable and they start changing as soon as the liquid blend comes out of the mixer. A desired morphology in a blend stays unchanged only if frozen in rapidly. During further processing (e.g. injection or compression molding) the blend has to be melted and the frozen-in morphology starts changing again. A coarsening of the phase dimensions and a change of the type of morphology may occur simultaneously. The interfacial tension driven changes in morphology can occur via different mechanisms, viz. coalescence, breakup, retraction and end pinching. Which of these mechanisms will be operative depends on the initial morphology in the blend.

Coarsening of the morphology during annealing is often described in terms of coalescence only (e.g. [1-3]). In droplet/matrix structures coalescence is indeed the only possible mechanism, whereas in fibrillar or co-continuous morphologies the other mechanisms may contribute. These mechanisms have different effects on the coarsening process both in terms of the extent and the rate of change of the phase dimensions as will be discussed in this chapter. If these other mechanisms are neglected, coalescence is often incorrectly considered to be the only mechanism causing the coarsening. Experimental evidence will be presented in this chapter demonstrating the dependence of the rate and the extent of coarsening in polymer blends on their initial morphology [4].

Furthermore, coarsening goes together with a change of morphology, e.g. a fibrillar morphology in a blend may change into a droplet/matrix morphology. Consequently, this change of morphology will also lead to a change of the blend properties. It is to be expected that a similar change of morphology occurs in blends with a co-continuous morphology. However, the co-

continuous morphology appears to be stable above a critical volume fraction of the minor phase [5-7]. Verhoogt [6] found that the co-continuous morphology in blends of 20% SEBS (a styrene-ethylene/butylene block copolymer) in PEE (a polyether-ester) broke up upon annealing leading to a dispersion whereas such a morphology in blends with 30 and 50% SEBS in PEE did not break up and the co-continuous morphology was preserved. The phase dimensions, however, increased. Similar results were found by Quintens [7] in blends of PC (polycarbonate) and SAN (styrene-acrylonitrile). A transition from a co-continuous structure to a dispersed phase structure occurred in the 70/30 PC/SAN blend with increasing annealing time. Coarsening of the phase dimensions in the 60/40 PC/SAN blends was found, whereas the co-continuous morphology was preserved. In this chapter a theoretical consideration is presented which predicts the existence of a critical volume fraction of the minor phase above which the co-continuous morphology is stable.

In absence of flow upon annealing, e.g. in a compression molding machine, the type of morphology changes and a coarsening of the phase dimensions is seen. In the case of flow, e.g. in injection molding, when the molten blend flows through a nozzle into a mold a recovery of the initial morphology both in terms of type and phase dimensions may occur as will be discussed in this chapter, too [8].

5.2 Theory

5.2.1 Stability of the morphology: break-up vs. retraction

The morphologies obtained after blending will start changing when left in a quiescent fluid state. This change is frequently considered to be caused by coalescence of droplets. However, fibrous or co-continuous structures can undergo coarsening via retraction or breakup leading eventually to droplets in most cases, suggesting coalescence to be the mechanism of coarsening which it was not. Obviously, the mechanism and, consequently, the rate and extent of coarsening depend on the morphology of the blend under consideration.

In fibrillar morphologies two different mechanisms may compete and depending on the length of the fibre, L, fibres can either break up or retract [9-11]. A first approach to determine whether a fibre breaks up or retracts is the comparison of the characteristic times for both interfacial driven processes. The breakup time of a fibre in absence of flow can be calculated with [9]:
\[ t_s = \frac{\eta_m B_{\text{fibre}}}{\sigma \Omega_m} \ln\left(\frac{0.81 B_{\text{fibre}}}{2 \alpha_0}\right) \]  

(5.1)

where \( B_{\text{fibre}} \) is the initial diameter of the fibre (typical 1 \( \mu \text{m} \)), \( \eta_m \) is the viscosity of the matrix phase (typical 1000 Pa.s), \( \sigma \) is the interfacial tension (typical 5 mN/m), \( \Omega_m \) is the dimensionless growth function and \( \alpha_0 \) is the initial disturbance on the surface of the fibre caused by thermal fluctuations (typical \( 10^9 \) m [13]). \( \Omega_m \) is shown in Fig. 5.1 as a function of the viscosity ratio, \( p = \eta_d / \eta_m \) [12], and \( \Omega_m = 0.07 \) at equal viscosities of both blend components [12].

![Graph showing \( \Omega_m \) and \( X_m \) as functions of \( p \) and \( \eta_d / \eta_m \)]

**Figure 5.1:** Theoretical values of the wave number, \( X_m \), and the growth function \( \Omega_m \) as a function of the viscosity ratio \( p = \eta_d / \eta_m \) [12].

The time necessary for the complete retraction of a fibre into a sphere can be calculated with [10]:

\[ t_r = \frac{3 B_{\text{fibre}} (\eta_m + \eta_d)}{\sigma} \ln\left(\frac{(L')^3 - 1}{6 L' - 5}\right) \text{ with } L' = 2 \frac{L}{B_{\text{fibre}}} \]  

(5.2)

where \( \eta_d \) is the viscosity of the dispersed phase (typical 1000 Pa.s).
Figure 5.2: The ratio of the characteristic breakup and retraction time (Eq.(5.1)/Eq.(5.2) as a function of the viscosity ratio, $p$, for $L/B=3$ and $6$.

Figure 5.3: Critical elongation ratio, $L/B_{\text{droplet}}$, with $B_{0,\text{droplet}}$ the diameter of the undeformed droplet, necessary to ensure breakup found experimentally $(\ast, o)$ [9] as a function of the viscosity ratio compared with calculated values (full line: Eq.(5.4)).
Stability of polymer blends: role of initial morphology

Breakup will occur only if the ratio of the characteristic times, $t_b/t_c$, is less than 1. This ratio is shown as a function of the viscosity ratio, $\nu$, in Fig. 5.2. From this graph it can be concluded that even short fibres with $L/B=3$, or better ellipsoids, can break up outside the range $0.1<\nu<10$. If the aspect ratio only slightly increases, e.g. $L/B = 6$, breakup becomes more favourable. However, Stone et al. [9] reported that within a broad range of viscosity ratios, $0.01<\nu<10$, the breakup of fibres (via sinusoidal distortions) only occurs in the case of highly extended fibres. A critical length of the fibres, expressed as an elongation ratio, above which breakup can occur is shown in Fig. 5.3 as a function of the viscosity ratio. The comparison of the characteristics times for breakup and retraction is obviously not suitable for the determination whether breakup or retraction occurs and for that reason an alternative approach is given in this chapter.

The existence of such a critical length above which a fibre can break up, can be understood using the theory for breakup of extended fibres. From calculations of the surface area of the sinusoidally disturbances it follows that, if the wavelength of the disturbance, $\lambda$, is larger than the circumference, $\pi B_{fibre}$, the interfacial area decreases when the amplitude of the disturbance increases [14]. The disturbances grow exponentially with time and at for certain $\lambda_m$, which is the dominant wavelength, the disturbance will grow the fastest. This dominant wavelength, expressed as a dominant wave number, $X_m=\pi B_{fibre}/\lambda_m$, is shown in Fig. 5.1.

It is asserted here that the length of a fibre should exceed this dominant wave length for breakup. At a shorter length this dominant wave length cannot exist and the growth of a disturbance is delayed. The critical aspect ratio, $(L/B_{fibre})_{cr}$, below which a fibre will not break up is given by:

$$
\left(\frac{L}{B_{fibre}}\right)_{cr} = \left(\frac{\lambda_m}{B_{fibre}}\right) = \frac{\pi}{X_m(\nu)}
$$

(5.3)

Stone [9] reported the length of the deformed droplet divided by the initial diameter, $B_{droplet}$, as shown in Fig. 5.3. When the deformed droplet is an ellipsoid then $L/B_{droplet} = (B_{fibre}/B_{droplet})^2$. The parameter $L/B_{droplet}$ as a function of the aspect ratio $L/B_{fibre}$ is given by:
\[
\frac{L}{B_{\text{droplet}}} = \left( \frac{L}{B_{\text{fibre}}} \right)^2 = \left( \frac{\pi}{X_m(p)} \right)^2
\]  
(5.4)

The critical value of \( L/B_{\text{droplet}} \) calculated with Eq. (5.4) is also shown in Fig.5.3. It can be seen that the results of Stone [9] can be described well up to \( p=1 \) above which some deviation can be seen. Here, the parameter \( Q_m \) will become almost 0 leading to high breakup times. The absolute values of \( L/B_{\text{droplet}} \) reported by Stone [9] are approximately a factor of 1.5 higher than the those calculated with Eq.(5.4).

Apart from a change of the morphology these interfacial driven processes do not result in a huge change of the phase dimensions as will be illustrated below. Complete breakup will occur within 17 s (solving Eq. (5.1) for the typical values given above). The final diameter of the droplets formed, \( B_{\text{droplet}} \), can be calculated with:

\[
B_{\text{droplet}} = B_{\text{fibre}} \left( \frac{3 \pi}{2 X_m} \right)^{3/2}
\]  
(5.5)

where \( X_m \) is a dominant dimensionless wave number characterizing the sinusoidal distortion on the liquid cylinder as shown in Fig 5.1. As an example, for equal viscosities of the blend components Tomotika's theory gives \( X_m = 0.56 \), which after break-up of the fibre leads to droplets twice as thick as the original fibre. The phase dimensions are doubled after approximately 17 s and do not change any further, as is shown in Fig.5.4, unless coalescence of the formed droplets would occur.

For moderately extended fibres (shaded area in Fig. 5.3) end pinching of the fibres can often be seen [9]. In this case the diameter of the resulting droplets will be about twice the diameter of the original fibre. Below a critical length (shown in Fig.5.3) retraction occurs [9]. Complete retraction of a fibre with, e.g. \( L/B_{\text{fibre}} = 6 \), will occur within 12 s (solving Eq.(5.2) for the typical values given above). The diameter of the droplet, \( B_{\text{droplet}} \), resulting from retraction is given by:

\[
B_{\text{droplet}} = B_{\text{fibre}} \left( \frac{2}{3} \right)^{1/3} \left( \frac{L}{B_{\text{fibre}}} \right)^{1/3}
\]  
(5.6)
Here, because $L/B_{fibre} \leq 6$ the droplets will be up to twice as thick as the original fibres. The phase dimensions are doubled within 12 s in the case of retraction and do not change anymore as is shown in Fig. 5.4.

5.2.2 Coalescence

After break-up or retraction of the fibres a further coarsening of the phase dimensions in blends is only possible if coalescence can occur. For coalescence two droplets have to meet each other. In a medium at rest, the approach of the droplets may be caused by gravity, Brownian motion or Van der Waals forces [1]. Due to the high viscosity of polymers and the small difference in density of the components, the influence of gravity and Brownian motion are expected to be negligible. In quiescent media Van der Waals forces between the droplets are the driving force for coalescence [1]. According to Fortély [1] many droplets in most blends are at such short distances from each other that coalescence between droplets starts immediately after mixing. In blends with a volume fraction of the dispersed phase, $\phi$, much higher than 0.1, many droplets practically touch, because a system of spherical droplets has its percolation threshold at $\phi_{perc} = 0.16$ [15].

The rate of coalescence depends on the mobility of the interface between the droplets and matrix. It is usually assumed that the interface in the case of polymers is partially mobile. For this case, coarsening of the droplets expressed as the increase of the radius ($R$) as a function of time can be described with the following equation [1]:

$$ R^2 = R_0^2 + \frac{32(6\pi)^2 \sigma^2 h_c^2}{3A \eta_d} \left[1 - \exp\left(-\frac{9\phi}{4(1-\phi)}\right)\right] t $$

(5.7)

in which $A$ is the Hamaker constant ($A \approx 10^{-20}$ J), $h_c$ is the critical distance at which the film between two droplets ruptures ($h_c = 5-500$ nm), $\phi$ is the volume fraction and $R_0$ is the droplet radius before coalescence takes place.

A compatibilizer can immobilize the interface. This leads to less coarsening. The droplet radius in the case of an immobile interface is then given by [1]:

\[ R^3 = R_0^3 + \frac{128 \pi \sigma^2 h_0^4}{3 \eta_m A} \left[ 1 - \exp \left( \frac{-9 \phi}{4(1-\phi)} \right) \right] t \] (5.8)

The dimensionless phase dimensions \( R/R_0 \) as a function of time with the volume fraction of the dispersed phase as a parameter are shown in Fig.5.4 (solving Eqs. (5.7) and (5.8) for the typical values given above). Although Forte [1] indicated that coalescence due to Van der Waals forces only takes place if the droplets touch, i.e. in the case of percolation, he did not take this into account in his model, which leads to Eqs. (5.7) and (5.8). This shows up clearly in Fig.5.4. Namely, in the case of 10 vol\%, which is below the percolation threshold value and only a few droplets will touch each other, the calculated phase dimensions nevertheless increase with approximately the same rate as the one at higher volume fractions.

**Figure 5.4:** Coarsening of the morphology expressed as an increase of the radius divided by the initial radius, \( R/R_0 \), of the domains of the minor component as a function of annealing time; : : : : break up (\( X_m=0.56; \) Eq.(5.5)) or retraction (\( L/B_{\text{fiber}}=6; \) Eq.(5.6)); ---: partially mobile interface (pmi; Eq.(5.7)); ---: immobile interface (imi; Eq.(5.8)). In all cases: \( \eta_m = \eta_d = 1000 \) Pa.s; \( \sigma = 5 \) mN/m; \( B_{\text{fiber}} = 1 \) \( \mu \)m; \( A = 10^{20} \) J; \( h_c = 5 \times 10^{-5} \) m; a, b and c represent blends with 10, 20 and 30 \% of the minor component, respectively.
Stability of polymer blends: role of initial morphology

From Fig. 5.4 it becomes clear that it is to be expected that the initial morphology of the blend plays a role in the coarsening process and that only in the case of coalescence a considerable coarsening can be found, especially for partially mobile interfaces. In this chapter it is demonstrated that different mechanisms for coarsening can be active in blends depending on the starting structures. In order to study these mechanisms two blend systems were used in which properly defined initial morphologies can be obtained, i.e. blends of polyamide/polyethylene and polystyrene/polyethylene.

5.2.3 Stability of a co-continuous morphology

Annealing of a polymer blend which exhibits a co-continuous morphology either results in a particle/matrix morphology or in a coarser co-continuous morphology [5,6,7]. It appears that a critical volume fraction of the minor phase can be distinguished above which the co-continuous morphology is stable. It is asserted here that this critical volume fraction can be understood by taking into account the same geometrical requirements of the co-continuous morphology which were already described in chapter 3. The co-continuous morphology was depicted there as an assembly of rodlike particles randomly oriented at their maximum packing density inside the major component. All the rods have touched each other and have 'coalesced' at their cross-over points. The ligaments between two cross-over points have a certain length which increases with increasing length of the rods, i.e. with decreasing volume fraction of the minor phase as can be calculated with Eq. (3.5). If the co-continuous morphology breaks up, then these filaments should break up. This breakup of ligaments or fibres only occurs above a certain length or aspect ratio as shown in Fig. 5.3 and which can be calculated with $1.5*\text{Eq.}(5.3)$ as was discussed above. This critical length may correspond to the length of the ligaments between two cross-over points as can be found in the assembly of randomly oriented rods. This length of such ligament, indicated here as an aspect ratio, will be maximally the aspect ratio of the total rod and in that case the filaments in the co-continuous morphology are connected by other ligaments at their endpoints. The volume fraction of the minor phase at which the co-continuous structure should not break up, can be calculated by combining Eq.(3.5) and $1.5*\text{Eq.}(5.3)$. The result is shown in Fig. 5.5.

In spite of the stability of the co-continuous morphology against breakup a coarsening of the phase dimensions of this structure can be seen. This can only occur if some parts of the network
structure break at one point rather than break up into separate droplets [16]. The broken ligament retracts keeping the network structure intact, but a coarser structure is formed.

![Diagram](image)

**Figure 5.5:** The volume fraction at which a co-continuous morphology once formed is stable against breakup into droplets. The dotted line is the result for PE/PS discussed in this chapter.

### 5.3 Experimental

Blends of polyethylene (PE) in nylon-6 (PA6) with 13, 23 and 33 vol% PE2 in PA6, were used to study the coarsening in a droplet/matrix morphology. Blends of polystyrene (PS) in PE with 15, 27 and 35 vol% PS in PE1, were used to study the coarsening of a fibrillar and a co-continuous morphology. The polymers used and their viscosities are listed in Table 5.1. The blends were prepared by single screw extrusion in conjunction with static mixing. A Collin laboratory single screw extruder equipped with a transport screw \((D = 20 \text{ mm}, L/D = 20)\) was used for feeding a static mixer, which contained 10 static mixing elements. The static mixing elements were of the type Ross ISG (15 mm diameter), which contained 4 channels with a diameter of 2.7 mm. The average shear rate in these channels was estimated to be \(22 \text{ s}^{-1}\). The extruded blends were quenched in water.
**Table 5.1:** Trade names of the polymers used and shear viscosities at $\dot{\gamma} = 22 \text{ s}^{-1}$ and $\dot{\gamma} = 0 \text{ s}^{-1}$ at $T_{\text{process}}$ (200°C in the case of PS and PE1; 250°C in the case of PE2 and PA6).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Trade name (manufacturer)</th>
<th>$\eta$ (Pa.s) at $T_{\text{process}}$</th>
<th>$\eta_0$ (Pa.s) at $T_{\text{process}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Hostyrene N2000 (Shell)</td>
<td>780</td>
<td>1500</td>
</tr>
<tr>
<td>PE1</td>
<td>Stamylan LD 2100TN00 (DSM)</td>
<td>1860</td>
<td>165000</td>
</tr>
<tr>
<td>PE2</td>
<td>Stamylan LD 2102TN26 (DSM)</td>
<td>540</td>
<td>2200</td>
</tr>
<tr>
<td>PA6</td>
<td>Akulon K 136 (DSM)</td>
<td>1500</td>
<td>2000</td>
</tr>
</tbody>
</table>

The extruded strands were annealed at 200°C (the PS/PE1 blends) and at 250°C (the PE2/PA6 blends). Different annealing times of 0, 0.5, 1, 2, 5 and 10 minutes were used. After annealing the samples were quenched in water. No macroscopic retraction of the strands should occur so that the change of morphology is the result of the microtheoretical processes only. For that reason the samples were annealed in a compression molding apparatus (Fontijne press).

Pellets of the blends, granulated after extrusion, were injection molded in an Arburg Allround (type: 170 CMD) injection molding machine at 200°C (the PS/PE1 blends) and at 250°C (the PE2/PA6 blends). Several process parameters involving the plastification/injection steps of the molding cycle were varied to study their effect on the morphology of the blends: 1. screw rotational speed (5-30 m/min), 2. injection rate into the mold (5-50 cm³/s), 3. residence time of the molten material in the reservoir before the nozzle (after this time the material is injected with 5 cm³/s), 4. nozzle diameter (2 and 3 mm) and 5. a static mixing element (Sulzer SMX) inserted before the nozzle. In order to isolate the effect of these parameters on the morphology, the material was injected in some cases directly into water instead of the mold.

The samples were broken in liquid nitrogen and extraction of the PS phase (from the PS/PE1 blends) and the PE2 phase (from the PE2/PA6 blends) with 2-butanol and iso-octane, respectively, was performed in a Soxhlet extraction apparatus during 3 days. This was sufficient for complete removal of the soluble fraction.

A scanning electron microscope (Philips XL 20) was used to study the morphology and the phase dimensions after extraction. The reported droplet radii and fibre diameters are the results of
50 to 100 measurements of the holes resulting after extraction. With the method described above the morphology of the blend perpendicular to the flow direction can be studied. However, the fibres cannot be detected in this way, because they are oriented in the flow direction. In order to examine the morphology parallel to the flow direction the samples surfaces were smoothed by removing a part of the sample parallel to the flow direction, using a diamond knife under liquid nitrogen.

5.4 Results and discussion

5.4.1 Initial morphology

The matrix viscosity and the viscosity ratio during processing were approximately the same in the blends of PE2 in PA6 and PS in PE1. Due to a higher interfacial tension in the PE2/PA6 blends ($\sigma$=11 mN/m [13]) compared with the PS/PE1 blends ($\sigma$=4.5 mN/m [14]) the morphology found in the two blend systems is expected to be different. The results of the extraction experiments are shown in Table 5.2.

Table 5.2: Percentage PE2 and PS extracted at several volume fractions of PE2 and PS in PE2/PA6 and PS/PE1 blends, respectively.

<table>
<thead>
<tr>
<th>vol% PE2 in PA6</th>
<th>% PE2 extracted</th>
<th>vol% PS in PE1</th>
<th>% PS extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0</td>
<td>15</td>
<td>84</td>
</tr>
<tr>
<td>23</td>
<td>3</td>
<td>27</td>
<td>99</td>
</tr>
<tr>
<td>33</td>
<td>24</td>
<td>35</td>
<td>100</td>
</tr>
</tbody>
</table>

In the PE2/PA6 blends, where droplets are present (see Fig. 5.6a, b and c), extraction of PE2 was only possible above its percolation threshold value of 16 vol% [15]. The morphology of the PS/PE1 blend with 15 vol% PS is fibrous as can be seen from Fig. 5.7d and confirmed by the amount of extractable PS, shown in Table 5.2. These fibres are oriented in the flow direction. Using Fig.5.7a only would lead to the incorrect conclusion of a droplet/matrix structure. The morphologies of the PS/PE1 blends with 27 and 35 vol% PS are co-continuous as is shown in Fig. 5.8a and d and as is confirmed by the amount of extractable PS, shown in Table 5.2.
Figure 5.6: Scanning Electron Micrographs of blends of PE2 in PA6 perpendicular to the flow direction (after extraction of PE); a, b and c represent the initial morphologies of blends with 13, 23 and 33 vol% PE (at t=0), respectively, and d, e and f represent the morphologies after 10 minutes annealing of 13, 23 and 33 vol% PE2, respectively.
Figure 5.7: Scanning Electron Micrographs of blends of 15 vol% PS in PE1 (after extraction of PS) as a function of the annealing time: a, b and c represent the morphologies perpendicular to the flow direction at t=0, 120 and 300 s, respectively; d, e and f represent the morphology parallel to the flow direction at t=0, 120 and 600 s, respectively.
Figure 5.8: Scanning Electron Micrographs of blends of 27 and 35vol% PS in PE1 perpendicular to the flow direction as a function of the annealing time (after extraction of PS): a, b and c represent the morphologies of the 27 vol% PS in PE1 blends at t = 0, 120 and 300 s, respectively, and d, e and f represent the morphology of the blends of 35 vol% PS in PE1 at t=0, 120 and 300 s, respectively.
5.4.2 Compression molding: absence of flow

5.4.2.1 Coarsening starting from droplets

The average diameter of the PE2 particles in the PE2/PA6 blends as a function of annealing time is shown in Table 5.3 and Fig. 5.9. Corresponding SEM pictures of PE2 particles in PA6 are shown in Fig. 5.6. In the case of 13 vol% PE2 no coalescence was found. The diameter of the PE2 particles in this blend only slightly increased after annealing which can be caused by retraction of ellipsoids into spherical droplets. The percolation threshold is about 16 vol%, so only a few droplets can touch leading to a low coalescence probability. Although the volume fraction in the blend with 23 vol% PE2 exceeds the percolation threshold value, limited coalescence occurs. It appears that only in the case of 33 vol% PE2 in PA6 a strong coarsening can be seen. This coarsening is the result of coalescence only, because fibres were absent in the initial morphology. The increase of the PE2 particle size can be described using the theory of Fortelny [1]. It appears that Eq. (5.7), valid in the case of a partially mobile interface, overestimates the increase of the phase dimensions (Fig. 5.10) even if the minimum critical thickness at which the film between two droplets ruptures, was used ($h_{\text{crit, min}} = 5 \times 10^{-9} \text{ m}$). The results can be better described by Eq. (5.8), valid for immobile interfaces, with a value of $h_c = 7 \times 10^{-9} \text{ m}$, although it is generally assumed that the droplet interface in polymer systems is partially mobile. This problem was perceived by Fortelny [1], too. A further discussion is beyond the scope of this chapter.

Table 5.3: Phase dimensions of PE2 droplets in PA6 (\(\mu\text{m}\)) as a function of the annealing time for different compositions.

<table>
<thead>
<tr>
<th>t (s)</th>
<th>11 vol% PE</th>
<th>23 vol% PE</th>
<th>33 vol% PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.4 ± 1.0</td>
<td>1.6 ± 1.3</td>
<td>1.9 ± 1.3</td>
</tr>
<tr>
<td>30</td>
<td>2.3 ± 0.9</td>
<td>2.3 ± 1.2</td>
<td>6.5 ± 4.0</td>
</tr>
<tr>
<td>60</td>
<td>2.5 ± 1.5</td>
<td>4.8 ± 2.4</td>
<td>6.4 ± 4.8</td>
</tr>
<tr>
<td>120</td>
<td>2.4 ± 1.4</td>
<td>4.7 ± 2.4</td>
<td>10.5 ± 7.4</td>
</tr>
<tr>
<td>300</td>
<td>2.6 ± 1.7</td>
<td>4.9 ± 2.8</td>
<td>15.0 ± 9.4</td>
</tr>
<tr>
<td>600</td>
<td>2.3 ± 0.9</td>
<td>6.6 ± 3.8</td>
<td>20.0 ± 15.0</td>
</tr>
</tbody>
</table>
Figure 5.9: Increase of the dimensionless diameter, $R/R_0$, of the domains of the PE2 phase in PE2/PA6 as a function of the annealing time; +, Δ and ○ represent 13, 23 and 33 vol% PE2 in PA6, respectively.

Figure 5.10: Increase of the dimensionless diameter, $R/R_0$, of the PE2 phase in PE2/PA6 blends as a function of the annealing time and comparison of the experimental results (○) of blends of 33 vol% PE2 in PA6 with the theory; ....: immobile interface ($h_c = 5 \times 10^{-9} \text{ m}$), ---: immobile interface ($h_c = 7 \times 10^{-9} \text{ m}$) and ---: partially mobile interface ($h_c = 5 \times 10^{-9} \text{ m}$). In all cases: $\eta_s = 2000 \text{ Pa.s}; \eta_d = 500 \text{ Pa.s}; \sigma = 11 \text{mN/m}; B_{\text{misc}} = 1.9 \mu \text{m}$. 
5.4.2.2 Coarsening starting from fibres

The blend with 15 vol% PS in PE1 was used to study the coarsening in blends with a fibre/matrix morphology. The corresponding SEM pictures of PS fibres in PE1 are shown in Fig. 5.7. The pictures representing the morphology perpendicular to the flow direction show a coarser structure after annealing. The pictures representing the morphology parallel to the flow direction show fibres which break up. This breakup is verified by the extraction experiments shown in Fig. 5.11. Prior to annealing about 80% PS could be extracted due to the fibrillar morphology. After annealing the fraction extractable PS decreases, because droplets are formed. The PS phase diameters are three times the diameters of the original fibres found after extrusion (Table 5.4).

Table 5.4: Phase dimensions of PS domains in PE1 (μm) as a function of the composition and annealing time.

<table>
<thead>
<tr>
<th>t (s)</th>
<th>15 vol% PS</th>
<th>27 vol% PS</th>
<th>35 vol% PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4 ± 0.2</td>
<td>0.6 ± 0.3</td>
<td>0.8 ± 0.4</td>
</tr>
<tr>
<td>30</td>
<td>0.5 ± 0.2</td>
<td>1.7 ± 1.2</td>
<td>2.7 ± 1.3</td>
</tr>
<tr>
<td>60</td>
<td>0.6 ± 0.2</td>
<td>2.7 ± 2.3</td>
<td>2.8 ± 1.7</td>
</tr>
<tr>
<td>120</td>
<td>0.8 ± 0.4</td>
<td>3.5 ± 2.7</td>
<td>3.3 ± 2.2</td>
</tr>
<tr>
<td>300</td>
<td>1.0 ± 0.4</td>
<td>3.9 ± 1.7</td>
<td>5.2 ± 3.5</td>
</tr>
<tr>
<td>600</td>
<td>1.3 ± 1.0</td>
<td>3.8 ± 2.9</td>
<td>9.6 ± 8.0</td>
</tr>
<tr>
<td>1800</td>
<td>1.3 ± 0.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

This experiment proves that coarsening at low volume fractions (below the percolation threshold value for droplets) only occurs if the initial morphology consists of fibres in a matrix as can be seen in Fig. 5.12. The diameter of the droplets after breakup is three times the diameter of the original fibre. Solving Eq. (5.1) for the experimental values -η_m = 165000 Pa.s, B_fibre = 0.4 μm, σ = 5 mN/m, Ω = 0.3 at η_PS/η_PE1 = 0.01 and α_0 = 10^9 m^2 gives τ_b = 224s. The breakup of these PS fibres, however, is already completed after 120 s. The fibres found in these systems do not exhibit smooth surfaces and it is to be expected that the initial disturbance, α_0, exceeds the theoretical value of
Figure 5.11: Fraction of PS extracted from the PE1/PS blends as a function of annealing time; ■, ▴ and ○ represent the blends with 15, 27 and 35 vol% PS in PE1, respectively.

Figure 5.12: Dimensionless diameter, $R/R_0$, as a function of the annealing time at a volume fraction below the percolation threshold value: (+): 13 vol% PE2 in PE2/PA6 blends (droplet/matrix) and (■): 15vol% PS in PS/PE1 blends (fibre/matrix).
$10^9$ m $[17,18]$. By using $\alpha_0 = 10^{-8}$ m the breakup time becomes 123 s which almost coincides with the experimental value. If the initial morphology consists of non spherical droplets the diameter only slightly increases due to the retraction of the droplets into a sphere as was found for the PE2/PA6 blend. Once a droplet/matrix morphology has been formed, no significant further coarsening takes place.

5.4.2.3 Coarsening starting from co-continuous morphologies

The blends with 27 and 35 vol% PS in PE1 possess a co-continuous morphology as can be concluded from the extraction experiments shown in Table 5.2. Extraction experiments were also used to follow the morphology change during annealing. Corresponding SEM pictures are shown in Fig.5.8, representing the morphology perpendicular to the flow direction.

The phase diameters in the blend with 27 vol% PS in PE1 after annealing were a factor of 6 higher than those found directly after extrusion (Table 5.4). The type of morphology changed during annealing as can be seen in Figs.5.8 and 5.11. The co-continuous structure broke up and a dispersion was formed. Less PS could be extracted. A further coarsening did not occur. The coarsening in this blend cannot be explained by break-up only, because then the phase dimensions should be only a factor of two or three higher than those of the original structures. From Fig.5.8a to c it can be seen that the co-continuous structure did not directly break up into droplets only. The breakup of the ligaments of the network will leave large fragments of the original ‘crossing points’ of the co-continuous structure (as shown in Fig.5.8b) which can retract leading to a much more coarser structure. In the PE2/PA6 blend with 23 vol% PE2 limited coalescence occurred and it is to be expected that coalescence in the blend with 27 vol% PS in PE1 is also limited. So, the coarsening in this PS/PE1 blend is mainly caused by breakup and retraction.

The co-continuous structure in the blend with 35 vol% PS in PE1 did not break up as can be concluded from Fig. 5.11. Coalescence is not to be expected because all the material already belongs to an interconnected phase. Annealing of this blend leads to a coarser structure, as shown in Fig. 5.8d, e and f, which must be caused by retraction only. Retraction of a 3-dimensional structure requires local ruptures $[16]$. These are to be distinguished from break-up of extended strands resulting in a number of droplets. The phase dimensions in the blends with 15 and 27 vol% PS in
PE1 remain constant after breakup, whereas those in the blend with 35 vol% PS still increased after 10 min, as shown in Fig. 5.13, due to retraction of the interconnected structure.

These results also indicate the existence of a critical volume fraction of around 30 vol% above which the co-continuous morphology does not breakup, something which has already been found by Verhoogt [6] and Quintens [7]. It was asserted above that this critical volume fraction is connected with the aspect ratio of the ligaments between two cross-over points. The calculated critical volume fraction shown in Fig. 5.5 is 35%, which was also found experimentally ($\eta_{PS}/\eta_{PE} = 0.01 \sim 35\%$ as shown in Fig. 5.5). The co-continuous morphology in the blend with 35 vol% PS did not break up. The aspect ratio will increase at lower volume fractions of the minor phase and breakup will become possible upon annealing as was indeed found experimentally by annealing the blend with 27 vol% PS in PE.

It is difficult to measure this ratio experimentally as can be concluded from Fig. 5.8a and d. By extracting the PE phase the PS network can be made visible which should facilitate a proper determination of the L/D of the PS phase. However, extraction of the PE phase is not possible without damaging the PS phase.

![Graph](image)

**Figure 5.13:** Increase of the dimensionless diameter, $R/R_0$, of the PS phase in PE1 as a function of the annealing time; ■, ▲ and ○ = 15, 27 and 35 vol% PS.
5.4.3 Injection molding: subsequent flow through a nozzle

From the above it can be concluded that the morphology of a polymer blend changes rapidly during the annealing in absence of flow. In order to maintain the desired morphology in the polymer blend the molten blend has to flow followed by a rapid solidification, which may be achieved in the injection molding machine. In this section the stability of the same PE2/PA6 and PS/PE1 blends during injection molding is studied.

5.4.3.1 Blends with a droplet/matrix morphology

The initial morphology in blends of PE2 and PA6 consisted of droplets of PE2 in PA6 as discussed above. The comparison of the phase dimensions after extrusion, $B_{\text{initial}}$, and after injection molding, $B_{\text{injection}}$, it can be concluded that the droplet/matrix morphology is preserved during the injection molding of these blends but for higher volume fractions some coarsening occurs (Table 5.5). The cycle time in the injection molding machine is about 2 min. The resulting morphology was compared with that obtained after compression molding for the same time. The coarsening during injection molding was less (Table 5.5). It is to be expected that coarsening of the droplet/matrix morphology takes place during the time that the material does not flow. In injection molding this happens inside the reservoir (melt cushion) to fill-up with melt to be injected. It seems that the subsequent flow through the nozzle and into the mold refines the morphology formed in the reservoir. This does not occur during the compression molding and it explains the above difference.

<table>
<thead>
<tr>
<th>Blend (vol% PE)</th>
<th>$B_{\text{initial}}$ (µm)</th>
<th>$B_{\text{injection}}$ (µm)</th>
<th>$B_{\text{compression}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1.4</td>
<td>1.6</td>
<td>2.4</td>
</tr>
<tr>
<td>23</td>
<td>1.6</td>
<td>1.7</td>
<td>4.7</td>
</tr>
<tr>
<td>33</td>
<td>1.9</td>
<td>3.9</td>
<td>10.5</td>
</tr>
</tbody>
</table>
Stability of polymer blends: role of initial morphology

5.4.3.2 Blends with a co-continuous or fibrillar morphology

The phase dimensions of the PS phase after injection molding are compared in Table 5.6 with the initial phase dimensions found after extrusion and the phase dimensions found after 2 min. compression molding. Some coarsening of the initial morphology was found probably due to the residence time in the melt cushion, but this coarsening was less than the coarsening found during compression molding. Due to the flow through the nozzle and into the mold the phase dimensions are reduced by the formation of elongated structures. The extraction experiments shown in Table 5.6 verify the presence of these elongated structures.

Table 5.6: The phase dimensions of the PS phase of the initial PEI/PS blend, \( B_{\text{initial}} \), the phase dimensions and the extraction results of the PS phase after injection molding, \( B_{\text{injection}} \), and after 2 min. compression molding, \( B_{\text{compression}} \).

<table>
<thead>
<tr>
<th>Blend (vol% PS)</th>
<th>( B_{\text{initial}} ) (( \mu \text{m} ))</th>
<th>( B_{\text{injection}} ) (( \mu \text{m} ))</th>
<th>% PS extracted (after injection molding)</th>
<th>( B_{\text{compression}} ) (( \mu \text{m} ))</th>
<th>% PS extracted (after compression molding (2 min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.4</td>
<td>0.6</td>
<td>90</td>
<td>0.8</td>
<td>25</td>
</tr>
<tr>
<td>27</td>
<td>0.6</td>
<td>1</td>
<td>100</td>
<td>3.5</td>
<td>29</td>
</tr>
<tr>
<td>35</td>
<td>0.8</td>
<td>1.5</td>
<td>100</td>
<td>3.5</td>
<td>95</td>
</tr>
</tbody>
</table>

These extraction experiments indicate that compression molding leads to breakup of the fibrillar morphology (15 vol%) and one of the co-continuous morphology (27 vol%), whereas the blend with 35 vol% PS did not break up. The co-continuous morphology after injection molding seems to be preserved as can be concluded from the extraction experiments (e.g. 27 vol% PS as shown in Table 5.6), whereas it was lost during compression molding. The SEM pictures (Fig. 5.14), however, show a rather irregular structure as if the minor phase was not distributed properly. There are several reasons that may lead to coarsening in injection molding. In order to classify their significance, the influence of some parameters of the injection molding process on the morphology of the PE/PS blends is examined separately in the following.
Figure 5.14: Scanning Electron Micrographs of blends of 27 vol% PS in PE1; a. initial, b. after injection molding, c. after injection molding; nozzle with mixing element

5.4.3.3 Process parameters

- Effect of screw rpm and flow through the nozzle

The effect of the screw speed without an injection step was examined by collecting the material into a water bath. This parameter determines the deformation rates that the blend experiences during melting and transport to the reservoir. Its effect, however, on the phase dimensions seems to be negligible (Fig.5.15). The time that the melt experiences this flow is relatively small.

The effects of the injection speed and the nozzle diameter are examined by collecting the molten blend in the reservoir followed by immediate injection through the nozzle into a water bath. These parameters are related. Higher speeds (flow rates) or smaller diameters result in shorter residence times and higher deformation rates. The amount of accumulated strain increases with decreasing nozzle diameter. The phase dimensions as a function of these parameters are shown in Fig.5.16. Obviously, these parameters do not play a role in the coarsening of the phase dimensions.
Figure 5.15: The diameter of the PS phase (μm) as a function of the screw speed. ■, ○ and + represent the blends with 15, 27 and 35 vol% PS, respectively.

Figure 5.16: The diameter of the PS phase (μm) in the blend with 27 vol% PS in PE1 as a function of the injection speed (cm³/s) for different diameters of the nozzle: 2 mm (■) and 3 mm (○).
- Residence time in the reservoir

The strongest changes of the morphology of the blend in injection molding takes place during the time that the material is not flowing, i.e. in the reservoir just before the nozzle. This waiting time is part of the injection molding cycle and cannot be avoided. The phase dimensions as a function of this time are shown in Fig. 5.17. It can be concluded that this time has a pronounced influence on the phase dimensions compared with the effect of the parameters described above.

From Fig. 5.17 it can be seen that a coarsening has already occurred within 2 min, which is about the cycle time during injection molding of small parts and much less than the time needed for larger products. Due to this, the morphology in injection molded products will always be coarser than the initial morphology of the blend, although it is less coarse than the morphology found after compression molding of the same blend. Due to the subsequent flow through the nozzle the final phase dimensions in injection molded parts are smaller than those found during compression molding, which are also shown in Fig. 5.17. This small refinement of the phase dimensions is caused by the stretching of the structures in the nozzle, explaining also the higher amount of extractable PS as compared to the amount of PS from the compression molded blends as shown in Table 5.6.

![Graph](image)

**Figure 5.17:** The diameter of the PS phase (µm) as a function of the residence time in the injection molding machine: ■, ○ and + represent the blends with 15, 27 and 35 vol% PS, respectively. The solid line represents the blend with 27 vol% PS in PE1, which was pressed in the compression molding machine.
Effect of Sulzer mixer

From the results presented above it can be concluded that the residence time in the injection molding machine leads to a coarser structure. The co-continuous morphology is preserved but the final structure is rather irregular. The subsequent flow through the nozzle reduces the phase dimensions. However, this flow is not sufficient and the initial phase dimensions are not regained. For that reason a static mixing element was added at the nozzle to enhance the effect of the nozzle flow and to obtain a certain level of re-mixing in the blend after the waiting time in the reservoir and before the material flows into the mold.

The phase dimensions of the PS phase in the PS/PE blends using the static mixing element are shown in Fig. 5.18. From this figure it can be concluded that the original phase dimensions found after extrusion are regained. The SEM pictures (Fig. 5.14c) show that a regular co-continuous morphology with a proper distribution of the minor phase is obtained similar to the morphology of the original blend.

![Graph showing the diameter of the PS phase (µm) in the blend as a function of the amount of PS (%) in PE1 prepared by different processing methods: + = extrusion (initial morphology), ○ = injection molding and ■ = injection molding with a static mixing element in the nozzle.](image)

**Figure 5.18:** The diameter of the PS phase (µm) in the blend as a function of the amount of PS (%) in PE1 prepared by different processing methods: + = extrusion (initial morphology), ○ = injection molding and ■ = injection molding with a static mixing element in the nozzle.
5.5 General discussion

It is obvious that the blend morphology plays an important role in the coarsening of polymer blends. Both the rate and the extent of the coarsening are strongly dependent on the initial morphology. If this initial morphology is a droplet/matrix structure coarsening takes place by coalescence of droplets. This is a comparatively slow process leading slowly but continuously to growing phase dimensions. From our results it appears that, contrary to prediction with Fortelny’s equations, the percolation threshold is indeed a threshold for coalescence. No appreciable coarsening takes place below this composition.

Coarsening in fibrous structures takes place by way of breakup and/or retraction leading eventually to droplet/matrix structures. This process is completed in a short time as compared to coalescence and results in final drop sizes approximately twice the fibre diameters. If the concentration of the resulting droplets is above the percolation threshold additional (slow) coalescence may occur.

In co-continuous structures significant coarsening can occur either by breakup and retraction at lower concentrations of the minor phase or by retraction only at higher concentrations. Droplets of a size 6 times the original ligament thickness can be formed at lower concentrations, apparently resulting from the crossing points of the network after breakup. After this breakup process no further coarsening takes place. Again this process takes place on a short time scale as compared to coalescence. At higher concentrations the co-continuous structure does not break up and only retraction is seen which leads to a co-continuous structure with continuously increasing phase dimensions. It appears that a critical volume fraction can be distinguished above which the co-continuous structure does not break up upon annealing. This composition can be predicted by depicting the co-continuous structure as an assembly of fibres and it can be related to the aspect ratio of the ligaments between the points where the fibres are connected. If the length of a ligament is smaller than the dominant wave length of a sinusoidal disturbance, then this filament will not break up. As such the co-continuous structure is inherently stable against breakup within a certain composition range. It is to be expected that there is a critical volume fraction for every immiscible blend system above which the co-continuous morphology does not break up on annealing.

Injection molding of the blends leads to less coarsening as compared to compression
molding. Furthermore, elongated structures present in the initial blend structure are reformed during the flow through a nozzle. In case of co-continuity, however, the obtained structure is rather irregular. The initial morphologies, with regard to both phase dimensions and type, are regained by using a static mixer installed in the nozzle.

The results obtained in this study clearly have important consequences for processing of polymer blends. It can be stated in general that droplet/matrix structures are not as vulnerable to the interfacial tension driven changes as fibrous or co-continuous structures are. Although the extent of coarsening in the latter structures is usually limited to an increase of phase size, the typical structures are quickly lost and changed into a droplet matrix structure with associated loss of typical properties. This implies that the compounding of blends with co-continuous morphologies and their processing to final products should be done preferably in one step. Alternatively, the morphology should be regenerated just before the final shaping step, e.g. by placing an efficient static mixer before the mold in injection molding.

5.6 Conclusion

Coarsening in polymer blends in a quiescent state can be caused by other mechanisms apart from coalescence. These interfacial driven processes have different consequences for the type and the phase dimensions of a certain morphology. For example, the phase dimensions increase in a droplet/matrix morphology due to coalescence if the volume fraction exceeds the percolation threshold. The type of morphology, however, remains the same. In a fibrillar morphology breakup occurs leading to a limited increase of the phase dimensions only, but the fibrillar morphology is lost on a short time scale. The same behavior was found for co-continuous morphologies at lower concentrations.

Above a ‘critical’ concentration the latter morphologies do not break up and a considerable coarsening is found due to retraction. This concentration is related to the aspect ratio of the filament between the points where the filaments are connected. If the length of this filament is smaller than the dominant wave length of a sinusoidal disturbance, then this filament will not break up. As such the co-continuous structure is inherently stable against breakup within a certain composition range.

During injection molding a coarsening of the blends with elongated structures occurs,
whereas the blends with droplet/matrix morphology remain unchanged. This coarsening is the result of breakup and retraction due to the absence of flow during the waiting time in the reservoir before the nozzle. This coarsening is considerably less than the coarsening of the blends during compression molding because the flow through the nozzle reduces the phase dimensions. The co-continuous structure is still found after injection molding, but the structure becomes rather irregular. The use of a static mixer before the nozzle has two results: the original phase dimensions are regained and a regular structure is formed.

5.7 References

13. Kuhn, W., Kolloid Z., 132, 94 (1953)
6. TENSILE PROPERTIES OF IMMISCIBLE POLYMER BLENDS

6.1 Introduction

The tensile properties of blends with different morphologies and at various compositions are studied in this chapter. It is well-known that the type and scale of the morphology in the blend determine the properties [1]. This holds especially for mechanical properties such as e.g. the tensile modulus. In the case of a droplet matrix-morphology the tensile modulus of a blend will largely be determined by the modulus of the matrix phase. The modulus of a fibrous blend can, on the other hand, be largely determined by the modulus of the dispersed (fibrous) phase, especially in oriented samples [2,3]. Co-continuous blends are expected to fall in between these extremes: neither of the blend components is expected to dominate the moduli of the blends and isotropic values may be obtained because of their interpenetrating phase structure.

The tensile properties of polyethylene/polypropylene (PE/PP) and polyethylene/polystyrene (PE/PS) blends as a function of composition and morphology, are compared with existing theoretical models. In literature several models can be found, which describe the modulus, strength and strain at break of blends in general [4-9], and the modulus of the fibrillar and the co-continuous morphology in particular [10-17]. A comparison is made between the predictions of these models and the experimental results, which should give more insight in the benefits of a co-continuous morphology in relation to the dispersed type of morphologies.

6.2 Theory

6.2.1 Tensile modulus

Tensile moduli of polymer blends are strongly dependent on the composition and morphology. In literature several models can be found which describe tensile moduli of blends as a function of the composition. Most of these models are valid for a given morphology, others leave the morphology unspecified. Changes of morphology with composition are common in polymer blends, such as the transformation of a dispersed morphology into a co-continuous morphology. For

this reason most models are applicable only within limited composition ranges.

The moduli of polymer blends generally range between an upper bound, \( E_U \), given by the parallel model [4]:

\[
E_U = \phi_1 E_1 + \phi_2 E_2
\]  
(6.1)

and a lower bound, \( E_L \), given by the series model [4]:

\[
\frac{1}{E_L} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2}
\]  
(6.2)

in which \( E_i \) and \( \phi_i \) are the modulus and the volume fraction of phase \( i \). Although the parallel and series models are, strictly speaking, valid only for simple and idealised structures, they are frequently used as limiting models regardless of morphology.

For particle/matrix morphologies the relation between modulus and composition has been given by Halpin [10]. Particles of the second blend component of uniform aspect ratio \( L/D \) are supposed to be oriented in one direction. The modulus in this direction, \( E_\parallel \), is given by:

\[
E_\parallel = E_1 \left( 1 + AB\phi_2 \right) \left( 1 - B\phi_2 \right)
\]  
(6.3.a)

with:

\[
A = 2 \frac{L}{D} \quad ; \quad B = \frac{E_2/E_1 - 1}{E_2/E_1 + A}
\]  
(6.3.b)

The modulus according to Eq.(6.3) is plotted in Fig.6.1 for \( L/D = 10 \). For aspect ratios larger than 100 the calculated moduli approach the upper bound (Eq.(6.1)), which was confirmed experimentally by Crevecoeur [3]. The modulus perpendicular to the direction of orientation, \( E_\perp \), is also given by Eq.(6.3), if \( A = 0.5 \) is used instead of \( 2L/D \) [10]. \( E_\perp \) is much lower than \( E_\parallel \), as is shown in Fig.6.1.
Figure 6.1: Modulus versus composition with \( E_t = 200 \text{ Mpa} \) and \( E_s = 2500 \text{MPa} \): (...) represent \( E_t \) and \( E_s \) with \( L/D = 10 \) upto 90 vol% phase 2 as calculated from Eq. (6.3); (----) and (--) represent \( E_{\text{random}} \) with \( L/D = 10 \) and 40 upto \( \phi_m = 45 \) and 10 vol% phase 2, respectively, as calculated from Eq.(6.4).

The tensile modulus for a randomly oriented dispersion is given by [11]:

\[
E_{\text{random}} = \frac{2}{\pi} \int_{0}^{\pi} E_{\theta} d\theta
\]

(6.4a)

in which \( E_{\theta} \) is the angular dependence of the tensile modulus. This modulus is:

\[
E_{\theta} = \frac{E_t E_s}{E_t + (E_s - E_t) \cos^4 \theta}
\]

(6.4b)

in which \( E_t \) and \( E_s \) have the same meaning as above. Two examples of moduli of random blends are shown in Fig.6.1, for different aspect ratios. Eqs. (6.3) and (6.4) are applicable at concentrations of the dispersed phase up to the maximum packing density of the dispersed particles. In the case of
a hexagonal packing of parallel rods this maximum packing density can be up to about 90 vol% whereas it is much lower for randomly oriented rods or for spheres. The maximum packing density of randomly oriented rods depends on their aspect ratio L/D and is given by [18]:

\[
\frac{1}{\phi_{\text{max}}} = 1.38 + 0.0376 \left(\frac{L}{D}\right)^{1.4}
\]  

(6.5)

An increase of the aspect ratio of the dispersed phase leads to a decrease of the maximum packing density and, consequently, to a smaller range of validity of Eq. (6.4). This is illustrated in Fig. 6.1 for values of L/D = 10 and L/D = 40 limiting the maximum composition for Eq. (6.4) to \( \phi = 43 \) vol\% and 12 vol\%, respectively.

For co-continuous polymer blends different equations for the tensile modulus as a function of the composition have been proposed. The relation given by Davies [14], assuming the blend to be macroscopically homogeneous and isotropic, takes the shape:

\[
\frac{1}{E^5} = \frac{1}{E_1^5} \phi_1 + \frac{1}{E_2^5} \phi_2
\]

(6.6)

It is supposed to be applicable for co-continuous structures without specifying any details.

Coran and Patel [15] proposed an equation which is intended to account for phase inversion at a certain composition of the blend. The modulus is expressed as a function of the upper and lower bounds using a fit parameter, \( n \), which is supposed to depend on wetting and compatibility and to give the point of phase inversion as \( \phi = (n-1)/n \):

\[
E = \phi_2^n (n\phi_1 + 1)(E_u - E_L) + E_L
\]

(6.7)

Lyngaae-Jørgensen et al. [16] have given a relation for the moduli of blends above the percolation threshold of the minor component:

\[
E = E_1 + (E_2 - E_1) \left( \frac{\phi_2 - \phi_c}{1 - \phi_c} \right)^T
\]

(6.8)
in which T = 1.7 - 1.9 and \( \phi_c \) is the percolation threshold; for spheres \( \phi_c = 0.16 \), for fibres \( \phi_c \) is much lower. Kolarik [17] introduced the cross orthogonal skeleton (COS) model for the mechanical properties of a co-continuous morphology. The modulus of the COS model is:

\[
E = E_1(1 - f)^2 + E_2 f^2 + \frac{2f(1-f)}{(1-f)/E_1 + \beta E_2}
\]

(6.9)

in which \( f \) is related to the volume fraction as \( \phi_1 = (1-f)^2(1+2f) \) [17].

The moduli calculated with Eqs.(6.6), (6.7), (6.8) and (6.9) are shown in Fig. 6.2. Despite the different backgrounds, the predictions of these theories do not differ very much.

![Figure 6.2: Modulus versus composition with \( E_1 = 200 \) MPa and \( E_2 = 2500 \) MPa: (---), (---), (-----) and (-----) calculated with Eq.(6.6), (6.7) with \( (n-1)/n = 0.5 \), (6.8) with \( T = 1.9 \) and \( \phi_{cr} = 0.01 \), and (6.9), respectively.](image)

Any relation for the tensile modulus of a polymer blend requires a proper definition of the structure to which it applies. A gradual change in structure from dispersed to fully co-continuous takes place in heterogeneous polymer blends on increasing the volume fraction of the minor component. In dilute systems droplet/matrix structures prevail. At higher volume fractions, starting
at the percolation threshold, interconnected structures of the minor component develop until at a still higher volume fractions all of the minor component is incorporated in a single continuous phase network inside the matrix component and a fully co-continuous morphology is obtained. This co-continuous morphology can exist over a range of compositions, depending on the blending conditions (chapter 3). Beyond this range, at still higher volume fractions, the phase network of the erstwhile matrix component starts breaking down until finally this component becomes dispersed. From this picture it will be clear that Eqs. (6.6), (6.7) and (6.8) cannot be expected to give a proper description of the moduli of the blends over a broad composition range. The relation of Lyngaae-Jørgensen et al. [16] does indeed account for the onset of percolation, however it does not account for the onset of full co-continuity. The COS-model [17] does account for full co-continuous morphologies, but its predictions hardly differ from the values obtained by Eqs. (6.6), (6.7) and (6.8).

In fully co-continuous blends both components form single continuous and interpenetrating structures. For low volume fractions of the minor component such a fully continuous structure can exist only if the ligaments of the phase network have an extended shape. By depicting this continuous phase network as a random assembly of rodlike particles at their maximum packing density, one obtains a crude model of a continuous phase network. The limiting volume fraction for existence of such a phase network will be given by Eq. (6.5) relating the composition limits to the aspect ratio of the network ligaments, which in turn can be related to the blending conditions. By applying Eq.(6.5) to both blend components a composition range is obtained within which fully co-continuous structures can exist. These fully co-continuous blends will have tensile moduli which are determined by the moduli of both components. Because of the interpenetrating network structure of these blends we expect these tensile moduli to exceed predictions by the traditional models for dispersed and co-continuous structures. Outside the composition range for full co-continuity the phase network breaks down and a gradual decrease of the moduli of the blends may be expected.

6.2.2 Strength and strain at break

The modulus of a blend can be predicted to some extent by considering the type of morphology as was already discussed above. In the case of an unknown type of morphology one may say that the moduli can be found between a lower and an upper limit calculated with Eqs. (6.1)
and (6.2). The effect of the morphology on properties such as the tensile strength, yield strength and maximum elongation at break, however, is more difficult to predict. These blend properties are not only determined by the properties of the separate blend components and the type of morphology, but also by the effect of, e.g., adhesion and the fracture mechanism in a blend. Some models for elongation at break and strength are summarized here.

Nielsen [5] derived an equation for the total elongation at break, $\varepsilon_b$, in the case of adhering rigid particles:

$$\varepsilon_b = \varepsilon_{b,1} \left(1 - \phi_2^3\right)$$

(6.10)

with $\varepsilon_{b,1}$ the total strain of component 1. In the case of non-adhering particles $\varepsilon_b = \varepsilon_{b,1}$. Plots of the elongation as a function of the volume fraction are shown in Fig.6.3. Similar results were obtained by Smith [6]. The fracture mechanism is not considered in these models.

Figure 6.3: Calculated elongation at break of a blend with rigid particles versus composition: (...) represent Eq.(6.10) in the case of adhering particles, (—) represent $\varepsilon_b = \varepsilon_1$ in the case of non adhering particles.
The tensile strength of a blend, $\sigma_t$, is given by [7]:

$$\sigma_t = \sigma_{t,1}(1 - \phi_2^2)^{\frac{2}{3}}$$  \hspace{1cm} (6.11)

with $\sigma_{t,1}$ the tensile strength of component 1. The blend consists of separate non-adhering particles within a matrix phase leading to a decrease of the tensile strength with increasing particle density. The particles introduce as it were voids. A similar equation was derived for the yield strength [8]:

$$\sigma_y = \sigma_{y,1}(1 - 1.21 \phi_2^3)^{\frac{2}{3}}$$  \hspace{1cm} (6.12)

Both equations are plotted in Fig.6.4. These equations both describe a decrease of the strength.

Equations for the tensile strength of a fibrillar morphology were derived by Piggot [12]. Two limiting cases can be distinguished:

1. For high contents of fibres, the fibres dominate the mechanical behaviour of the blend, i.e. when the fibres break, fatal failure appears and the blend breaks. The total blend strength is [12]:

$$\sigma_t = \phi_f \sigma_f + (1 - \phi_f)\sigma_m \frac{E_m}{E_f}$$  \hspace{1cm} (6.13)

with $\phi_f$, $\sigma_f$, and $E_f$ are the volume fraction, tensile strength and the modulus of the fibre, respectively, and $E_m$ is the modulus of the matrix phase.

2. For low fibre contents, the mechanical behaviour of the blend is determined by the matrix, since the fibres cannot follow the plastic deformation of the matrix. The fibres are pulled out, when the deformation approaches the yield strain of the matrix, and they do not contribute to the stress anymore. The fibres can be considered as voids and the strength can be calculated with:

$$\sigma_t = \sigma_m (1 - \phi_f)$$  \hspace{1cm} (6.14)

with $\sigma_m$ the tensile strength of the matrix phase.
Eq. 6.14 is a similar equation as Eq.(6.12) and (6.13) described above. These contributions are also shown in Fig.6.4. In spite of the strength of the reinforcing particles an increase of the tensile strength is only found at higher volume fractions of this reinforcing phase. Gergen [13] presented a ‘fibre tensile’ model for co-continuous morphologies, but the results of this theory hardly differs from the plots shown in Fig 6.4.

These plots predicts a kind of concave curve which is indeed found experimentally for different polymer blends. According to Kolarik [9] this behaviour is the result of the poor interfacial adhesion between the blend components.

![Graph showing the relationship between σ (MPa) and vol% phase 2.](image)

**Figure 6.4:** Calculated strength versus composition. Tensile strength: (—), (..a...) and (..b...) represent predictions of Eqs.(6.11), (6.13) and (6.14). Yield strength: (−) represent predictions of Eq.(6.12). In all cases: \( \sigma_1 = 10 \text{ MPa}, \sigma_2 = 35 \text{ MPa}, E_1 = 200 \text{ MPa} \) and \( E_2 = 2500 \text{ MPa} \).
6.3 Experimental

Two grades of polystyrene (PS), two grades of low density polyethylene (PE) and two grades of polypropylene (PP) shown in Table 6.1, were used to prepare the PE/PS and PE/PP blend series shown in Table 6.2. Nine different compositions (9, 17, 27, 35, 46, 56, 67, 77 and 88 vol% PS in PE and 9, 18, 28, 37, 47, 58, 69, 79 and 89 vol% PE in PP) were made by extrusion at 200°C. The mixing equipment consisted of a 20 mm Collin laboratory extruder equipped with a transport screw, and a static mixer in series with the extruder containing 10 Ross ISG 15 mm diameter mixing elements. Each element contains 4 channels with a radius of 0.135 cm. The average shear rate in the channels was estimated to be 22 s⁻¹. The extruder was equipped with a film extrusion die with an opening of 100 mm width and 1.5 mm thickness. Directly after leaving the extruder the film was cooled rapidly by compressed air. The film was collected with take-up rolls.

Co-continuity in the blends was checked by extraction experiments. The strands were broken in liquid nitrogen and during 3 days extraction of the PS or PE phase was performed in a Soxhlet extraction apparatus with 2-butanone and iso-octane, respectively. This was sufficient for complete removal of the soluble fraction. The samples were checked whether they were self supporting after extraction. Five pieces of the extruded strands were used to obtain an average value. In the case of co-continuity 100% of the PS phase from the PE/PS blends and 100% of the PE phase from the PE/PP blends can be extracted [19]. It was not possible to extract the PE or PP phase from the PE/PS and PE/PP blends, respectively, without damaging the remaining phase. For that reason the upper limit for the composition range of co-continuity could not be determined. This limit, however, can be estimated from the stability of the samples after extraction.

From the extruded films several test bars were punched out parallel and perpendicular to the original flow field. The test pieces were dumb-bell shaped (ISO/DIS 8256A); the cross section being 2.5*1.5 mm and the length being approximately 60 mm. The tensile measurements were done with an Instron Universal testing machine. Stress-strain curves were determined at a speed of 10 mm/min. From these curves the tensile modulus and strength were determined. Five test bars were tested for each composition both parallel and perpendicular to the original flow direction.
Table 6.1: Trade names and shear viscosities at $\dot{\gamma} = 22$ and 30 s$^{-1}$ (200°C) of the polymers used.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Trade name (manufacturer)</th>
<th>Viscosity (Pa.s) ($22$ s$^{-1}$)</th>
<th>Viscosity (Pa.s) ($30$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>Hostyrene N2000 (Shell)</td>
<td>780</td>
<td>-</td>
</tr>
<tr>
<td>PS2</td>
<td>Hostyrene N7000 (Shell)</td>
<td>2400</td>
<td>-</td>
</tr>
<tr>
<td>PE1</td>
<td>Stamylan LD 2100TN00 (DSM)</td>
<td>1860</td>
<td>1585</td>
</tr>
<tr>
<td>PE2</td>
<td>Stamylan LD 2102TN26 (DSM)</td>
<td>960</td>
<td>830</td>
</tr>
<tr>
<td>PP1</td>
<td>Stamylan PP 19MN10 (DSM)</td>
<td>-</td>
<td>450</td>
</tr>
<tr>
<td>PP2</td>
<td>Stamylan PP 13E10 (DSM)</td>
<td>-</td>
<td>1690</td>
</tr>
</tbody>
</table>

Table 6.2: Blends studied in this chapter, the expected volume fractions for the upper limit of co-continuity, $\phi_u$, (estimated) and for the lower limit of co-continuity, $\phi_l$, measured experimentally.

<table>
<thead>
<tr>
<th>Series</th>
<th>Blend components</th>
<th>$\phi_u$ (vol %) upper limit (estimated)</th>
<th>$\phi_l$ (vol %) lower limit (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>PS1,PE1</td>
<td>56</td>
<td>35</td>
</tr>
<tr>
<td>II</td>
<td>PS1,PE2</td>
<td>56</td>
<td>46</td>
</tr>
<tr>
<td>III</td>
<td>PS2,PE2</td>
<td>78</td>
<td>56</td>
</tr>
<tr>
<td>IV</td>
<td>PE2,PP1</td>
<td>79</td>
<td>27</td>
</tr>
<tr>
<td>V</td>
<td>PE1,PP2</td>
<td>79</td>
<td>27</td>
</tr>
</tbody>
</table>
6.4 Results and discussion

The blend systems PE/PS (series I, II and III) and PP/PE (series IV and V) were chosen for their differences in composition range for full co-continuity (chapter 3 and 4). Apart from checking the validity of Eqs.(6.6) to (6.9) in the case of tensile moduli, this enables a comparison of blends with the same composition but with differenter morphologies. The results of the extraction experiments are shown in Table 6.3 and the corresponding lower limiting volume fractions together with estimates for the upper limits are shown in Table 6.2. From this Table it can is seen that co-continuity in series I, II and III can be found at 35-56 vol% PS1 in PE1, 46-56 vol% PS1 in PE2, 56-77 vol% PS2 in PE2 and 28-79 vol% PP in PE (both series). The properties of these blends are compared, as will be discussed in detail below.

Table 6.3: Percentage of PS or PE extracted from the blends of series I-III or series IV/V, respectively, as a function of the volume fraction.

<table>
<thead>
<tr>
<th>% PS in blend (series)</th>
<th>% PS extracted (I)</th>
<th>% PS extracted (II)</th>
<th>% PS extracted (III)</th>
<th>% PE in blends (series)</th>
<th>% PE extracted (IV)</th>
<th>% PE extracted (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>39</td>
<td>15</td>
<td>34</td>
<td>9</td>
<td>76</td>
<td>36</td>
</tr>
<tr>
<td>17</td>
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<td>48</td>
<td>18</td>
<td>65</td>
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</tr>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>58</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 6.5: Stress strain plots of the PE/PS blend systems (series I). (---) represent PE and PS (PE breaks above 200%); (.....) represents 27 vol% PS in PE; (--) represents 46 vol% PS and (-----) represents 88 vol% PS.

Figure 6.6: Stress strain plots of the PE/PP blends system (series IV) (---) represent PE and PP (PE breaks above 200% and PP breaks above 400%); (...) represents 30% PE and (---) represents 40% PE in PP.
Some typical stress strain curves of some PE/PS and PE/PP blends are shown in Fig. 6.5 and Fig 6.6, respectively. The moduli of these blend systems are discussed in section 6.4.1. From Fig. 6.5 it can be concluded that PE yields and both a yield strength (at low strain) and a tensile strength (above 200 % strain) can be measured, whereas for PS only a tensile strength can be measured at low strain. In the case of the PE/PS blends the yield strength and the tensile strength are difficult to distinguished and for that reason only the yield strength measured at low strain is considered.

From Fig. 6.6 it can be concluded that the yield strength and the tensile strength in the case of PP differs considerably. The yield strength and the tensile strength of the blends both at measured at low strain hardly differ. For that reason the yield strength is considered in this chapter. This yield strength and elongation at break for the different blend systems are studied in section 6.4.2.

6.4.1 Tensile Modulus
6.4.1.1 PE/PS-blends

The moduli of the blends of series I, II and III as a function of the composition are shown in Figs. 6.7, 6.8 and 6.9, respectively, both for samples taken parallel and perpendicular to the original flow direction. The values of these moduli are compared with the values predicted by Eqs.(6.6) to (6.9). For the sake of simplicity only the predictions of Eq.(6.6) are shown in Figs. 6.7, 6.8 and 6.9.

Co-continuity in blends of series I is found at 35-56 vol% PS1 in PE1. The moduli of the blends exhibiting a co-continuous morphology are higher than the one calculated with Eqs. (6.6) to (6.9). Above 56 vol% PS some anisotropy can be seen due to some skin-core effects. Although no fully continuous PS phase was obtained the modulus of the samples with 27 vol% PS is obviously raised to a higher level. In this blend more than 80% of the PS phase was extracted.

The blends of series II exhibit a co-continuous morphology in a narrow composition range: 46-56 vol% PS1 in PE2. In contrast to the blends of series I the blends of series II have anisotropic properties caused by the skin core structures. Only in the case of full continuity of the PS phase in the blend with 46 and 56 vol% PS an isotropic material was obtained. The modulus of this isotropic material is higher than the values calculated with Eqs. (6.6) to (6.9).
Figure 6.7: Young's modulus versus composition for PE/PS blends (Series I). ● and O represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6.6) (full line). The composition limits for co-continuity are indicated with (....).

Figure 6.8: Young's modulus versus composition for PE/PS blends (Series II). ● and O represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6.6) (full line). The composition limits for co-continuity are indicated with (....).
Co-continuity in series III was found within a composition range of 56-78 vol% PS. Above 36 vol% PS the modulus of the blend is already raised. Although no full co-continuity was found more than 80% of the PS phase could be extracted. The moduli of the blends in case of full co-continuity were higher than the equivalent moduli of series I with the same composition where no co-continuity was found. Predictions of Eq.(6) to (9) can not be used in this case, again.

![Graph](image)

**Figure 6.9:** Young's modulus versus composition for PE/PS blends (Series III). ● and ○ represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6.6) (full line). The composition limits for co-continuity are indicated with (....).

### 6.4.1.2 PE/PP blends

The moduli of the blends of series IV as a function of the composition are shown in Fig. 6.10. Co-continuity in these blends is found within a broad composition range: 28-79 vol% PP in PE2. The moduli of the blends exhibiting a co-continuous morphology are higher than the ones calculated with Eqs. (6.6) to (6.9), just as for blends of PE/PS. The PE/PP blends exhibit this behaviour over the entire broad composition range within which full co-continuity can be generated. The same behaviour was found for blends of series V.
Figure 6.10: Young's modulus versus composition for PE/PP blends (Series IV). ● and O represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6.6) (full line). The composition limits for co-continuity are indicated with (...).

6.4.2 Strength and elongation at break

The yield strength of the blends of series I and III as a function of the volume fraction PS are shown in Figs. 6.11 and 6.12, respectively. Both Figures show that the yield strength of the PE-rich blends hardly decrease as a function of the PS volume fraction, whereas the yield strength of the PS-rich almost collapses as the volume fraction of the PE phase increases. The blends of series II showed a pronounced skin-core structure and for that reason they are not suitable to study the effect of the morphology on the yield strength.

The blends of series I exhibit a co-continuous morphology at 35-56 vol% PS. In this range the yield strength slightly increases and this increase cannot be described by any of the existing relations. At higher volume fractions of the PS phase (>75 vol%) the yield strength increases and this yield strength can be described as if the particles of the PE phase are voids within the PS phase.

The blends of series III exhibit a co-continuous morphology at 56-77 vol% PS. From the above it may be expected that in this composition range both phases will contribute to the strength
of the blend. However, the yield strength collapses by increasing the PE volume fraction as can be concluded from Fig.6.12. Again, this collapse can be described by considering the PE phase as voids. This collapse may be the result of the high stresses which have built up in the blend at the moment of fracture. The PS phase breaks first because its elongation at break is rather low (2%). Due to the high stresses built up in the blend the PE phase will also break and no effect of co-continuity on the yield strength within this range can be seen.

The yield strength in blends of PE/PS hardly increased as a function of PS. By contrast, in the case of PE/PP blends the yield strength increases with increasing amount of PP as shown in Fig.6.13. This increase may be ascribed to the co-continuous morphology found within a wide composition range. However, the results presented for the PE/PS blends indicate that the co-continuity in this system hardly results in better properties and other factors such as fracture mechanism, should be considered, too.

**Figure 6.11:** Yield strength versus composition for PE/PS blends of series I (●). (---) represent Eqs.(6.13) and (6.14) and (……) represents Eq.(6.11).
Figure 6.12: Yield strength versus composition for PE/PS blends of series III (+). (----) represent Eqs.(6.13) and (6.14) and (......) represents Eq.(6.11).

Figure 6.13: Yield strength versus composition for PE/PP blends: + and □ represent series IV and V, respectively.
**Figure 6.14:** Elongation at break versus composition for PE/PS blends. +,○ and ● represent series I, II and III, respectively. These values are compared with Eq. (6.10).

**Figure 6.15:** Elongation at break versus composition for PE/PP blends. + and □ represent series IV and V, respectively. These values are compared with Eq. (6.10).
Tensile properties of polymer blends

The maximum elongation at break is shown in Fig. 6.14 for blends of series I, II and III. It can be concluded that the elongation at break collapses above 10% PS in PE independently of the type of morphology of the blend. This result can more or less be predicted using Eq. (6.10). The maximum elongation at break is shown in Fig. 6.15 for blends of the PE/PP of series IV and V. This maximum elongation at break of both blend components is rather high. At intermediate composition this elongation at break is lower as predicted by Eq 6.10.

The tensile behaviour of PP/PE blends behaviour differs from that found in the PS/PE blends. Both PE and PP do not break at low elongation (as shown in Fig. 6.15 and if, for example, PE yields at a certain stress, the PP phase will not break and starts yieding at a somewhat higher stress leading to an overall higher yield strength of the blend. The result is an overall higher strength of the blend, which follows an additive rule of mixture. This different behaviour compared with that of the PE/PS blends is explained in literature [9] by the difference of the interfacial adhesion. It may be expected that this adhesion in blends with PE/PP is better than in blends with PE/PS due to the lower interfacial tension of PP/PS. However, it is more likely that the difference of yield behaviour of PP and PS plays a role. PS already breaks at a low elongation and the stress after PS fracture will be beared by PE only until the PE breaks, too.

6.5 General discussion

Fully co-continuous blends are found to be characterized by values of their Young’s moduli which are high and isotropic. These high values exceed the predictions of existing models and are near to the upper bound for mixtures. This is illustrated in Fig. 6.16 which summarizes the results for the PE/PS blends. These high moduli of co-continuous blends are probably the result of a very effective stress transfer in the fully interpenetrating phase networks. This is not accounted for by existing models for moduli of polymer blends, perhaps with exception of the COS model. However, the COS model appears to predict values approaching the upper bound only if the moduli of the blend components differ many orders of magnitude, which is not the case in our blends.

The level of the moduli of co-continuous blends approaches the parallel model and appears to be isotropic, which means that in these blends both phases fully contribute to the blend modulus in all directions. Such a level cannot otherwise be obtained in polymer blends, except in fibrous
blends and than only in one direction provided these blends are perfectly oriented. This makes co-continuous morphologies much more effective than fibrous morphologies for reinforcing purposes. The high level of moduli and isotropic behaviour of co-continuous blends is not confined to one single composition, but can be achieved over a wide composition range, dependent on processing conditions (chapter 3 and 4).

By creating a co-continuous structure instead of a droplet-matrix structure in a given blend the modulus of the blend can be significantly raised, depending on the ratio of the moduli of the blend components and the composition. For example, in a blend of 30% PS in PE changing the droplet matrix structure into a fully co-continuous structure will raise the modulus from approximately 400 to approximately 750 MPa, resulting in almost a doubling of the stiffness of the material. This makes co-continuous morphologies a versatile means of obtaining new materials.

Figure 6.16: Young's modulus versus composition for PE/PS blends in the case of co-continuous morphologies (0, □ and △ represent series I, II and III, respectively) and a dispersion (● and ▲ represent series I and III, respectively) These experimental values are compared with Eq.(6.1) (.........) and Eq.(6.6) (full line).
By contrast, the effect of the co-continuous morphology on the yield strength and elongation at break is not as straightforward as the effect on the modulus. The strength of a PS/PE blend increased in the case of the continuity of the PS minor phase which can be described with a kind of upper bound mixing rule. However, at higher PS volume fraction fracture of the PS phase simultaneously leads to fracture of the PE phase independently of the PE phase structure. This behaviour was not found in PE/PP blends where the strength of the blend increased with increasing amount of PP.

In order to describe strength and elongation at break the knowledge of the properties of the separate blend components alone is not sufficient. The adhesion between the two phases may play a role [9], but the results of the PE/PS and PE/PP blends indicate that the different yield behaviour of the blend components also plays a role. PS, for example, which does not yield, may introduce some stress concentrations leading to brittle fracture within the PE phase and for that reason the fracture mechanism of the blend components and the one of the total blend should be considered, too.

6.6 Conclusions

Blends of polyethylene/polystyrene and polyethylene/polypropylene with a co-continuous morphology show high isotropic tensile moduli. These high moduli exceed predictions by the models valid for co-continuous morphologies and approach the parallel model. Changing the structure from a droplet-matrix to a co-continuous structure at a given composition can result in a quite significant increase in modulus.

The yield strength or elongation at break do not depend clearly on morphology and the properties of the blend components alone. It is to be expected that the yield or fracture behaviour of the separate blend components and the adhesion between the blend components play a role, too.
6.7 References

7. MULTI-COMPONENT BLENDS: recycling

7.1 Introduction

Consumer plastics recycling is nowadays in a very dynamic stage of development and implementation. In order to preserve our natural resources and reduce the disposal of solid waste [1], various approaches to collecting and recycling plastics are taking place [2,3]. Getting the right materials in the right form for reclamation and at reasonable costs is a difficult hurdle to overcome. Furthermore, no constant distribution of the different types of plastics, such as polyethylenes, polypropylenes, styrenics, polyvinylchlorides and polyethylene terephthalates [4-6], is found in this waste and a constant set of properties cannot be achieved. For that reason separation of the different types of plastics is preferable. The possible markets for these recycled materials are the production of lumber, low pressure pipes, dustbins or insulation [7]. In some cases the recycled plastic can be used for its original purpose by blending it with virgin material, e.g. some shopping bags contain at least 50% of recycled low density polyethylene [8].

Separation, however, is costly and complete sorting is economically nonviable and sometimes impossible. Hence the plastic recycling industry is usually faced with a source of a commingled mixture. In the case of recycling of polyolefins, a commingled blend of polyethylenes (low density and high density) and polypropylenes is inevitable. Due to the incompatible nature of most polymers [9,10], even PE and PP, the commingled polymeric mixtures are poor in their mechanical performance [2,3,11,12,13,14,15].

Several studies were devoted to possibilities of improvement of the mechanical properties of PE/PP blends by incorporation of an additional component [12-15], which is usually a compatibilizer. Theoretically, a limited amount of such compatibilizers (<1 wt%) should already give a better dispersion due to a decrease of the interfacial tension [16,17] and eventually lead to better properties. In practice, however, at least 5 wt% of these relatively expensive compatibilizers are required [12-15] in order to improve the mechanical properties leading to unacceptably high prices of the recycled plastics as compared to the prices of virgin plastics.

From the above it can be concluded that separation and/or compatibilization of the different plastics may be preferable, but both, however, are economically not attractive. The goal of this
research was to enhance certain properties of multicomponent waste to an acceptable level by mixing it with at most 30 wt% of a PS rich waste stream without using a compatibilizer. In order to reduce production costs even more the possible products should be made directly after blending of the different polymers and the plastic waste is not pelletized after the first mixing step. With this method a certain class of properties can be defined for certain applications, e.g. lumber [18]. It is asserted here that the PS minor phase should be a continuous phase in order to ensure a certain minimum level of properties. In chapter 6 it was shown that the tensile moduli of blends with a continuous PS phase, i.e. a co-continuous morphology of PS and PE, are high in all directions in contrast to the ones of fibrillar morphologies which are high in one direction only. In this chapter blends of PS in LDPE/PP and its properties are studied in order to describe the possibilities of this method.

7.2 Experimental

One grade of polystyrene (PS, Hostyrene N2000 (Shell)), one grade of polypropylene (PP, Stamylan PP 13E10 (DSM)) and two grades of low density polyethylene (PE1, Stamylan LD 2100TN00 (DSM); PE2, Stamylan LD 2102TN26 (DSM) ) were used to prepare the PS/PE, PE/PP and PS/ (PP/PE) blend series shown in Table 7.1. An important part of the plastic waste consists of packaging [19]. These materials are often made using the film blowing process in which high viscous grades of the different plastics are used. For that reason PP and PE1, which are relatively high viscous grades, are used in this chapter representing typical packaging materials. In addition to the three component blends blends of PE1/PP, PE1/PS and PE2/PS were made as a reference.

The mixing equipment consisted of a 20 mm Collin laboratory extruder equipped with a transport screw, and a static mixer in series with the extruder containing 10 Ross ISG 15 mm diameter mixing elements. Each element contains 4 channels with a radius of 0.135 cm. The average shear rate in the channels was estimated to be 22 s⁻¹. The extruder was equipped with a film extrusion die with an opening of 100 mm width and 1.5 mm thickness. Directly after leaving the extruder the film was cooled rapidly by compressed air. The film was collected with take up rolls.

Co-continuity in the blends was checked by extraction experiments. The strands were broken in liquid nitrogen and extraction of the PS or PE phase was performed during 3 days in a Soxhlet extraction apparatus with 2-butanol and iso-octane, respectively. This was sufficient for complete
removal of the soluble fraction. The samples were checked whether they were self supporting after extraction. Five pieces of the extruded strands were used to obtain an average value. In the case of co-continuity 100% of the PS phase from the PS/PE and PS/PE/PP blends and 100% of the PE phase from the PE/PP blends can be extracted. It was not possible to extract the PE or PP phase from the PE/PS and PE/PP blends, respectively, without damaging the remaining phase. For that reason the upper limit for the composition range of co-continuity could not be determined. After extraction of the PS phase from the PS/PE/PP blends the PE phase can be extracted as described above. This was done for some blends of series IV in order to determine the structure of the PE phase in PP. A scanning electron microscope (Philips XL 20) was used to study the morphology of the blends after extraction of the minor phase.

Table 7.1: Blends studied in this work., and the lower limit of co-continuity measured experimentally($\phi_{,PS}$ in PE/PS blends and $\phi_{,PE}$ in PE/PP blends).* (PP/PE premixed)

<table>
<thead>
<tr>
<th>Series</th>
<th>Blend components</th>
<th>$\phi_s$ (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(experimental)</td>
</tr>
<tr>
<td>I</td>
<td>PS, (0.7PE1/0.3PP)</td>
<td>27</td>
</tr>
<tr>
<td>II</td>
<td>PS,(0.7PE1/0.3PP)*</td>
<td>20</td>
</tr>
<tr>
<td>III</td>
<td>PS,(0.3PE1/0.7PP)</td>
<td>35</td>
</tr>
<tr>
<td>IV</td>
<td>PS,(0.3PE1/0.7PP)*</td>
<td>27</td>
</tr>
<tr>
<td>V</td>
<td>PE1,PP</td>
<td>27</td>
</tr>
<tr>
<td>VI</td>
<td>PS,PE1</td>
<td>35</td>
</tr>
<tr>
<td>VII</td>
<td>PS,PE2</td>
<td>46</td>
</tr>
</tbody>
</table>

From the extruded films several test bars were punched out parallel and perpendicular to the original flow field. The test pieces were dumb-bell shaped (ISO/DIS 8256A); the cross section being 2.5*1.5 mm and the length being approximately 60 mm. The tensile measurements were done with an Instron Universal testing machine. Stress-strain curves were determined at a speed of 10 mm/min. From these curves the tensile modulus and strength were determined. Five test bars were tested for each composition both parallel and perpendicular to the original flow direction.
Pellets of the blends were used to make bars (10*4*60 mm) for impact testing, using an Arburg Allrounder (type 170 CMD) injection molding machine. A notch of 2 mm (top radius of 0.25 mm) was made using the Automatic Notchvis. The impact tests were done using a Zwick Pendulum Impact tester with an energy of 2.75 J. Five bars of each sample were used.

![Image of Scanning Electron Micrographs]

**Figure 7.1:** Scanning Electron Micrographs of blends the PS/PE/PP blends with 30 wt% PS: a, b, c and d represent series I, II, III and IV, respectively, after extraction of PS.

### 7.3 Results

#### 7.3.1 PS/PE/PP blends

Co-continuity at lower volume fractions of PS, e.g. at 30 vol% PS, is only possible if the viscosity of the major phase is rather high as was discussed in chapter 3. Since a considerable amount of the plastic waste consists of packaging (42% [19]) the PP/PE major phase usually meets
this requirement. Four series of PE/PP/PS blends were made as shown in Table 7.1. Blends of series I and II consist of a PE rich phase, whereas blends of series III and IV consist of a PP rich phase. The blends of series I and III were made starting from three separate phases. The PE and PP phase of the blend series II and IV were premixed before PS was added. In all blend series PS is continuous around 30 vol%. In Figure 7.1 some SEM pictures are shown. From these pictures it appears that the PS phase exhibits a more regular structure in the case of premixing.

The moduli of the blends of series I and II are shown in Fig. 7.2 and those of series III and IV are shown in Fig. 7.3. From these pictures it appears that premixing of PE/PP does not affect the modulus of the blend. The lines in these Figures are calculations using Eq. 6.1 with $E_{\text{PP/PE}}$ deduced from Fig 6.10. This graph shows that, in contrast to the PS/PE blends of chapter 6, the moduli of these three component blend systems are lower than the upperbound values given by the parallel model. The measured modulus of the PE/PP blends as shown in Fig.6.10 were those of the blends with a co-continuous morphology of PP in PE. It is to be expected that either some degradation has occurred or the PP/PE morphology has changed.

![Graph showing Young's modulus versus PS volume fraction](image)

**Figure 7.2:** Young's modulus versus PS volume fraction for the PS/PE/PP blends with a PE:PP of 70:30. (Δ and • represent series I and II, respectively). (---: calculated with Eq.(6.1)).
Figure 7.3: Young’s modulus versus PS volume fraction for the PS/PE/PP blends with a PE:PP of 30:70. (+ and □ represent series III and IV). (....: calculated with Eq.(6.1)).

The morphology of the PE/PP blend fraction can be studied by extracting the PE phase after extracting the PS phase. From the results described in chapter 4 it is expected that the PE/PP blends exhibit a co-continuous morphology within a broad composition range. In Fig.7.4 some SEM pictures are shown of the PS/PE/PP blend after extraction of the PS phase and after extraction of the PE phase. By comparing the morphology with the morphology of a PP/PE blend it can be concluded that the PE phase diameters are smaller in the PP/PE/PS blends. These smaller dimensions result in less stable elongated structures and a dispersion of PE in PP rather than a continuous phase of PE in PP is obtained. The calculations shown in Figs. 7.2 and 7.3 are based on a value for $E_{PE/PP}$ for a co-continuous structure, which cannot be used in the calculations of the modulus of a three component blend.

The yield strength of the blends of series I and II is shown in Fig 7.5 and that of series III and IV is shown in Fig 7.6. From these graphs it can be concluded that PS does not increase the yield strength. This was also found for the PE/PS blends as shown in Fig. 6.12 and 6.13. Furthermore it appeared that premixing of PE and PP does not affect the yield strength of the blends. The elongation at break of these blends is low, too, which was also found for blends of PE and PS (chapter 6).
Figure 7.4: Scanning Electron Micrographs of: a. series IV with 35 vol% PS after extraction of the PS phase. b. series IV with 35 vol% PS after extraction of the PS and PE phase. c. series VI with 30 vol% PE after extraction of the PE phase.

The impact strength of these three component blends is approximately 2 kJ/m². This low value is the result of mixing with PS. From the comparison of the impact strength of blends VI and VII in Figure 7.7, which exhibit a co-continuous and a dispersed morphology, respectively, it appears that this low impact strength does not depend on the type of the morphology [20]. The impact strength of both blend systems rapidly decreases with increasing amount of PS. This decrease is the result of the debonding of the PS phase leading to voids [21]. Due to the deformation of the blends these voids grow, leading to a fatal fracture.
Figure 7.5: Yield strength versus PS volume fraction for the PS/PE/PP blends with a PE:PP of 70:30 (△ and ○ represent series I and II, respectively).

Figure 7.6: Yield strength versus PS volume fraction for the PS/PE/PP blends with a PE:PP of 30:70. (+ and □ represent series III and IV).
Figure 7.7: Impact strength versus composition of the PE/PS blends; □ and ■ represents series VI and VII, respectively.

7.3.2 PP/PE blends

The morphology and the tensile properties of blends of PE/PP were already discussed in chapter 6 of this thesis. The blends exhibit a co-continuous morphology within a broad composition range (30-70 vol% PP). Both the tensile strength and the tensile modulus increase linearly with the amount of PP in the blend. The impact strength of the PE/PP blends of series V is shown in Fig 7.9. From this graph it can be concluded that the impact strength decreases rapidly with increasing amount of PP. Above 30 vol% PP the impact strength of the blend is as low as that of the PP component. Mixing of PS with PP/PE results in blends with low impact strenghts. This impact strength, however, was already low at high volume fractions of PP.

7.4 General discussion

Since most plastic waste is reused for lumber applications it is useful to consider the modulus of the blend as a guideline [18]. The modulus of blends of PE and PP is shown in Fig.7.10. From this Figure it can be deduced that the modulus varies between 200 MPa, which is rather low, and
Figure 7.9: Impact strength versus composition of the PE/PP blends.

Figure 7.10: Young’s modulus versus PP volume fraction for the PE/PP blends with (●) and without 30wt% PS (○)
1200 MPa. The composition of the waste stream is not expected to be constant and in the case of a PE rich waste the modulus of the blend may be too low for lumber applications [18]. The PP fraction in the blend increased the modulus of the blend as shown in Fig.7.10. For design purposes this increase, however, cannot be used, because PP is very sensitive to degradation leading to a lower modulus. In the case of highly degraded PP this increase may be negligible. The use of 30% PS as a reinforcing phase ensures a minimum level of the modulus as shown in Fig.7.10, which is approximately 750 MPa (0.3*2500) if PS is continuous. The impact strength is low even the case of PE/PP blends in which the PP amount exceeds 30%. For lumber applications the impact strength is a less important parameter.

In this chapter a potential approach for reuse of plastics is shown. This approach gives a possibility to ensure certain properties for certain applications. Mixing of the waste stream with PS in an extra processing step seems to increase the costs of this method. This mixing, however, can be a part of the shaping process (e.g. extrusion of tubes or profiles) in one step and the material is not pelletized anymore.

In practice this compounding step is also a part of the process in the case of separated plastics which are usually blended with virgin material. The properties of the recycled materials after separation of the different types of plastics are in most cases deteriorated due to thermal degradation [22,23,24]. Especially polypropylene is very sensitive to degradation. The properties of the recycled polypropylene can be drastically lowered after one or more recyclings steps and it needs to be restabilized by adding new stabilising agents [25,26]. The recycled polypropylene can be blended with virgin polypropylene to obtain a polypropylene with intermediate properties [27]. However, one should realize that this approach can be used only for certain waste streams. Other waste streams may require different methods. E.g. a colorless pure LDPE stream should be reused in shopping bags, whereas darkly colored pure LDPE can be used as garbage bags. Our approach is a possible method for recycling multi-component waste, which is difficult to split up into the pure components.

7.5 Conclusion

Mixing 30 wt% PS with a multi component waste stream will ensure a certain level of the modulus of the blend. This level can be used to define a certain class of products. The impact
strength normally decreases dramatically due to mixing with PS. However, this impact strength was already low for the PE/PP blends at higher PP contents.

The PE/PP blends exhibit a co-continuous morphology within a broad composition range. This co-continuity is lost by mixing these blends with PS due to a decrease of the phase dimensions of either PP or PE phase, leading to breakup.

7.6 References
7. Recycled plastic lumber to be key growth area?; *Plastic in the environment*; 31, 5 (1996)
8. CONCLUDING REMARKS

One of the main aims of this study was to explore methods to obtain a co-continuous morphology in a blend of polystyrene and multi-component plastic waste. Such a co-continuous morphology is expected to ensure high tensile properties. From chapter 1 it can be concluded that the formation of these morphologies and the effect of certain process parameters is poorly understood. For that reason some good defined two component polymer blends were used to study the factors described above.

The formation of the morphology in general and the co-continuous morphology in particular is studied in chapter 2. It was found that the initial morphology consists of sheets which break up by the formation of holes in these sheets. The holes will grow and a network will be formed between these holes. This network may break up leading to a dispersion or remains stable and a co-continuous morphology is formed. So, the sheets are the precursors of this co-continuous morphology. This study gave a better insight in the morphology development in general, too. It was found that the formation of sheets in the initial state quantitatively explains the rapid decrease of the phase dimensions which is often described in literature. The final phase dimensions depend on the breakup of sheets rather than the capillary number used up to now. A proper knowledge of the stability of sheets during processing will give the opportunity to describe the formation of the morphology in general both qualitatively and quantitatively.

The breakup of sheets results in a network of ligaments (fibres) which are more or less randomly oriented. This picture gives in fact some geometrical requirements for co-continuity in a blend, i.e. randomly oriented elongated particles in a matrix, which should be stable. By considering these requirements a model was developed (chapter 3) which describes the composition at which co-continuity is possible as a function of the process parameters such as the viscosities, the interfacial tension, the phase dimensions and the mixing conditions. The effect of these parameters are studied in chapter 3 and 4 and it appears that the effect of these parameters can be predicted successfully by the model.

These new insights give the possibility to control the formation of a co-continuous morphology. By a proper choice of the mixing process and the commercial grades of the blend
components the co-continuous morphology can be obtained within a desired composition range.

The blend once formed during extrusion is usually frozen in to ensure its stability. In a subsequent shaping process, e.g. compression molding or injection molding these blends will be re-melted. In chapter 5 it is described that the morphology starts changing again due to several interfacial processes, such as break-up, retraction and coalescence. The change of morphology in droplet/matrix and fibre/matrix morphologies is rather straightforward. By contrast, the change of a co-continuous morphology appears to depend on the volume fraction. A coarsening of the phase dimensions occurs but above a certain volume fraction these morphologies do not break up into droplets. The morphology is then inherently stable. If the change of the phase dimensions does not affect the desired properties, e.g. modulus, then a rapid solidification of the blend in the mold is not required. If the phase dimensions should remain as small as possible, e.g. to ensure a certain toughness, then this rapid solidification is still required.

The mechanical properties of blends with a co-continuous morphology are described in chapter 6. The moduli of the blends with a co-continuous morphology are high in all directions, whereas those of a fibrillar morphology is only high in one direction. The effect of the co-continuous morphology on strength and strain can not properly be deduced from this chapter. It is clear that other factors such as the fracture mechanism cannot be ignored.

One of the aims of this study was to explore the possibilities of recycling of multi-component polyolefine waste. From chapter 7 it can be concluded that mixing 30 wt% PS with such waste streams will ensure a certain level of the modulus of the blend. This level can be used to define a certain class of products. The impact strength of the material normally decreases dramatically when mixed with PS. However, this impact strength was already low for the PE/PP blends at higher PP contents. However, one should realize that this approach can be used only for certain waste streams. Other waste streams may require different approaches.
SUMMARY

This thesis deals with the formation, stability and properties of polymer blends which exhibit a co-continuous morphology. In chapter 1 a brief discussion is given concerning the co-continuous morphology. Existing mixing theories can be used to some extent to describe the forming of droplets and fibres in a blend by taking into account the effect of the process parameters - e.g. interfacial tension, viscosities, mixing conditions. They, however, are not applicable for co-continuous morphologies, which are usually considered to be simply an intermediate type of morphology. The theories for co-continuity do not incorporate the above parameters and for that reason they usually fail. The stability of polymer blends during annealing can be estimated by taking the above parameters into account. The effect of these parameters in the case of a co-continuous morphology is not as straightforward as that in the case of dispersed structures. The co-continuous structures do not break up above a critical volume fraction. The goal of this study was to explore a possible recycling process for multi-component waste by mixing it with 30 wt% polystyrene leading to a co-continuous morphology. However, several new insights had to be obtained before this study could be done successfully.

In chapter 2 the morphology development in an extruder is studied. The morphology of blends of polystyrene and polyethylene prepared by single screw extrusion and static mixing is shown to consist initially of sheet-like structures and subsequently of co-continuous structures. These co-continuous structures either break up into droplets or threads or become the final morphology depending on the mixing conditions and the rheological properties of the blend. The rapid decrease of phase dimensions during blending can quantitatively be described by deformation of sheets in shear flow and not by deformation of droplets into threads. The final phase dimensions are found to be largely determined by the sheet thickness at the onset of breakup of the sheets. The type of morphology obtained after breakup can change during further processing without changing the phase dimensions significantly.

In chapter 3 a model for phase continuity in polymer blends based on geometrical requirements for co-continuous structures is presented. The minor phase of a fully co-continuous blend is considered as a dispersion of randomly oriented rods at their maximum packing density in the major phase. An existing empirical relation between this packing density and the aspect ratio of the rods in conjunction with micro-rheological requirements for the existence of such rods results in an equation describing the critical volume fraction of the minor phase for complete co-continuity as a function of the matrix viscosity, the interfacial tension, the shear rate and the phase dimensions. This equation naturally leads to a range of compositions within which fully co-continuous structures can exist. It is demonstrated that existing relations between the volume fraction at phase inversion and the viscosity ratio of the blend components are not generally valid. Experimental evidence obtained by blending of polystyrene and polyethylene shows that the new model quantitatively predicts trends in the critical volume fraction as a function of the viscosities of both phases. The critical composition for full co-continuity is found to decrease with increasing viscosity of the matrix phase, leading to a broader composition range. The opposite was found for the effect of the interfacial tension in chapter 4 in blends of polyethylene/polystyrene, polyethylene/propylene and polyethylene/polyamide. The effect of this factor is composed of two counteracting effects, viz. the stability of the co-continuous morphology and the phase dimensions. The latter effect is smaller
than the former. An absolute prediction is not yet possible because the phase dimensions cannot a priori be predicted, but have to be measured.

In Chapter 5 coarsening of the phase dimensions in polymer blends in a compression molding machine is studied in blends of different morphologies demonstrating the dependence of the rate and extent of coarsening on the initial morphology. In blends of polyethylene/polyamide with a droplet/matrix structure coarsening via coalescence is found only above the percolation threshold for spherical particles (16 vol%). The rate of coalescence in the droplet/matrix structure is shown to obey the theory of Fortetny for coalescence of droplets in quiescent media and no constant level of the phase dimensions is reached. Below a volume fraction of 0.16 limited coarsening is found only for fibrillar and co-continuous morphologies in blends of polyethylene/polystyrene. In this case coarsening does not proceed via coalescence but via retraction and break-up. This leads to a droplet/matrix morphology in which no further coarsening is found. In these cases the coarsening of the phase dimensions and a change of structure occurs simultaneously. A critical volume fraction of the minor component within the major component can be distinguished above which the co-continuous morphology in a polymer blend remains stable during annealing of the blend. This critical composition can be understood by depicting the co-continuous structure as an assembly of fibres randomly oriented at their maximum packing density. These fibres have 'coalesced' at their cross-over points. The length of the filament between two cross-over points decreases with increasing volume fraction of the minor phase. At a certain length the dominant wavelength of the sinusoidal disturbances is larger than the length between two cross-over points and the disturbances will not grow further. Consequently, the filament can not break up. The critical volume fraction above which breakup of the co-continuous structure during annealing is not possible, is found to be around 30 vol% of the minor phase. The morphology in immiscible polymer blends also changes during injection molding. If the initial morphology is co-continuous, injection molding of the blends that have been compounded in an extruder leads to coarse and irregular structures, whereas droplet/matrix morphologies remain unchanged. The changes are caused by the long residence time in the injection molding machine, which promotes the breakup and retraction of the continuous minor phase. By using a static mixing element in the nozzle both the co-continuous morphology and the original phase dimensions were recovered.

In Chapter 6 blends of polyethylene/polystyrene and polyethylene/polypropylene which exhibit a co-continuous morphology at various compositions are made to examine the effect of co-continuity on the tensile modulus. The moduli of these co-continuous blends appeared to be high in all directions and reach the value of the upper limit. The yield strength and strain at break are both hardly affected by the existence of the co-continuous morphology. Other factors - e.g. fracture mechanism - should be considered, too, which was not done in this study.

In Chapter 7 it is shown that mixing 30 wt% PS with a multi component waste stream will ensure a certain level of the modulus of the blend. This level can be used to define a certain class of products.
SAMENVATTING

In dit proefschrift worden de vorming, de stabiliteit en de eigenschappen van polymeermengsels met een co-continue morfologie bestudeerd. In hoofdstuk 1 wordt een korte discussie beschreven over de kennis betreffende deze co-continue morfologie. Bestaande mengtheorieën kunnen gebruikt worden om de vorming van druppels en vezels in een mengsel te beschrijven door het effect van de volgende parameters in acht te nemen: grensvlakspanning, viscositeiten en de mengcondities. Ze zijn echter onbruikbaar om de vorming van een co-continue morfologie te beschrijven. Vaak wordt gedacht dat deze morfologie alleen bestaat gedurende een korte tijd in de menger. De theorieën, die wel geacht worden om de vorming van een co-continue morfologie te beschrijven, nemen de bovengenoemde parameters niet mee en zijn daardoor onbruikbaar. Het gedrag van polymeermengsels gedurende ‘annealing’ is niet altijd voorspelijk. In blends met een co-continue morfologie blijkt namelijk een kritische volume fractie the zijn waarboven zo’n morfologie niet opbreekt. De stabilititeit van deze mengsels kan dan niet geschat worden met behulp van bovengenoemde parameters. Het doel van deze studie is het verkennen van een mogelijke herverwerkingsproces voor plastic afval. Aan dit afval wordt 30 w% polystyreen toegevoegd zodanig dat een co-continue morfologie gevormd wordt. Echter, de vorming en stabilititeit van de co-continue morfologie moet dan wel beter begrepen worden.

De vorming van de morfologie in een extruder wordt beschreven in hoofdstuk 2. Het is aangetoond dat in mengsels van polystyreen en polyetheen eerst lagen gevormd worden, die vervolgens opbreken tot een netwerk, de co-continue morfologie. Afhankelijk van de mengcondities en de rheologische eigenschappen van de uitgangsmaterialen zal deze co-continue morfologie opbreken, waardoor de lagen gescheiden worden, of stabiel blijven. De vorming van lagen in de eerste mengstappen verklaart ook de snelle afname van de fase afmetingen in het begin van het mengproces. De uiteindelijke fase afmetingen blijken af te hangen van het moment waarop de gevormde lagen opbreken. De morfologie kan na het opbreken van de lagen nog wel veranderen, maar de fase afmetingen zullen min of meer constant blijven.

In hoofdstuk 3 wordt een model voor fase continuïteit beschreven gebaseerd op de geometrische voorwaarden voor continuïteit. De minderheidsfase van een volledig co-continue morfologie wordt beschouwd als een dispersie van random georiënteerde staven met de maximale pakingsdichtheid in de meerderheids fase. Een combinatie van een bestaande empirische relatie voor deze maximale pakingsdichtheid en de eisen voor stabiliteit van vezels in een mengsel leidt tot een formulering, die de kritische volume fractie in geval van volledige co-continuïteit als een functie van de matrix viscositeit, de grensvlakspanning, de afschuifensnelheid en de fase afmetingen beschrijft. Deze relatie leidt tot een samenstellingssgebied voor volledige co-continuïteit. De bestaande relaties, die de co-continuïteit in een mengsel beschrijven als een functie van de viscositeitsverhouding, blijken niet algemeen geldig te zijn. Experimenten met polystyreen/polyetheen mengsels tonen aan dat het model trends van de volume fractie voorspelt als een functie van de viscositeiten van beide fase in plaats van alleen de viscositeitsverhouding. De kritische volume fractie neemt af als de matrix viscositeit toeneemt wat kan leiden tot een breed samenstellingssgebied voor co-continuïteit. In hoofdstuk 4 wordt een tegenovergesteld effect van de grensvlakspanning beschreven in mengsels van polyetheen/polystyreen, polyetheen/polypropaan en polyamide/polyetheen. De grensvlakspanning bepaalt zowel de stabiliteit van de co-continue morfologie (direct effect), als de
fase afmetingen in het mengsel (indirect effect). Het effect van de laatste parameter op de stabilititeit van de co-continue morfologie blijkt in dit geval echter minder sterk te zijn. Omdat de fase afmetingen pas gemeten worden nadat het mengsel gevormd is, is een voorspelling van de kritische samenstelling a priori niet mogelijk.

In hoofdstuk 5 wordt de stabilititeit van polymeer mengsels beschreven. De mate en de snelheid van vergroeiing van de fase afmetingen in een gesmolten mengsel in een pers blijken afhankelijk te zijn van de morfologie in dit mengsel. In polyetheen/polyamide mengsels met een druppel/matrix morfologie wordt de vergroeiing voornamelijk veroorzaakt door coalescentie van de druppels. Coalescentie blijkt echter alleen plaats te vinden boven de percolatie grens van druppels (16 vol%). De snelheid van coalescentie kan dan beschreven worden met behulp van een theorie van Fortelny. Experimenten met polystyreen/polyetheen mengsels tonen aan dat bij volumefracties, die kleiner zijn dan deze percolatiegrens voor druppels, slechts een beperkte vergroeiing plaats vindt in blends met een vezel/matrix of een co-continue morfologie. De vergroeiing wordt in dit geval veroorzaakt door retractie en opbreken van de morfologie tot een druppel. Naast een beperkte vergroeiing verandert dan ook de structuur. Als de volumefractie van de minderheidsfase toeneemt dan vertonen mengsels met een co-continue morfologie boven een kritische volumefractie een afwijkend gedrag. Ze breken niet meer op. Deze kritische volumefractie kan geschat worden door de geometrische eisen van het model beschreven in hoofdstuk 3 in acht te nemen. De staven in dit model zullen op de plaatsen waar ze elkaar raken samengevlooid zijn. De lengte van een filament tussen deze raakpunten wordt kleiner bij een toenemende volumefractie van de staven. Op een bepaald moment kunnen de sinusvormige verbuigingen niet meer gevormd worden omdat de golflengte kleiner is dan de lengte tussen twee raakpunten. De staven kunnen dan niet opbreken. Deze kritische volumefractie is ongeveer 30 vol% van de minderheidsfase. Gedurende het spuitgieten van mengsels blijkt een mengsel met een druppel/matrix morfologienuwelijk te veranderen, terwijl in een mengsel met een co-continue morfologie onregelmatige en grote structuren gevormd worden. Deze vergroeiing is het gevolg van de lange verblijftijd in de spuitgietmachine, waardoor de continue minderheidsfase kan opbreken. Het plaatsen van een statische mengel in de spuitmond blijkt zowel de gewenste afmetingen als de gewenste morfologie terug te winnen.

In hoofdstuk 6 worden polyetheen/polystyreen en polyetheen/polypropaan mengsels met een co-continue morfologie bij verschillende samenstellingen bestudeerd. De modulus van de blends met een co-continue morfologie is hoog in alle richtingen en ze bereiken het niveau van de moduli berekend met het parallel model. De zwichtspanning en de breukrek worden echter niet beïnvloed door de continuïteit van de minderheidsfase. Andere factoren, zoals het breukmechanisme, moeten ook in acht genomen worden. Dit is niet gedaan in deze studie.

In hoofdstuk 7 wordt aangetoond dat het mengen van 30 vol% polystyreen in een meer-fase mengsel een bepaald niveau van eigenschappen zal garanderen. Dit niveau kan gebruikt worden om een bepaald type produkt te definiëren.
CURRICULUM VITAE

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