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Co-continuous morphologies in polymer blends: the influence of the interfacial tension

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Abstract

The influence of the interfacial tension on the composition range within which fully co-continuous polymer blend structures can exist is studied for different blends with selected matrix viscosities and viscosity ratios. The critical composition for full co-continuity is found to increase with increasing interfacial tension, narrowing the composition range. The effect of the interfacial tension on the critical composition is composed of two counteracting effects, i.e. the stability of the co-continuous morphology and the phase dimensions. The latter effect is smaller than the former. The experimental results can quantitatively be predicted by a model published earlier, provided the phase dimensions are measured separately. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Co-continuous morphology; Interfacial tension

1. Introduction

Blending of polymers is an effective way to obtain materials with specific properties. Most polymers are immiscible, therefore blending usually leads to heterogeneous morphologies. The type and dimensions of the morphology determine the properties of the blend. The type of morphology, which is formed during processing, depends on the nature of the polymers (interfacial tension, viscosities and the ratio of these viscosities), their volume fractions and the processing conditions. Of all possible morphologies, the co-continuous morphology shows an unique combination of the characteristics of both polymer components [1–3].

A co-continuous morphology is a non-equilibrium morphology that is generated during mixing of two polymers. As such, it is an unstable morphology, and it starts changing through filament break-up and retraction as soon as the fluid blend comes out of the mixer. However, the blend may remain co-continuous, if it is frozen fast. Considerable attention has been given to the conditions that make co-continuous morphologies possible in blends during the mixing. It has been generally suggested that co-continuity occurs at the phase inversion point. Existing empirical relations [4–6] and theories [7,8] give a volume fraction for phase inversion as a function of the viscosity ratio, as shown in Fig. 1. However, many experimental results [9] cannot be described with these relations (Fig. 1). By basing the phase inversion point on the viscosity ratio of the components only, these relations neglect the influence of the blending conditions and material properties, e.g. the interfacial tension. Moreover, 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, a co-continuous network can only exist if the minor blend component consists of structures with an extended shape [9]. These structures can be formed and remain so only under appropriate blending conditions. For this reason, it is to be expected that the existence of a co-continuous morphology in the blend will be strongly dependent both on the processing conditions, e.g. the stress levels, and the processing properties of the blend components, e.g. the matrix viscosity, viscosity ratio and interfacial tension. In a previous paper [9], an equation has been derived that describes the critical volume fraction of the minor phase for complete co-continuity as a function of the matrix viscosity, interfacial tension, shear rate and phase dimensions, and it was shown that a high viscosity of the matrix component was favourable for co-continuity over a broad composition range in blends of commercial grades of polyethylene and polystyrene. In the present paper, we examine the influence of the interfacial tension. Results for the following blend systems: polyethylene/polystyrene, polyethylene/polyamide and polyethylene/polypropylene will be compared with the predictions by the model.

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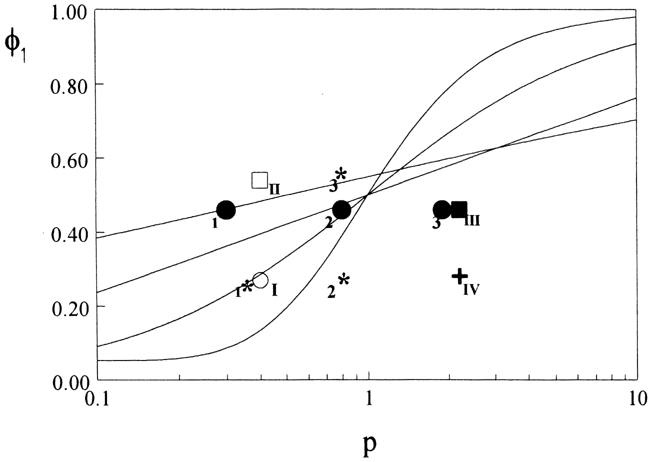

Fig. 1. Phase inversion as a function of the viscosity ratio, $p = \eta_d/\eta_m$, according to several empirical relations summarized in Ref. [9]. * and ●: points found for PE/PS systems in Ref. [9]. □, ○, ■ and + : points corresponding to series I–IV, respectively, described in this paper.

2. Theory

In this paragraph, a summary is given of the theory in Ref. [9], which describes the composition limits within which co-continuous morphologies are to be expected, and a brief description of the dual role of the interfacial tension. Our study concerns polymer blends with fully co-continuous structures, i.e. both phases form single continuous interpenetrating structures. For low volume fractions of either component, a fully continuous structure can exist only if it is made up of extended structures. The continuous minor phase is depicted as an assembly of rod-like particles randomly oriented and at their maximum packing density inside the matrix (major component). At this packing density, all the rods have touched each other and have 'coalesced' at their cross-over points. This picture is, admittedly, a gross simplification, but it captures the essential geometrical conditions for the minor phase to become continuous. This type of geometry is the prerequisite for full co-continuity.

The maximum packing density (ϕ_{max}) of randomly oriented rods depends on their aspect ratio L/B, where L is the length and B is the diameter of the particle [10]:

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

The existence and stability of the elongated structures in the blend are determined by the value of the capillary number [9]:

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

with σ the interfacial tension, η_m the viscosity of the matrix phase and $\dot{\gamma}$ the shear rate. At high values of Ca, the shear stress, $\eta_m\ \dot{\gamma}$, overrules the interfacial stress, σ/B, and the particles are stretched (distributive mixing). As L/B increases, Ca decreases. When a critical value, $Ca = 1$, is reached [11], the interfacial stress destabilizes the elongated particles and break-up occurs (dispersive mixing). This indicates that the minimum value of B, for which the cylindrical particles are still stable, can be found from Eq. (2) by setting $Ca = 1$.

In order to relate the capillary number to the maximum packing density of the elongated structure, Eq. (2) ($Ca = 1$) together with the condition for the conservation of the volume of the extended particle:

$$\frac{B}{2R_0} = \left(\frac{2}{3}\right)^{1/3}\left(\frac{L}{B}\right)^{-1/3} \tag{3}$$

are combined with Eq. (1).

The final relation is [9]:

$$\frac{1}{\phi_{d,cc}} = 1.38 + 0.0213\left(\frac{\eta_m \dot{\gamma}}{\sigma} R_0\right)^{4.2} \tag{4}$$

Eq. (4) 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. 2 shows the limit for co-continuity ($\phi_{d,cc}$) according to Eq. (4) as a function of ($\eta_m\ \dot{\gamma}/\sigma$) and R_0, a size which is determined by the particulars of the blending process. The experimental data in Fig. 2 correspond to that in Fig. 1. The three points $●_{1,2,3}$ of Fig. 1 become one in Fig. 2, because the different blend systems have the same matrix phase and interfacial tension. This is also the case in the blends corresponding to $*_1$ and $*_2$. The results of the present study will be shown separately (Fig. 5), because they largely overlap with the other data points.

Eq. (4) 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. Eq. (4) does not include the viscosity ratio as an independent variable, whereas the empirical relations shown in Fig. 1 show a dependency of $\phi_{d,cc}$ on this ratio only. In our model, for a given viscosity

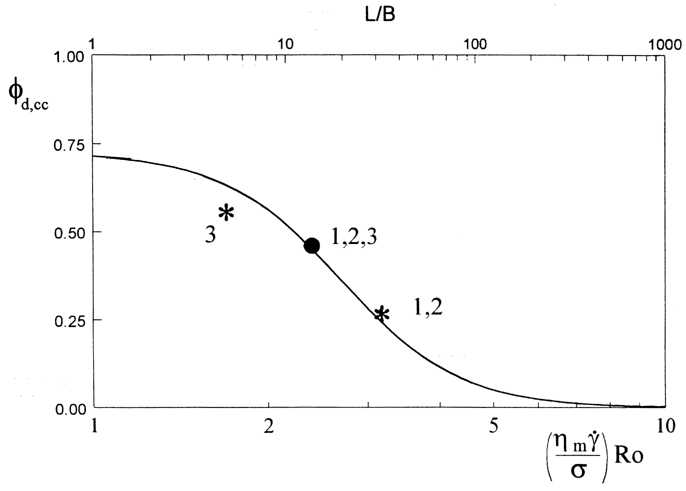

Fig. 2. Composition for the onset of full co-continuity as a function of $\eta_m \dot{\gamma}/\sigma$ and R_0 [9] according to equation (4) (solid line); ($\bullet_{1,2,3}$) corresponds to points $\bullet_1$, $\bullet_2$ and $\bullet_3$ in Fig. 1, because the matrix viscosity and interfacial tension are the same. The points $*_{1,2}$ and $*_3$, correspond to $*_1$, $*_2$ and $*_3$ in Fig. 1, respectively.

ratio, different values of $\phi_{d,cc}$ can be obtained depending on the choice of η_m or η_d. This explains why the experimental results can not be described by the relations shown in Fig. 1. In fact, all sorts of dependencies of $\phi_{d,cc}$ on the viscosity ratio can be obtained experimentally, depending on the way in which the variables, e.g. η_d and η_m are varied in the experiments, as was shown in Ref. [9].

From Fig. 2 and Eq. (4), it can be seen that the volume fraction at which co-continuity is possible decreases as the matrix viscosity (η_m) increases, and co-continuity becomes possible over a wider range of compositions for the same phase size. This was verified experimentally in Ref. [9]. The value of R_0 and the resulting diameter B calculated from Eq. (3) appeared to correspond to the minimum phase dimensions found in the blends during mixing [9].

The influence of the interfacial tension on composition range is two-fold. 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), 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 $\phi_{d,cc}$ 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 $\phi_{d,cc}$. This indirect effect can, as yet, not be quantified. It can be accounted for in Eq. (4) by measuring the phase dimensions separately afterwards. The direct effect is stronger than the indirect effect, as will be shown below.

3. Experimental

The polymers that were used to form the experimental blends are shown in Table 1. Four series of blends (I, II, III and IV) were made, each consisting of five blends with volume fractions of about 10–50 vol% of the minor component. Their characteristics are listed in Table 2.

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 s^{-1} and temperatures of 200 and 250°C (the conditions inside the mixer) are also shown in Table 1.

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 four channels with a radius of 1.35 mm [9]. The average shear rate in the channels was estimated to be 22 s^{-1}. The extruded strands were

Table 1
Trade names and shear viscosities at $\dot{\gamma} = 22\ s^{-1}$ of the polymers used

Sample code	Trade name (manufacturer)	Viscosity (Pa.s) at 200°C	Viscosity (Pa.s) at 250°C
PS1	Hostyrene N2000 (Shell)	780	160
PS2	Hostyrene N7000 (Shell)	2690	1154
PE1	Stamylan LD 2100TN00 (DSM)	1860	1210
PE2	Stamylan LD 2102TN26 (DSM)	960	540
PA6	Akulon K 136 (DSM)	-	1500
PP	Stamylan PP 19MN10 (DSM)	450	-

Table 2
Blend components, processing temperature, interfacial tension, viscosity ratio, matrix viscosity of the prepared blends and the lower limits of co-continuity measured experimentally

Series	Blend components	Temperature (°C)	σ (mN/m)	Viscosity ratio	η_m (Pa.s)	$\phi_{d,cc}$ (%)
I	PS1 in PE1	200	4.5^{a}	0.4	1860	27
II	PE2 in PA6	250	10.7^{a}	0.4	1500	56
III	PS2 in PE2	250	3.5^{b}	2.1	540	46
IV	PE1 in PP	200	0.8^{b}	2.1	445	28

[a] From Ref. [22].
[b] From Ref. [23].

quenched in water. PA6 was dried before mixing for seven days in a vacuum oven at 80°C.

Co-continuity in the blends was checked by extraction experiments [12]. The strands were broken in liquid nitrogen, and extraction of the PS (in PS/PE blends) or PE (in PE/PP and PE/PA6 blends) was performed in a Soxhlet extraction apparatus with 2-butanon (PS) or iso-octane (PE) for three days. This was sufficient for the complete removal of the soluble fraction. The samples were checked as to 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 (in PS/PE) or 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 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 50–100 measurements of the holes resulting from the extraction.

4. Results and discussion

The main experimental results for the different series are summarized in Table 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 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, e.g. 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.

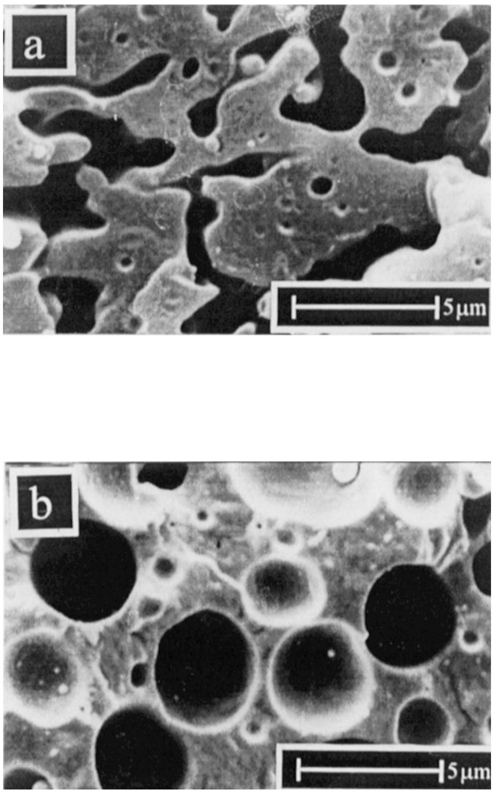

Fig. 3. Scanning Electron Micrographs of blends of: (a) series I with 35 vol% PS in PE; and (b) series II with 33 vol% PE in PA6.

4.1. A high matrix viscosity

Series I and II are compared here. They both have a matrix with a relatively high viscosity, but they differ in their values of the interfacial tension. Both from the SEM pictures (Fig. 3) and the extraction measurements (Fig. 4), it

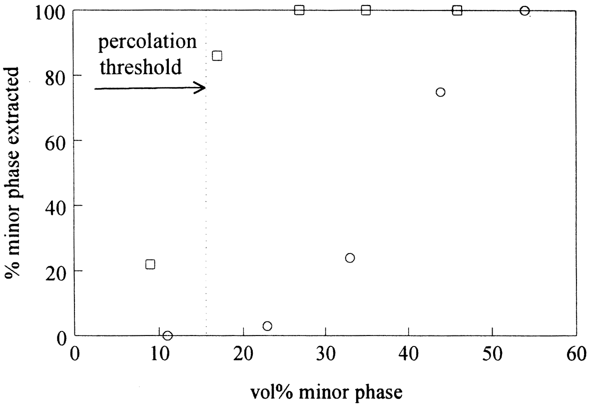

Fig. 4. %PS (□) and PE (o) extracted from the blends of series I and II, respectively, as a function of the blend composition.

Table 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

Series I (PS/PE)				Series II (PE/PA)			
Vol% PS	B (μm)	% PS extracted	Ca_{min}	Vol% PE	B (μm)	% PE extracted	Ca_{min}
9	0.43 ± 0.17	22	1.2	11	1.41 ± 1.01	0	0.6
17	0.49 ± 0.16	86	1.4	23	1.59 ± 1.31	3	0.5
27	0.61 ± 0.33	100	1.3	33	1.88 ± 1.28	24	1
35	0.84 ± 0.35	100	2.2	44	2.21 ± 1.32	75	1.5
46	0.99 ± 0.39	100	2.8	54	—	100	> 1

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.

The value for the minimum capillary number is shown in Table 3, calculated from the number average value of B minus its standard deviation. It can be seen in this table that all blends in this series have experienced distributive mixing ($Ca_{\mathrm{min}} > 1$). Although the minimum capillary number is larger than 1, no co-continuity is found at volume fractions lower than 27 vol% PS in PE. The measured phase dimensions at these compositions, however, are not only filament thicknesses, but also the diameters of droplets formed by break up of the thinnest filaments. When a filament breaks up in a series of droplets, these droplets have twice the diameter of the original filament. This leads to an apparently higher minimum capillary number [9].

The results can be described with Eq. (4) by using $2R_0 = 0.7$, as shown in Fig. 5. From this value, the filament thickness of the PS phase, B, can be calculated, which is still stable in the case of co-continuity. Solving Eq. (1) for $\phi = 0.27$ and putting the result into Eq. (3) with $2R_0 = 0.7\ \mu$m gives $B = 0.23\mu$m. 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 3) [9].

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)] are both evident in the comparison of series I and II. Comparing the SEM pictures, shown in Fig. 3, 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 those in blends of series I (Table 3). By introducing $2R_0 = 1.4\ \mu$m, which is twice the value of $2R_0$ in series I, in Eq. (4), 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 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 was the case in series I.

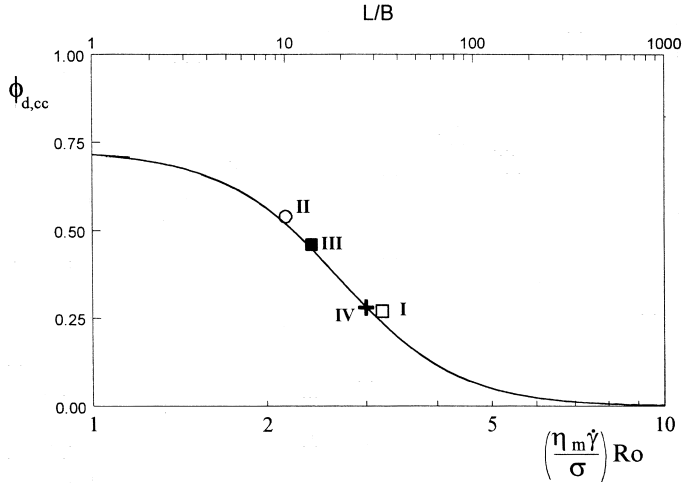

Fig. 5. Composition for onset of full co-continuity as a function of $\eta_m\,\dot{\gamma}/\sigma$ and R_0 according to equation (4); experimental results of series I (□, $2R_0 = 0.7\ \mu$m), II (○, $2R_0 = 1.4\ \mu$m), series III (■, $2R_0 = 1.4\ \mu$m) and IV (+ , $2R_0 = 0.5\ \mu$m).

The volume fractions at which full co-continuity begins in both systems are shown in Fig. 1. The older empirical relations cannot describe these results. In Fig. 5, a comparison of the experimental results with calculations using Eq. (4) is shown (□, ○). The parameter R_0 (which is proportional to the minimum phase dimensions found in the two systems), differs by a factor of 2, which is also measured in the SEM pictures of the 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 a high interfacial tension will lead to a small range at which co-continuity is possible.

In addition to the different compositions 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 none of the minor component can be extracted from the PE/PA6 blends. Lyngaae-Jørgensen and Utracki [12] 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 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.

4.2. 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) and the SEM pictures (e.g. Fig. 6*a*). 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. 6*a*). The 46 vol% PS blend has experienced distributive mixing, and a co-continuous morphology is indeed found at this composition.

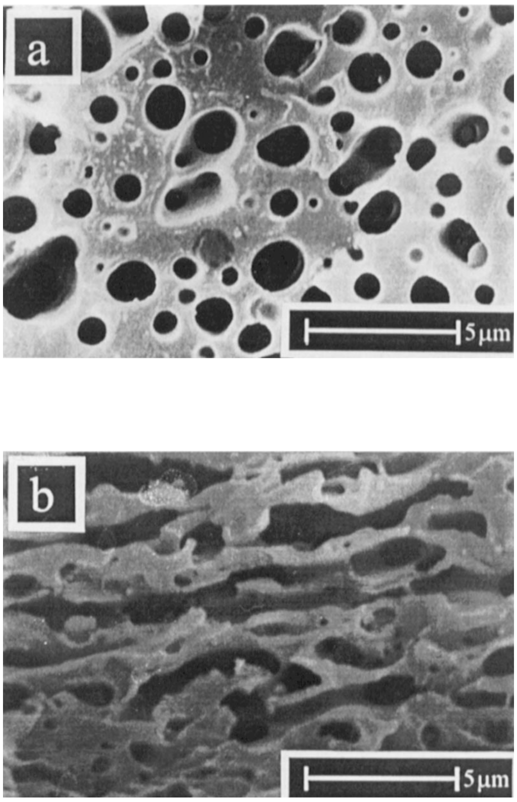

Fig. 6. Scanning Electron Micrographs of blends of: (a) series III with 35 vol% PS in PE; and (b) series IV with 37 vol% PE in PP.

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 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. 6*a* 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. 6*b*. The minimum phase dimensions found in series IV in the case of co-continuity are smaller than those found in series III, see Table 4. The calculated minimum capillary

Table 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

Series III (PS/PE)				Series IV (PE/PP)			
Vol% PS	*B* (μm)	%PS extracted	$Ca_{\min}$	Vol% PE	*B* (μm)	%PE extracted	$Ca_{\min}$
9	0.51 ± 0.21	16	0.5	9	0.43 ± 0.18	76	1.5
17	0.63 ± 0.27	16	0.6	18	0.40 ± 0.15	70	1.5
27	0.59 ± 0.22	62	0.6	28	0.54 ± 0.25	100	1.8
35	0.80 ± 0.36	86	0.7	37	0.69 ± 0.37	100	2.0
46	1.48 ± 0.67	100	1.4	47	1.05 ± 0.48	100	3.5

numbers are also shown in Table 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, 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 the break-up of the thinnest filaments during mixing have twice the diameter of the original filament. This leads to an apparently higher minimum capillary number [9], as was already discussed above. Calculations using Eq. (4) are shown in Fig. 5. The blends of series III are described with a value of $2R_0 = 1.4\ \mu\text{m}$, while series IV are described using a value of $2R_0 = 0.5\ \mu\text{m}$ (■, +).

5. General discussion

The experiments described in this paper 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 [4–8], in which the viscosity ratio is the only parameter, cannot account for this effect. It is, however, predicted correctly by the model described in this paper.

The interfacial tension plays a two-fold role in this model. First, it determines the stability of the extended structures required for obtaining full co-continuity, in conjunction with the matrix viscosity and shear rate. It enters directly into the model via the capillary number: an increasing value of σ will decrease the value of $\phi_{\mathrm{d,cc}}$ in Eq. (4) if other paremeters are kept constant. Second, σ 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 [13–15]. There is growing evidence that blend morphologies are usually generated via the mechanism of sheet formation [16–19]. The final phase dimensions appear to be determined by the process of sheet break-up. This sheet break-up occurs at a critical sheet thickness due to the growth of interfacial disturbances on the sheet surface. It is to be expected that these interfacial disturbances depend on micro-rheological paramaters (e.g. viscosity and interfacial tension) and on the process conditions, in a fashion not yet fully understood [20,21]. After sheet break-up, the phase dimensions do not change very much [19].

The effects of the phase dimensions and interfacial tension on $\phi_{\mathrm{d,cc}}$ are counteracting and can even cancel each other out. From the results presented in this paper, 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 small 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.

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 a model published earlier provided the phase dimensions are measured separately.

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