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Co-continuous morphologies in polymer blends with SEBS block copolymers

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Abstract

Stable co-continuous morphologies are found over a wide composition range in blends of styrene/(ethylene–butylene) based block copolymers (SEBS) and polypropylene (PP) when they are processed below the block copolymer's order–disorder transition (ODT), i.e. when the block copolymers are microphase-separated. Blending at higher temperatures, i.e. when the block copolymer shows a single-phase melt, also leads to a reasonably wide composition range of co-continuity but when annealing takes place at these temperatures the blends show an increase in their phase domains and the composition range decreases significantly. Annealing of the co-continuous PP/SEBS blends when the block copolymers are microphase-separated hardly influences the phase sizes and composition range. Blending the same block copolymers with polymethyl methacrylate or polyoxymethylene, leading to blends with much higher interfacial tensions, results in a much smaller composition range of co-continuous morphologies than was found in the PP/SEBS blends, whatever the processing temperature be. It is demonstrated that breakup and retraction can be severely limited or even stopped at lower blending temperatures, therefore fulfilling the condition for stability of co-continuous morphologies. The (non-)breakup or (non-)retraction behaviour of elongated structures strongly depends on a complex combination of parameters, including phase size, yield stress and interfacial tension. Therefore the formation of stable co-continuous morphologies also strongly depends on these parameters. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Co-continuous morphology; Blends; Block copolymer

1. Introduction

Blending of thermoplastic polymers is an elegant method to obtain new materials. The properties of these polymer blends are to a large extent determined by the morphology, i.e. the size, shape and distribution of the components [1]. Factors governing the morphology are composition, interfacial tension, processing conditions and rheological properties of the components. In general, polymer blend morphologies can be divided into three classes, i.e. dispersed, stratified and co-continuous morphologies. Dispersions of droplets of the minor phase in a matrix of the major phase are most common. These types of blends are often used in rubber modification of brittle polymers [1–4]. The minor phase can also be dispersed as fibres, for example in self-reinforcing polymer blends [5–7]. In these kinds of blends the properties are mainly improved in the direction of the fibres. Stratified morphologies are developed to enhance barrier properties [8]. We are interested in co-continuous morphologies because an interesting feature of these morphologies is that both the components, in all directions, can fully contribute to the properties of the blend.

It was long believed that co-continuous morphologies are mainly formed close around the point of phase inversion. In earlier articles we have shown that co-continuous morphologies are not formed at a single volume fraction, such as a point of phase inversion, but rather over a range of volume fractions [9–13]. This range of volume fractions strongly depends on the processing conditions and the rheological properties of the components.

The condition for the formation of co-continuous morphologies, especially at low concentrations, is the existence of stable elongated structures that do not show breakup or retraction, whatever their origin (there is some discussion in the literature, whether the formation of polymer blends proceeds via the droplet deformation/breakup mechanism [14, 15] or by a sheet forming mechanism [16, 17]). A co-continuous morphology can be depicted by an interconnection of these stable elongated structures.

These elongated structures in co-continuous morphologies are in fact non-equilibrium states in quiescent conditions and will change form because of the interfacial tension. There are several interfacial tension driven

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Table 1
Blends, processing temperatures (T_p) and interfacial tensions (σ)

System	Blends	T_p (°C)	σ (mN/m)
I	PP/SEBS 1657	190°C, 250°C	0.9[a]
II	PP/SEBS 1652	210°C	—
III	PMMA/SEBS 1657	190°C, 250°C	2.9[a]
IV	PMMA/SEBS 1652	210°C	—
V	POM/SEBS 1657	190°C	13.8[b]
VI	POM/SEBS 1652	190°C	

[a] Determined at 250°C with the breaking thread method.
[b] Determined at 230°C with the breaking thread method.

mechanisms by which a fibre can change shape, including Rayleigh distortions [18–20], retraction and end-pinching [21, 22]. We have shown that these mechanisms are important, not only in the formation [13] of polymer blends but also for the stability [13, 23] of non-equilibrium morphologies during further processing.

An interesting feature of blends with thermoplastic elastomers (TPEs) is that co-continuous morphologies can be obtained over a wide composition range [11–13]. In an earlier article [13] the formation of such a wide composition range was related to the specific rheological properties of a poly(ether–ester) multiblock copolymer. Crystallization of the PTMT blocks in this specific TPE leads to phase separation into micro-domains. These phase-separated domains, acting as physical crosslinks, are responsible for the unique (rheological) properties of the poly(ether–ester) [24]. A detailed knowledge of the rheological and thermal properties of the poly(ether–ester), related to the specific microstructure, enabled us to control the formation and stability of co-continuous morphologies [13, 23]. Another interesting feature is that the network structures of TPEs can stabilize the blend morphology against interfacial tension driven coarsening during further processing because of the resistance to retraction [25, 26] or the presence of a yield stress in the melt [27, 28].

The objective of this article is to examine in which way the interfacial tension and specific rheological properties of SEBS block copolymers, related to the presence of amorphous micro-domains, affect the formation and stability of co-continuous morphologies in blends with SEBS block copolymers. Therefore two SEBS block copolymers are blended with several pseudoplastic polymers, resulting in blends with different interfacial tensions. The formation and stability of co-continuous morphologies as well as the range of compositions where co-continuous morphologies are found will be related to the interfacial tension driven processes, such as breakup and retraction of polymer fibres.

2. Experimental

2.1. Materials

The polymers used were a polyoxymethylene (POM Delrin 150; DuPont) a polymethyl methacrylate (PMMA LG 156; ICI), two polypropylenes (PP Stamylan P13E10 and PP Stamylan 19MN10; DSM) and two styrene/(ethylene–butylene) based block copolymers (SEBS Kraton G1652 and SEBS Kraton G1657; Shell). The SEBS G1652 is a triblock copolymer with a styrene to rubber ratio of 29/71 wt.%. The SEBS G1657 has a styrene to rubber ratio of 13/87 wt.% and it consists of 65% triblock and 35% diblock.

2.2. Rheology

Flow curves were determined with a twin-bore capillary rheometer (Rosand RH 7/8-2) in the shear rate region 10^1–$10^3\ s^{-1}$. The capillaries had a diameter of 1 mm and lengths of 4 and 20 mm. Bagley and Rabinowitsch corrections were applied on all results.

Dynamic shear experiments were performed on a Rheometrics RMS 800 rheometer in the plate–plate configuration with a plate diameter of 25 or 50 mm and a gap of 2 mm. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were measured as a function of temperature in the frequency range of 10^{-2}–10^2 rad/s with a strain varying from 0.1% to 5%. It was made sure that all the experiments were done in the linear viscoelastic regime. Steady shear experiments were performed on the same apparatus, now operating in the cone–plate configuration. Measurements were carried out in the low shear rate range (10^{-4}–$10^{-1}\ s^{-1}$).

2.3. Processing

Blends were prepared over the total composition range with steps of 10 vol% on 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 four channels with a radius of 0.135 cm. The average shear rate in the channels was estimated to be $30\ s^{-1}$. The extruded strands were quenched in water. Samples were annealed in a compression moulding apparatus, without applying pressure on the samples, and subsequently quenched in water. The prepared blends, processing temperatures (T_p) and interfacial tensions (σ) calculated from breakup experiments are shown in Table 1.

2.4. Morphology

The morphology was characterized by means of a Philips XL20 scanning electron microscope (SEM) and extraction experiments. The SEBS phase was extracted with a selective solvent, i.e. *iso*-octane for the blends with PP and POM and cyclohexane for the PMMA blends. The combination of extraction experiments and SEM is essential in determining whether a blend is co-continuous or not. A blend is only considered fully co-continuous if 100% of one component

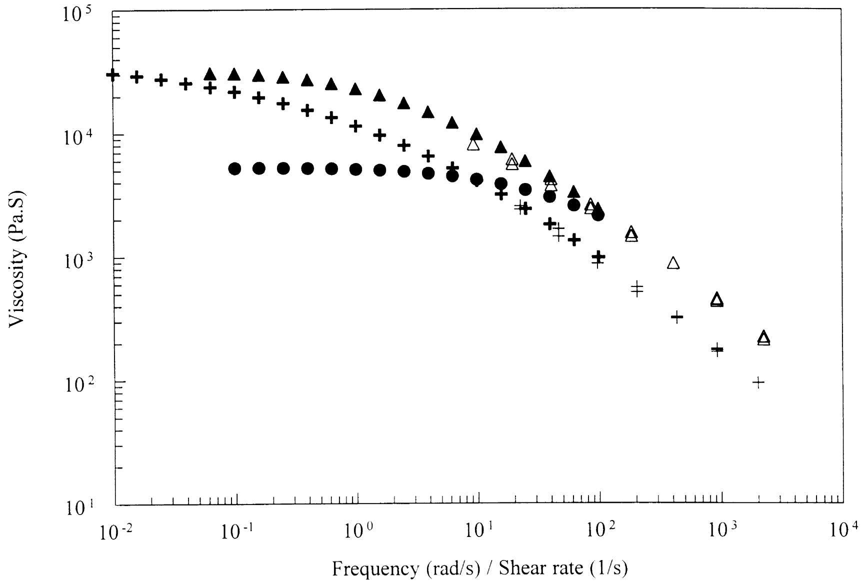

Fig. 1. Viscosity as a function of frequency/shear rate of PMMA (▲, △), POM (●) and PP (✚, +) determined at 190°C, with results from the capillary viscometer designated with open symbols and the results from the plate–plate rheometer designated with filled symbols.

can be extracted and the remaining piece is still self-supporting.

2.5. Breakup and retraction

Fibres of PP 19MN10, PMMA and POM were obtained by melt spinning from a capillary rheometer. The SEBS 1657 block copolymer was compression moulded in 1 mm thick plates to serve as matrix component. Before the materials were used it was made sure that no residual stresses were present by allowing the matrix as well as the fibres to relax for 24 h in a vacuum stove, after they had been cleaned with alcohol. Great care was taken to avoid contamination in further actions. A sandwich was made of, from the inside to the outside, the fibre, matrix, a glass slide and a piece of silver-foil. The sandwich was placed in a hot stage with a Mettler temperature control that was mounted under an optical microscope (Jenapol), and heated to the experiment's temperature. The microscope was equipped with a video camera. The experiments were recorded on a VHS video recorder, from which video prints could be made. Short fibres were obtained by simply cutting a long fibre into small pieces with a sharp surgeon's knife.

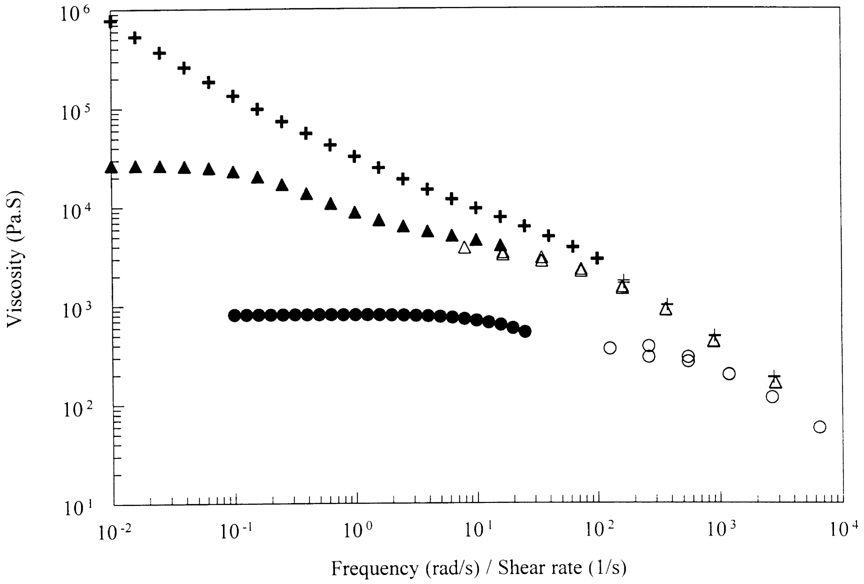

Fig. 2. Viscosity as a function of frequency/shear rate of SEBS 1657 determined at 190°C (▲, △) and 250°C (●, ○) and of SEBS 1652 determined at 210°C (✚, +), with results from the capillary viscometer designated with open symbols and the results from the plate–plate rheometer designated with filled symbols.

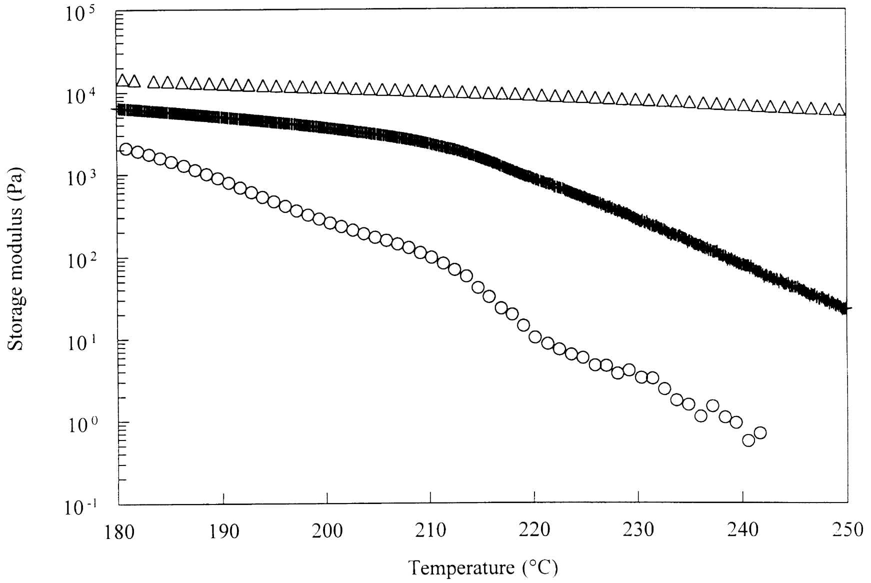

Fig. 3. Storage modulus vs. temperature of SEBS 1657 measured at 0.1 rad/s (○) and 1.0 rad/s (+), and SEBS 1652 measured at 0.1 rad/s (△).

3. Results and discussion

3.1. Rheology of the polymers

The used POM, PMMA and PP show normal pseudoplastic behaviour, at all measured temperatures (only 190°C is shown for the sake of clarity), when the viscosity is plotted as a function of frequency/shear rate, i.e. shear thinning at the highest shear rates and frequencies measured and a Newtonian flow behaviour at low frequencies (Fig. 1). The Cox–Merz rule is applicable in all the cases, i.e. the measured shear viscosity and complex viscosity overlap perfectly.

The viscosity plotted as a function of frequency/shear rate for the SEBS block copolymers is shown in Fig. 2. At 250°C the SEBS 1657 melt behaves comparable to the other pseudoplastics, with a Newtonian plateau at low shear rates and shear thinning behaviour at higher rates. When the experiment temperature is 190°C an extra shear thinning region is evident between 0.1 and 1.0 rad/s indicating that at this temperature the blocks are phase-separated into amorphous domains. The curve for the SEBS 1652 shows shear thinning behaviour over the complete range of frequencies and shear rates measured. Again this is a strong indication of melt structure and the extreme shear thinning behaviour at low shear rates can be associated with a melt yield stress.

The temperature at which the microphase-separated state changes into a single-phase state is called the order–disorder transition (ODT) or microphase separation transition (MST). This transition can be found by two different

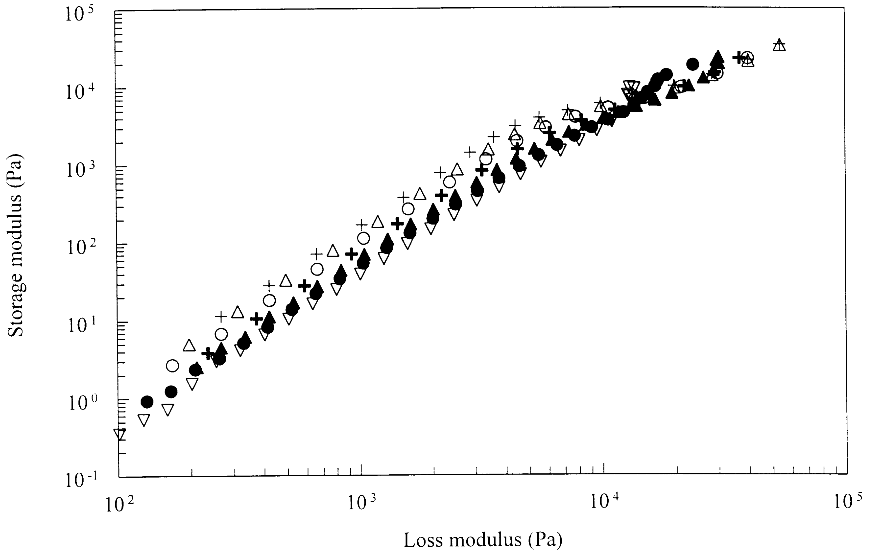

Fig. 4. Storage modulus vs. loss modulus of SEBS 1657 measured at 190°C (+), 200°C (△), 210°C (○), 220°C (+), 230°C (▲), 240°C (●) and 250°C (▽).

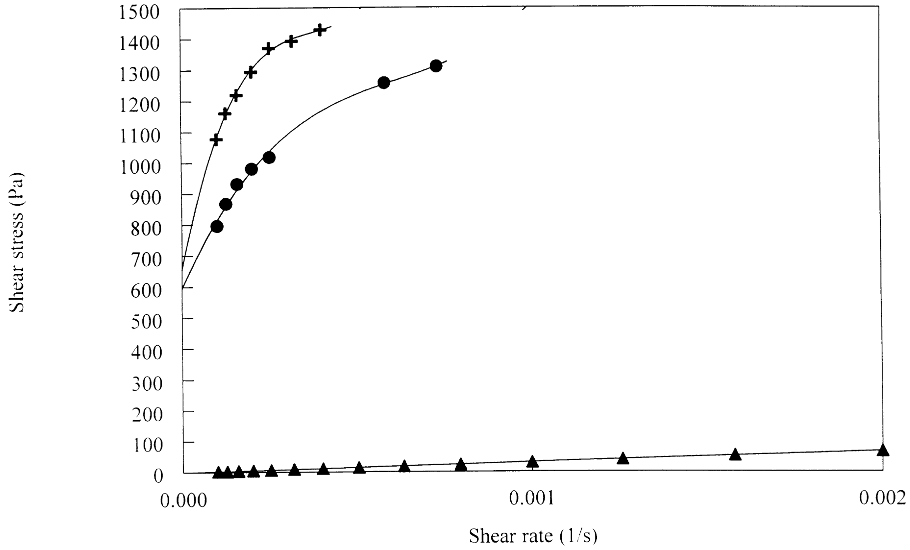

Fig. 5. Shear stress as a function of shear rate of SEBS 1657 determined at 190°C (▲) and of SEBS 1652 determined at 190°C (+) and 210°C (●).

rheological methods. The first method, suggested by Han et al. [29–31], is to plot the storage modulus (G') versus the loss modulus G''. For polymer microstructures changing with temperature different curves of G' versus G'' are expected. If the microstructure does not change with temperature, as is the case in a homogeneous melt, the curves should coincide. The temperature at which curves of G' versus G'' ceases to vary with temperature can therefore be regarded as the ODT. The second method is to measure the storage modulus (G') as a function of temperature [32–38]. The ODT can be identified by a sharp drop in the storage modulus upon heating.

Fig. 3 shows the plots of the storage modulus vs. temperature for SEBS 1657 and SEBS 1652. There is a distinct change in the slope between 210°C and 220°C of the curve of the storage modulus of SEBS 1657. By extrapolating the curve sections below 210°C and above 220°C to their intersection we obtained an ODT of 212°C for the SEBS 1657 block copolymer. When the storage modulus of SEBS 1652 is plotted versus temperature there is no change in the slope and therefore this block copolymer does not show an ODT, in the sense that in this temperature range the block copolymer stays microphase-separated.

The storage modulus of the SEBS 1657 is plotted as a function of the loss modulus in Fig. 4 for a range of temperatures. The curves show a temperature dependence up to at least 230°C meaning that according to Han's criterion the ODT for this polymer should exceed 230°C, which is a much higher temperature than that derived from Fig. 3. It was shown by other authors [32, 33, 37] that using the Han method can lead to an overestimation of the ODT which they related to the persistance of composition fluctuations well into the single-phase region.

It can be concluded though that the SEBS 1657 block copolymer is microphase-separated at temperatures below 212° and that SEBS 1652 does not show a single-phase melt at all temperatures measured. Proper knowledge of the exact temperature range where physical crosslinks are present is essential to explain the formation and stability of co-continuous morphologies in blends with these block copolymers.

Melt structure in block copolymers can be associated with a melt yield stress and therefore, we tried to make an estimate of this yield stress for both SEBS block copolymers. This was done by simply extrapolating the shear stress measured as a function of the shear rate in a conventional cone-and-plate rheometer to zero shear rate (Fig. 5). Although a proper determination of the magnitude of a yield stress requires specification of the relevant time scale and use of a constant stress rheometer, the results as shown in Fig. 5 are sufficient for the present purpose, i.e to obtain the order of magnitude. Despite the presence of a melt structure at 190°C, in case of SEBS 1657, an extrapolated shear stress of 0 Pa is found meaning that no yield stress could be measured with this method. For the SEBS 1652 an extapolated shear stress of around 600 Pa was found at 210°C and an extapolated shear stress of around 700 Pa can be obtained at 190°C. The extrapolation is somewhat arbitrary but it is sufficient for the present purpose, i.e. to obtain the order of magnitude of the yield stress.

3.2. Morphology

The morphologies of SEBS 1657/PP blends, processed at 190°C, in the composition range of 20/80 until 60/40 are depicted in Fig. 6. The SEM micrographs show the PP matrix (grey sections) that is left after the SEBS phase was extracted (dark sections). The same blends but processed at 250°C are depicted in Fig. 6(d)–(f). The results of the extraction experiments, showing the percentage SEBS extracted, for both processing temperatures and the total composition range are given in Table 2. It is evident from the SEM micrographs and the extraction results that in

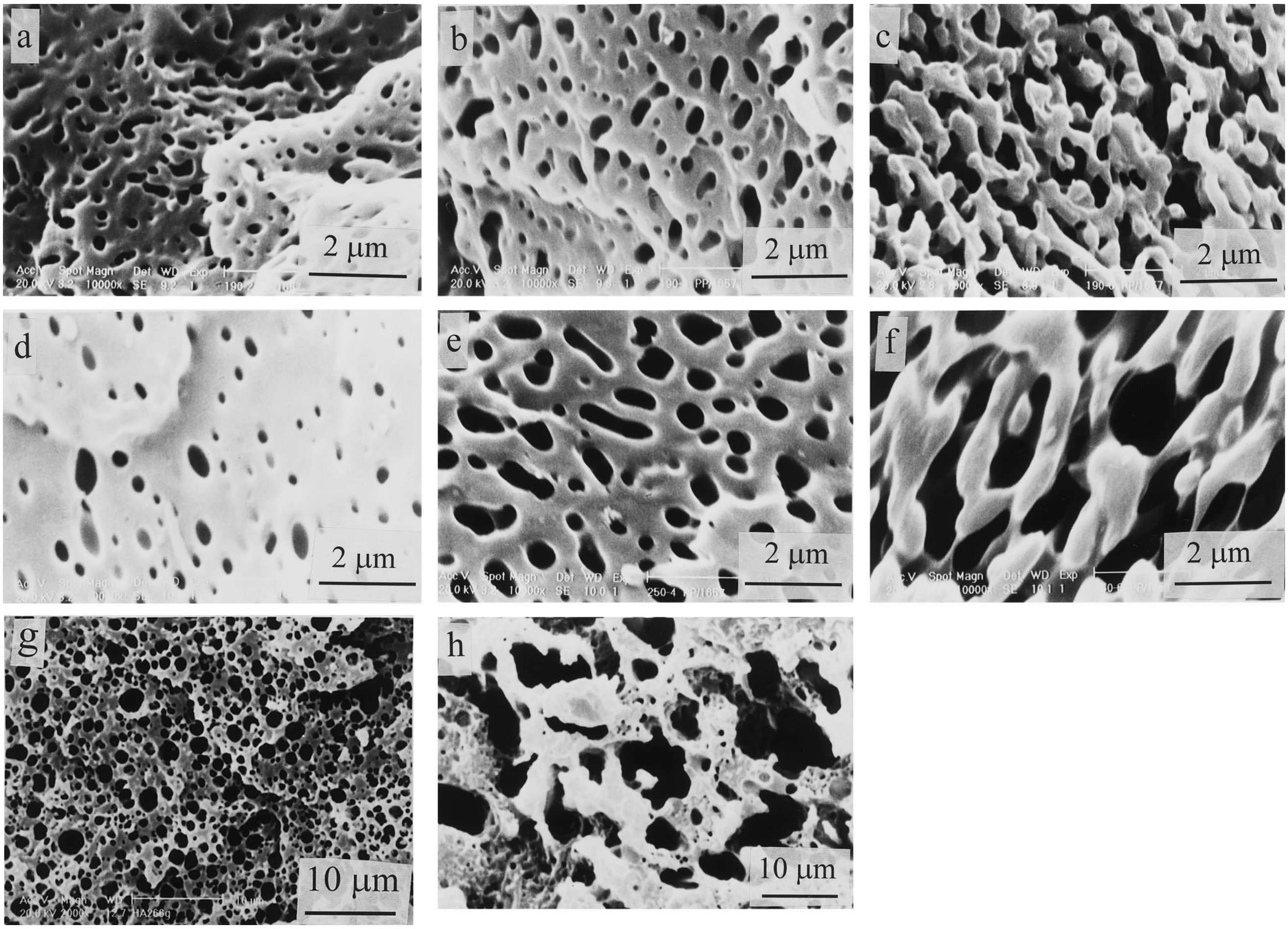

Fig. 6. SEM micrographs of SEBS 1657/PP blends (20, 40 and 60 vol% SEBS) processed at 190°C (a)–(c) and processed at 250°C (d)–(f) and of SEBS 1657/POM blends (20 and 40 vol% SEBS) processed at 190°C (g)–(h).

the SEBS 1657/PP blends, processed at 190°C, both polymers are continuous in the composition range 20–70 vol% SEBS. The blend with 10 vol% SEBS shows a droplet/matrix morphology. The blends with 80 and 90 vol% SEBS did not fall apart upon extraction but the remaining structure collapsed upon solvent evaporation. Therefore no clear SEM micrographs could be obtained. These blends are either co-continuous or some transition morphology in between a co-continuous and a dispersed morphology was formed. When the same SEBS 1657/PP blend is processed at 250°C, where the block copolymer shows normal pseudoplastic behaviour, the range of full co-continuity shifts to 30–70 vol% SEBS. The 10 and 20 vol% blends show clear droplet/matrix morphologies and the 90 vol% blend was no longer self-supporting after the SEBS phase had been extracted, indicated with a dash in Table 2, meaning that PP was dispersed in the SEBS matrix. The 80 vol% blend did not fall apart upon extraction but the remaining structure collapsed upon solvent evaporation indicating a transition morphology. The extraction results of the SEBS 1652/PP blends are also given in Table 2. These results show (together with SEM analysis) that full co-continuity is found in the composition range 30–60 vol% SEBS. The 70–90 vol% blends did not fall apart upon extraction but the remaining structure collapsed upon solvent evaporation and therefore no clear SEM-micrographs could be obtained. Again these blends are either co-continuous or show a transition morphology. The blends with 10 and 20 vol% SEBS 1652 show clear dispersed morphologies.

It becomes clear from the aforementioned results that co-continuous morphologies can be obtained over a wide composition range in PP/SEBS blends. It is also evident that this range (and the range of intermediate morphologies) becomes smaller when SEBS 1657 shows pseudoplastic behaviour and no physical crosslinks are present in the SEBS melt. Although this effect is significant it is not as explicit as it is in the case of polystyrene/poly(ether–ester) blends [13]. This may be related to the low interfacial tension between PP and SEBS (0.9 mN/m, obtained with the breaking thread method). It was shown by Willemse et al. that the range of co-continuity in blends of ordinary pseudoplastics increases with decreasing interfacial tension [39]. The effect of physical crosslinks and resulting elastic rheological properties on the range of co-continuity in SEBS blends may therefore be overshadowed by the effect of low interfacial tension. In order to prove this point, the SEBS

Table 2
Percentage of SEBS extracted of blends processed at the designated temperature and subsequently quenched. The samples indicated with (—) are no longer self-supporting after extraction. The characteristics of the different blends I–VI can be found in Table 1

Vol% SEBS	I (190°C)	I (250°C)	II	III (190°C)	III (250°C)	IV	V	VI
10	15	12	11	74	25	0	0	0
20	100	63	26	100	100	58	26	0
30	100	100	99	100	—	100	56	26
40	98	96	100	—	—	100	92	86
50	95	100	100	—	—	100	98	94
60	98	100	100	—	—	—	—	96
70	97	99	99	—	—	—	—	99
80	100	100	100	—	—	—	—	98
90	100	—	100	—	—	—	—	—

block copolymers are also blended with PMMA and POM resulting in blends with higher interfacial tensions.

The extraction results of these blends can also be found in Table 2 and SEM micrographs of SEBS 1657/POM blends in the composition range 20–40 vol% are depicted in Fig. 6(g)–(h).

When the SEBS 1657/POM system is processed at 190°C the range of co-continuity is limited to 40–50 vol% SEBS. At all other compositions clear dispersed morphologies were formed. The POM blends with SEBS 1652, the block copolymer that shows more elastic rheological properties, processed at 190°C show full co-continuity in the composition range 50–80 vol% SEBS. At the other compositions dispersed morphologies were formed. Similar results are obtained when PMMA is blended with block copolymers, i.e. a limited range of co-continuity (20–30 vol% SEBS 1657 at a processing temperature of 190°C and 20 vol% SEBS 1657 when processed at 250°C) in the PMMA/SEBS 1657 blends and a somewhat wider range (30–50 vol% SEBS 1652) in the PMMA/SEBS 1652 blends was obtained.

The formation of co-continuous morphologies, especially at very low volume fractions must be attributed to stable interconnected elongated structures that had formed during processing. It becomes clear from the aforementioned results that the presence of physical crosslinks in the block copolymers, meaning highly elastic rheological properties, has some effect on stabilizing these elongated structures. However these stable elongated structures can only exist if the stress that breaks up these elongated structures, the interfacial tension, is not too high. When the interfacial forces become larger than the stabilizing forces resulting from the physical crosslinks, the elongated structures are not stable and in this case co-continuous morphologies are only formed in a small composition range. This will be discussed later in more detail.

3.3. Stability

One of the main disadvantages of co-continuous morphologies is their intrinsic instability during further processing or annealing. As a result of the interfacial tension between the two phases the interfacial area will be reduced when the blend is kept at elevated temperatures.

This can lead to an increase in the phase size of the co-continuous blend or the co-continuous morphology breaks up into a droplet/matrix morphology, as was shown in a earlier article [23]. To examine the effect of the physical crosslinks in the SEBS block copolymers on the stability and range of co-continuity, all PP/SEBS blends were annealed for 5 min at the temperature of processing.

The morphologies of SEBS 1657/PP blends in the composition range of 20/80 until 60/40, that were annealed for 5 min at 190°C, are depicted in Fig. 7(a)–(c). The same blends but processed and annealed for 5 min at 250°C are depicted in Fig. 7(d)–(e). The results of the extraction experiments, showing the percentage SEBS extracted, for both annealing temperatures and the total composition range are given in Table 3. When the SEBS 1657/PP blends are annealed for 5 min at 190°C the composition range of full co-continuity shifts from 20–70 vol% to 30–70 vol% SEBS and the phase sizes increase from ~0.4 to ~0.8 μm. Annealing the SEBS 1657/PP blends that were processed at 250°C leads to a shift in the range of co-continuity from 30–70 vol% to 40–50 vol% SEBS and the phase sizes of the co-continuous blends increase from ~0.5 to ~2 μm. The SEBS 1652/PP blends do not show a shift in the range of co-continuity and hardly an increase in phase size, upon annealing. These results clearly show that during annealing the coarsening of co-continuous morphologies can be inhibited and that co-continuity can be maintained over a wide composition range when physical crosslinks are present, meaning that the yield stress or the elasticity of the block copolymer seems to stabilize the morphology. When the SEBS 1657 block copolymer shows normal pseudoplastic rheological behaviour, co-continuous morphologies either break up into dispersed morphologies or show a large increase in phase size.

3.4. Breakup and retraction

As stated in the Introduction, the condition for the formation of co-continuous morphologies, especially at low volume fractions, is the existence of stable elongated

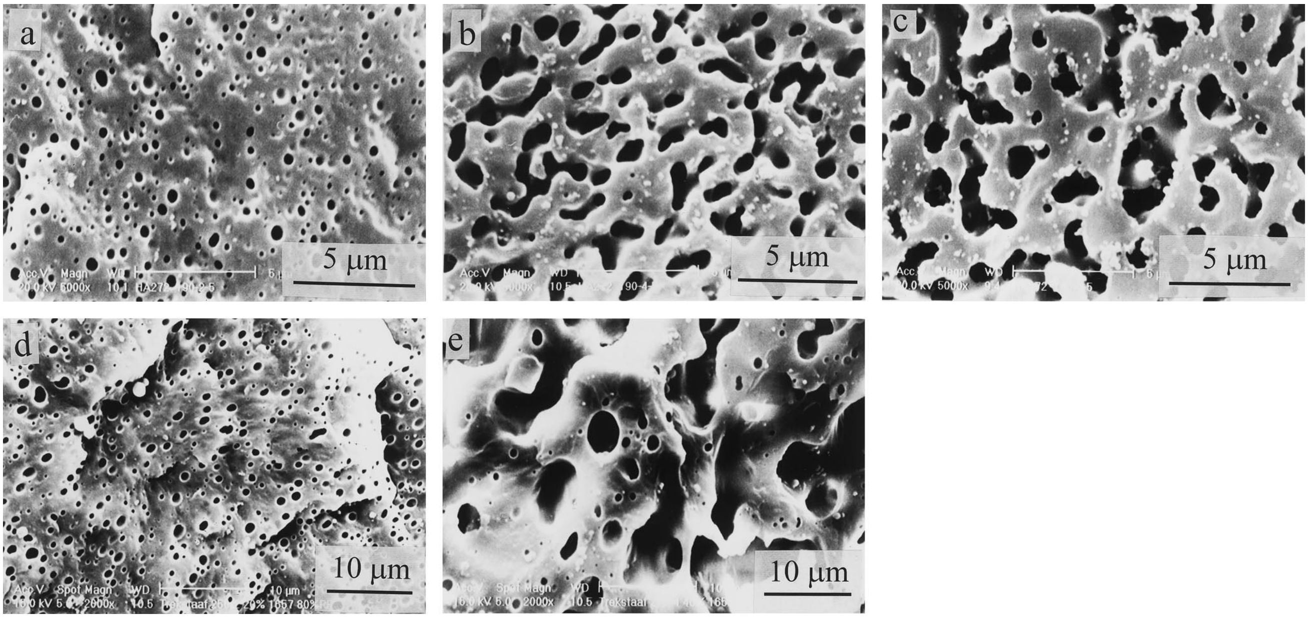

Fig. 7. SEM micrographs of SEBS 1657/PP blends (20, 40 and 60 vol% SEBS) processed and annealed at 190°C (a)–(c) and processed and annealed at 250°C (d)–(f).

structures that do not show breakup, end-pinching or retraction. Therefore these mechanisms for a PP, PMMA or POM fibre imbedded in a SEBS 1657 matrix were explicitly examined in the same temperature range as that of the blending experiments.

A typical example of the breakup behaviour of a PP thread in a SEBS 1657 matrix at 250°C is illustrated in Fig. 8. At the deformation rates involved both polymers show a Newtonian plateau in viscosity and therefore the breakup can be described according to Tomotika's theory for Newtonian fluids [19,20]. A reasonably regular sinusoidal distortion develops after which the thread breaks up in droplets separated by one wavelength and in between these droplets the formation of small satellite droplets can be seen. The resulting radius of the large droplets is almost equal to $1.9R_0$. A linear relationship between the logarithm of the dimensionless distortion (α/R_0) versus time was obtained (α is the distortion amplitude and R_0 the initial thread radius). The slope of this line is equal to the growth rate (q) of the distortions. Measurements at the last stage of breakup, i.e. where bead strings and satellite droplets are formed, are not taken into account.

When the minor phase in a polymer blend is continuous it consists of interconnected elongated ligaments, with a not very large aspect ratio (L/D). Therefore the retraction or end-pinching mechanisms, as described by Stone et al. [21, 22], may be as important as the classical breakup mechanism. The retraction mechanism, at 250°C, for short PP fibres imbedded in a SEBS 1657 matrix is illustrated in Fig. 9. At first the ends of the thread become almost spherical to produce a dumb-bell shape, after which the spherical ends are pulled towards the thread's centre and engulf the cylindrical portion of the thread as they move, finally resulting in a sphere. The retraction process described here is similar to that found for Newtonian fluids by Stone et al.

When PMMA fibres were used instead of PP fibres and the experiment temperature is 250°C, the same breakup and retraction mechanisms were observed as described earlier. The total breakup or retraction time is somewhat shorter, as compared to the breakup time for PP fibres, because of the higher interfacial tension between PMMA and SEBS.

For threads of ~70 μm diameter the time scale for breakup is in the order of minutes. In real blending conditions though the diameters are typical around 1 μm, resulting in completely different time scales for breakup. The time for breakup, t_b (s), for a viscous thread imbedded in a viscous matrix under quiescent conditions can be expressed as [27]

$$t_b = \frac{1}{q}\ln\left(\frac{0.82R_0}{\alpha_0}\right) \tag{1}$$

in which the distortion growth rate q (s^{-1}), is given by

$$q = \frac{\sigma}{2\eta_m R_0}\Omega(\lambda, p), \tag{2}$$

where α_0 is the initial distortion amplitude (m), R_0 is the initial thread radius (m), σ is the interfacial tension (N/m), λ is the wavelength of a sinusoidal distortion (m) and $\Omega(\lambda,p)$ a dimensionless growth rate [19]. When the interfacial tensions, as given in Table 1, are used and a relative initial distortion of $\alpha_0/R_0 = 0.1$ is assumed the calculated breakup time for a PP thread of 1 μm is of the order of 23 s and the breakup time for a PMMA thread of 1 μm is of the order of 6 s.

The time scales for retraction of a polymer fibre can be

Table 3
Percentage of SEBS extracted of blends processed and annealed for 5 min at the designated temperature. The samples indicated with (—) are no longer self-supporting after extraction. The characteristics of the different blends I and II can be found in Table 1

Vol% SEBS	I (190°C)	I (250°C)	II
10	0	2	0
20	31	36	0
30	100	87	98
40	100	99	100
50	100	100	100
60	100	—	99
70	100	—	96
80	100	—	—
90	—	—	—

expressed as [40, 41]

$$q_r = \frac{\sigma}{\chi R_d \eta_e}, \tag{3}$$

where q_r (s^{-1}) is the retraction growth rate, R_d (m) is the radius of the droplet after relaxation, η_e (Pa s) an effective viscosity that is a function of the matrix viscosity and the fibre viscosity and χ a hydrodynamic coefficient. Several other authors [42–44] have proposed similar relations for the time scale of retraction. The time scale for retraction is even smaller than the time scale for Rayleigh distortions leading to very small retraction times, of the order of a few seconds, for typical blend dimensions ($\sim$1 μm).

These calculations show that non-equilibrium morphologies cannot exist for a very long time at this temperature. Although the breakup time of the PP fibres may be long enough for extended structures to be solidified upon quenching, these fibres are certainly not stable upon annealing. Therefore co-continuous morphologies in PP/SEBS 1657 blends are found over a reasonable broad range after processing, mainly because of the low interfacial tension [39]. However after annealing the composition range of the co-continuity is limited, as was evident from the aforementioned results. The breakup and retraction times for PMMA fibres are so small that the non-equilibrium morphologies in PMMA/SEBS 1657 blends cannot exist for a period of time long enough to be solidified upon quenching or stay stable upon annealing. Therefore co-continuous morphologies in PMMA/SEBS 1657 blends are only found in a limited composition range after processing and annealing at this temperature.

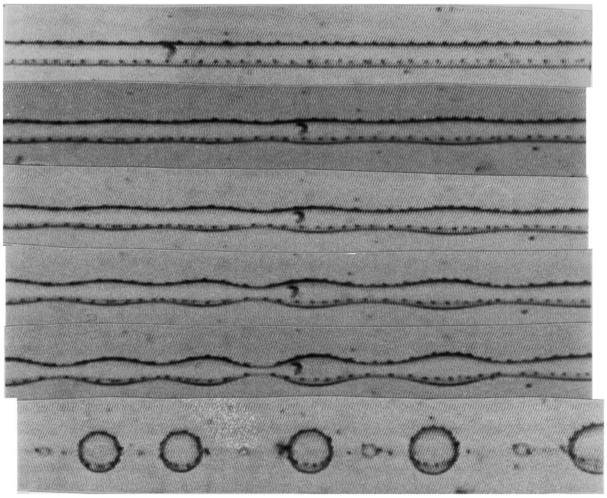
Fig. 8. Breakup process of a PP thread imbedded in a SEBS 1657 matrix at 250°C. Photographs taken at 0, 25, 29, 33, 37 and 60 min.

When a POM fibre of around 70 μm is imbedded in a SEBS 1657 matrix at 190°C the same breakup and retraction behaviour was found as shown in Figs. 8 and 9, despite the non-Newtonian behaviour of the SEBS 1657 at this temperature. The breakup behaviour of PMMA or PP fibres imbedded in a SEBS 1657 matrix at 190°C is completely different. Fibres with a diameter of around 70 μm simply do not break up and their retraction is severely limited. A similar non-breakup and non-retraction phenomena have been reported earlier for poly(ether–ester) fibres imbedded in polystyrene [13]. Owing to the non-Newtonian behaviour of the SEBS 1657 at this temperature Tomotika's theory cannot be applied in these cases. Although Palierne [45] extended Tomotika's theory to viscoelastic systems, his theory cannot explain the non-breakup behaviour. An approximation, proposed by Elmendorp [27, 28], to explain the observed phenomena is to use a yield stress as the limiting force for preventing breakup. This approximation is based on the assumption that a distortion is unable to grow if the pressure difference, which is generated in the thread by the different radii of curvature, is smaller than the yield stress. The pressure difference between positions in the thread with maximal and minimal radius can be expressed as

$$P_s = \frac{2\alpha'\sigma}{R_0}\left(\frac{1}{1 - 1.5\alpha'^2} - X^2\right), \tag{4}$$

where $\alpha' = \alpha/R_0$ is the relative distortion and $X = 2\pi R_0/\lambda$ the dimensionless wavenumber. The pressure difference (P_s) at a certain deformation can be calculated if the radius of the thread and interfacial tension are known. The interfacial tensions are given in Table 1, for X the value for the dominant wavenumber (X_m) corresponding to the viscosity ratio is used, and for α' a value of 0.1 is assumed. The calculated pressure differences for four different radii and X_m can be seen in Table 4.

From the steady shear experiment we could not obtain a yield stress for the SEBS 1657 block copolymer, but the non-breakup phenomena and the presence of physical cross-links at this temperature strongly indicate that the block copolymer must have a yield stress. When the radius of the PMMA fibres in breakup experiments was only 20 μm a limited distortion was observed that did not grow any further. We therefore assume that the SEBS 1657 should have a yield stress of around 22 Pa (Table 4).

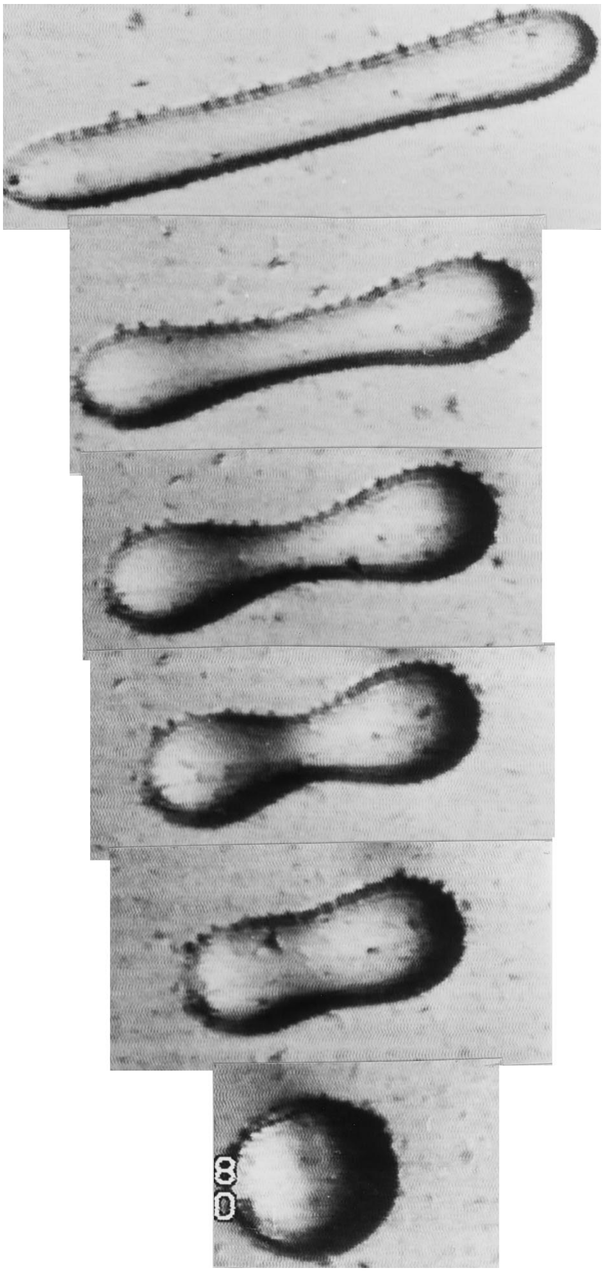

Fig. 9. Retraction process of a PP thread imbedded in a SEBS 1657 matrix at 250°C. Photographs taken at 0, 14, 21, 28, 35 and 53 min.

When a yield stress of 22 Pa is assumed it by far exceeds the calculated pressure difference for a PMMA or PP thread radius of 35 μm and therefore no breakup should occur according to Elmendorp's approximation. This is in agreement with the experimental results. The calculated pressure difference for a POM fibre of 35 μm does exceed the assumed yield stress. Therefore a POM fibre of 35 μm should break up, which is also in agreement with the experimental results. When a radius of 0.5 μm is assumed, which is typical for blending conditions, the calculated pressure differences (for all three systems) by far exceed the yield stress. This means that in blending conditions breakup can occur at 190°C and flow is possible despite the presence of physical crosslinks. This can explain why co-continuous morphologies in PMMA/SEBS 1657 and POM/SEBS 1657 blends are only found in a limited composition range. The wide range of co-continuous morphologies found in PP/SEBS 1657 blends is therefore mainly related to the low interfacial tension of this system [39] and not to the presence of crosslinks or a yield stress. The reasonable wide range of co-continuity that is still present in the PP/SEBS 1657 blend after 5 min of annealing can be explained by the coarsening process of co-continuous blends that is not stopped but severely slowed down when physical crosslinks are present, as was shown in an earlier article [23].

The pressure differences for fibres imbedded in a SEBS 1652 matrix can also be estimated when it is assumed that the interfacial tensions are the same as for the SEBS 1657 blends. The results for the 4 different radii, all in the range of blending conditions, are shown in Table 5.

When typical blend dimensions are considered for each system, i.e 0.2 μm for the PP blends, 0.5 μm for the PMMA blends and 2 μm for the POM blends, it becomes clear from Table 5 that the calculated pressure differences for these dimensions are very close to the yield stress for each particular system. This means that reasonably large fibres during processing are stable but the thinner ones will break up. This is in quite good agreement with the actual blending experiments where co-continuous morphologies were found over a somewhat broader range than in the SEBS 1657 blends (where pressure differences are much larger than the yield stress), but the range of co-continuity was still limited (for example 30–50 vol% SEBS in PMMA/SEBS 1652 blends and 50–80 vol% SEBS in POM/ SEBS 1652 blends). As the pressure difference for the PP/SEBS 1652 blend for typical blend dimensions (0.2–0.5 μm) is very close to or smaller than the yield stress, extended structures are stabilized. This might explain why these blends are stable upon annealing at this temperature.

The breakup and retraction experiments clearly show that breakup and retraction can be severely limited or even stopped, and therefore the condition for existence co-continuous morphologies can be fulfilled, i.e. the formation of stable elongated structures that do not show breakup or retraction. It is also shown that the (non-)breakup and (non-)retraction behaviours strongly depend on parameters such as interfacial tension, phase

Table 4
Dominant wavenumbers (X_m) and calculated pressure differences for four different radii for blends with SEBS 1657

System	X_m	P_s (Pa)			
		$R_0 = 35$ μm	$R_0 = 20$ μm	$R_0 = 0.5$ μm	$R_0 = 0.2$ μm
I	0.53	3.8	6.6	264	661
III	0.51	13	22	876	2190
V	0.53	5.4	94	3748	9370

Table 5
Yield stresses, dominant wavenumbers (X_m) and calculated pressure differences for four different radii for blends with SEBS 1652

Systems	Yield stress (Pa)	X_m	P_s (Pa)			
			$R_0 = 2$ μm	$R_0 = 1$ μm	$R_0 = 0.5$ μm	$R_0 = 0.2$ μm
II	600	0.5	69	138	275	688
IV	600	0.4	248	496	992	2480
VI	700	0.35	1232	2465	4929	12323

size and yield stress. Therefore, if one of the components shows a yield stress or physical crosslinks are present, this is certainly not a guarantee that stable elongated structures are formed and maintained during processing. Stable co-continuous morphologies, over a wide composition range, are therefore only obtained when a complex combination of parameters, i.e. phase size (also related to processing conditions), yield stress and interfacial tension, are such that breakup and retraction can be stopped or slowed down.

4. Conclusions

Stable co-continuous morphologies can be obtained over a wide composition range in PP/SEBS blends because of the low interfacial tension and the presence of physical crosslinks. When the same SEBS block copolymers are blended with PMMA or POM, resulting in blends with higher interfacial tensions, co-continuous morphologies are found over much smaller composition range. If crosslinks are present in the block copolymer the breakup and retraction can be severely limited or even stopped, meaning that elongated structures are stable and therefore co-continuous morphologies can be formed. It is shown that the (non-)breakup or (non-)retraction behaviour of elongated structures strongly depends on a complex combination of parameters, including phase size, yield stress and interfacial tension. The presence of physical crosslinks only is therefore not a guarantee for the formation of stable co-continuous morphologies over a wide composition range.

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