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Formation and stability of co-continuous blends with a poly(ether-ester) block copolymer around its order–disorder temperature

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Abstract

Co-continuous morphologies are found over a wide composition range (30–80 vol%) in blends of a polystyrene thermoplastic and a poly(ether-ester) thermoplastic elastomer when they are blended below the block copolymer's order–disorder transition (ODT). This range decreases with increasing processing temperature and becomes limited when both polymers show pseudo-plastic behaviour. Annealing of the co-continuous blends below the ODT hardly influences the phase sizes and composition range, but when annealing takes place at higher temperatures the blends show an increase of their phase domains and the composition range decreases. The condition for the formation of co-continuous morphologies, especially at low volume fractions, is the existence of stable interconnected elongated structures, that do not show breakup or retraction. Breakup and retraction experiments on poly(ether-ester) fibres embedded in a polystyrene matrix make clear that these mechanisms can be severely limited or even stopped and therefore the condition for the existence of co-continuous morphologies is fulfilled.
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1. Introduction

An elegant method to obtain new materials is blending of thermoplastic polymers. 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 intrinsically 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 components, in all directions, can fully contribute to the properties of the blend.

At low concentrations of the minor phase a dispersed morphology is most likely to be formed. Further increase in the amount of the minor phase will lead to the formation of a more continuous dispersed phase until a fully continuous structure has formed inside the matrix phase. Such a morphology where both phases form completely continuous structures will be referred to as a co-continuous morphology. Co-continuous morphologies are often formed close around the point of phase inversion. In the literature several relations have been proposed to predict the point of phase inversion. Through these semi-empirical models the point of phase inversion is related to some of the rheological properties of the components. Avgeropoulos et al. [9] used the torque ratio as the viscoelastic characteristic of the materials and included therefore all forces, such as elongation and shearing forces, that act upon the polymers during the blending process. This resulted in a relation between the torque ratio and the composition. Paul and Barlow [10] offered a theoretical prediction for blends prepared at low shear rates, based on the same ideas but now using the viscosities as the characteristics of the components. These ideas were

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expressed in an equation by Jordhamo et al. [11] and later generalized by Miles and Zurek [12] as:

$$\frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})} = \frac{\phi_1}{\phi_2} \tag{1}$$

where η_i is the viscosity of polymer i at the shear rate of blending and ϕ_i is the composition of polymer i at which phase inversion occurs. Other models to predict the point of phase inversion were derived by Metelkin and Blekht [13], based on the filament instability concept, and by Utracki [14] which is based on a dependence of the viscosity on the volume fraction of monodispersed hard spheres in a matrix. Most of these models only take into account the viscous characteristics of the polymers and do not account for important mixing parameters such as interfacial tension and elasticity. It is therefore not too surprising that several deviations were found [15–19], sometimes leading to small adjustments of the existing relations [17,18]. Furthermore, these relations only give a single volume fraction for phase inversion rather than a range of volume fractions at which co-continuity is possible. A model describing the volume fraction limits where co-continuity is possible is therefore more appropriate. Such a model has been developed by Willemse et al. [19], based on geometrical and micro-rheological requirements for existence of co-continuous morphologies. This resulted in a relation describing the limits of co-continuity ($\Phi_{\mathrm{d,cc}}$), i.e. the volume fraction at which the dispersed phase becomes fully continuous, as a function of the matrix viscosity (η_{m}), shear rate ($\dot{\gamma}$), interfacial tension (σ) and droplet radius (R_{d})

$$\frac{1}{\phi_{\mathrm{d,\,cc}}} = 1.38 + 0.0213\left(\frac{\eta_{\mathrm{m}}\dot{\gamma}}{\sigma}R_{\mathrm{d}}\right)^{4.2} \tag{2}$$

Dependent on the shape of the dispersed particles, continuity of the minor phase can already occur at low volume fractions. In the case of spherical droplets the percolation threshold is 0.158, whereas this value will be much lower for randomly orientated fibres [20]. The formation and stability of such fibres will be strongly dependent on the processing conditions and the processing properties of the blend components. Although there is some discussion in the literature as to whether the formation of polymer blends proceeds via the droplet deformation/breakup mechanism [21,22] or by a sheet forming mechanism [23,24], the condition for the formation of co-continuous morphologies is the existence of stable elongated structures that do not show breakup or retraction, whatever their origin.

Co-continuous morphologies as well as fibres in matrix morphologies are in fact non-equilibrium states in quiescent conditions and will change form due to the interfacial tension. There are several interfacial tension-driven mechanisms by which a fibre can change shape, including Rayleigh distortions [25–27], retraction and end-pinching [28,29]. These mechanisms are important, not only in the formation of polymer blends, but also for the stability of non-equilibrium morphologies during further processing.

When a thermoplastic elastomer (TPE) is blended with a normal thermoplastic [30–36] or another TPE [37–43], co-continuous morphologies are often formed. Verhoogt and co-workers [42,43] showed that co-continuous morphologies could be found over a wide range of compositions when two TPEs, i.e. a SEBS block copolymer and a semi-crystalline poly(ether-ester) multiblock copolymer, were blended. Full co-continuity was found down to 20% SEBS meaning that during processing fibres or elongated domains of the SEBS block copolymer must have been formed. Although it is believed that network structures of TPEs stabilize the blend morphology against interfacial tension-driven coarsening during further processing because of resistance to retraction [30,31] or the presence of a yield stress in the melt [44,45], the blends reported by Verhoogt et al. were not completely stable during further annealing.

A well-known phenomenon in TPEs is the order–disorder transition. The blocks that are phase-separated into microdomains will dissolve into a homogeneous melt when the temperature is raised above a certain value. This temperature is called the order–disorder transition (ODT) or microphase separation transition (MST). We have reported on a wide ODT in a semi-crystalline poly(ether-ester) multiblock copolymer which was related to the complex melting behaviour of the crystalline polyester blocks [46]. Melting in this block copolymer results in a one phase liquid and no separate segmental mixing occurs at higher temperatures. The ODT in this case is therefore entirely caused by melting. In the temperature range of the ODT the rheological behaviour of the multiblock copolymer changes from highly elastic to pseudo-plastic [46].

The objective of this paper is to examine if the ODT, and therefore the presence of physical crosslinks, of this poly(ether-ester) multiblock copolymer affects the formation and stability of co-continuous morphologies. Therefore the multiblock copolymer is blended with a pseudo-plastic polystyrene (PS) in the temperature range of the ODT. 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 interfacial tension-driven processes, such as breakup and retraction of polymer fibres.

2. Experimental

2.1. Materials

The polymers used were Arnitel EM400, supplied by Akzo Nobel (currently by DSM), Hostyrene N2000 and Hostyrene N7000, provided by Shell. Arnitel EM400 is a poly(ether-ester) multiblock copolymer, consisting of 40 wt% hard, crystalline poly(tetra methylene terephthalate) segments and 60 wt% soft, amorphous poly(tetra methylene oxide) segments. The melting and crystallization characteristics of this polymer as well as the rheological properties are described in Ref. [46]. Prior to usage the polymers were dried at 95°C in a vacuum-stove.

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} to 10^2 rad/s with a strain of 5% or 30%. It was made sure that all 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} to 10^{-1} s^{-1}).

2.3. Processing

Blends of PS N7000 and Arnitel EM400 were prepared in two ways. On a two-roll mill (Schwabentahn) with roll speeds of 0.136 and 0.163 m/s. The gap between the two rolls was 1.10 mm resulting in a average shear rate of 150 s^{-1} [47]. The blends processed at 200°C were scraped off the mill after 12 min and directly quenched in water at room temperature. At higher processing temperatures (210 and 220°C) the processing time was reduced to 7 min. Blends were prepared over the total composition range with steps of 10 vol%. In the same composition range blends were also prepared 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} at 200°C and 75 s^{-1} at 220°C. 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.

2.4. Morphology

The morphology was characterized by means of a Philips XL20 scanning electron microscope (SEM) and extraction experiments. The PS phase was extracted, in 7 days at room temperature, with 2-butanone as the solvent. 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 the PS can be extracted and the remaining poly(ether-ester) is still self-supporting.

2.5. Breakup and retraction

Fibres of the poly(ether-ester) were obtained by melt spinning from a capillary rheometer at 220°C. The PS N2000 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 PS matrix as well as the poly(ether-ester) fibres to relax for 24 h in a vacuum-stove at 95°C, 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 poly(ether-ester) fibre, PS 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 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.

3. Results and discussion

3.1. Rheology of the polymers

The viscosity versus shear rate curves of PS N7000 determined at 200, 210 and 220°C are shown in Fig. 1(a) with the open symbols for the capillary rheometer experiments and the filled symbols for the dynamic shear experiments. The polymer shows shear thinning behaviour over almost the complete range of measured shear rates and frequencies, only showing Newtonian flow behaviour at the lowest frequencies measured. The Cox–Merz rule is applicable, i.e. the measured shear viscosity and complex viscosity overlap perfectly, in all cases. For the PS N2000 the viscosity versus shear rate curves in the same temperature range are presented in Fig. 1(b). The only difference with the PS N7000 is the lower viscosity and the more explicit Newtonian flow behaviour at low frequencies.

The viscosity versus shear rate curves of the poly(ether-ester) block copolymer in the same temperature range, shown in Fig. 1(c), are somewhat more complex. At 220°C the melt behaves comparable to the polystyrenes, with a Newtonian plateau at low shear rates and shear thinning behaviour at higher rates. The Cox–Merz rule is also applicable at this temperature. If the experiment temperature is 200 or 210°C the flow curves do not show a Newtonian plateau in viscosity. Shear thinning behaviour over the complete range of measured shear rates is found, which is an indication of a crystalline structure in the melt. As a result the Cox–Merz rule fails at these temperatures.

The extreme shear thinning behaviour shown in Fig. 1(c) can be associated with a melt yield stress. Therefore, we tried to make an estimate of this yield stress for the poly(ether-ester) at several temperatures. 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 [48]. 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 [49], the results as shown in Fig. 2 are sufficient for the present purpose, i.e. to demonstrate the existence of a yield stress as a function of the temperature and to obtain the order of magnitude. For experiments carried out at 200°C an extrapolated shear stress of 3800 Pa is found. At 210°C the stress has diminished to around 500 Pa and at 220°C no stress could be measured at these small shear rates.

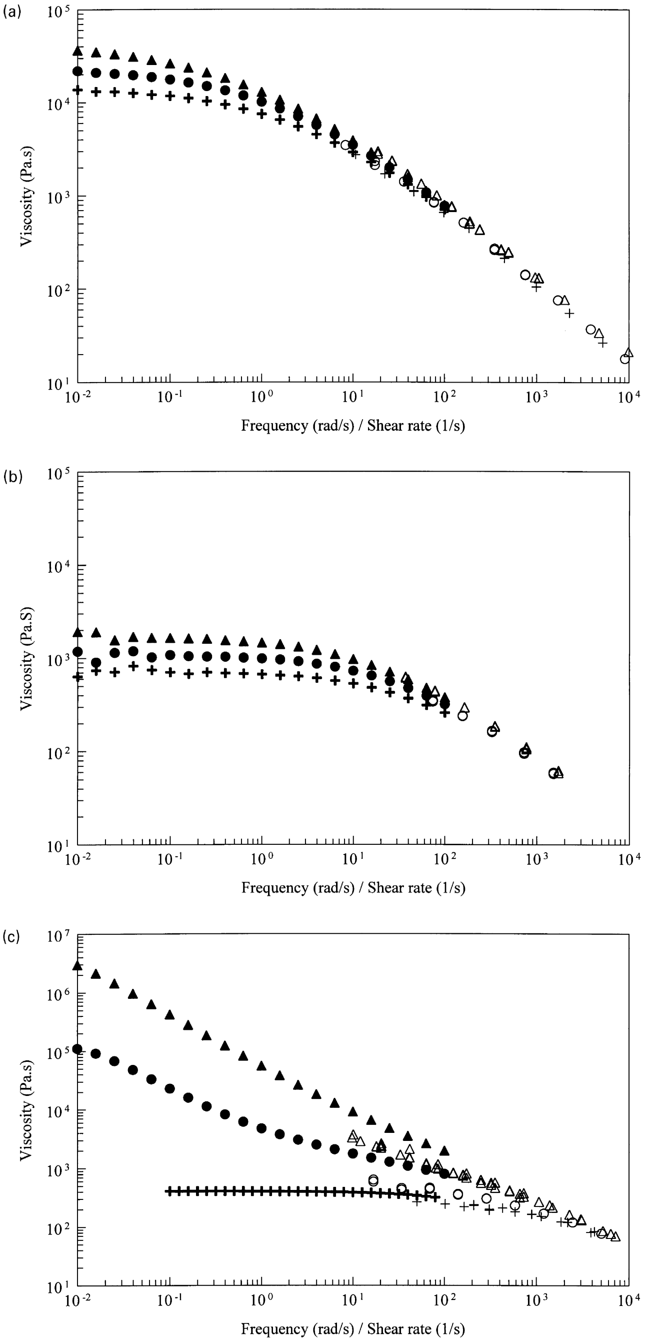

Fig. 1. Flow curves of (a) PS N7000, (b) PS N2000 and (c) poly(ether-ester) determined at 200°C (▲;△), 210°C (●;○) and 220°C (+ ; +).

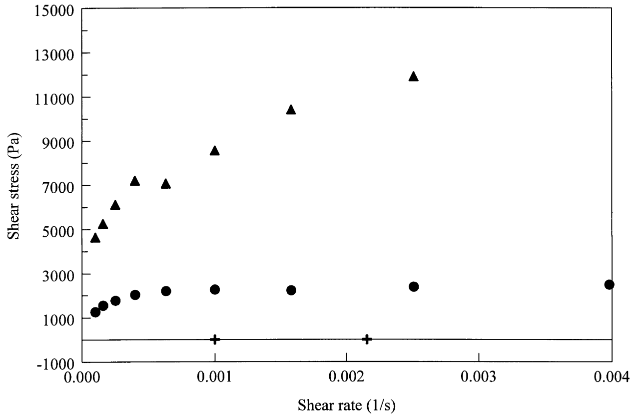

Fig. 2. Shear stress as a function of shear rate for the poly(ether-ester) at 200°C (▲), 210°C (●) and 220°C (+).

The gradual change in rheological behaviour of this polymer over a wide range of temperatures, as shown in Fig. 3, is described in more detail in Ref. [46]. This change is shown to be caused by a gradual decrease in crystallinity resulting in a transition which takes place, upon heating, from below 207 to 224°C. This wide transition implies a large processing window in which the rheological properties change from highly elastic, with a distinct yield stress, to normal pseudoplastic. Proper knowledge of the exact temperature range is essential to explain the formation and stability of co-continuous morphologies in blends with this polymer.

3.2. Morphology

The morphologies of PS/poly(ether-ester) blends in the composition range 30/70 until 70/30, that were processed at 200°C on the two-roll mill and subsequently quenched, are depicted in Fig. 4(a–c). The SEM micrographs show the poly(ether-ester) matrix (grey sections) that is left after

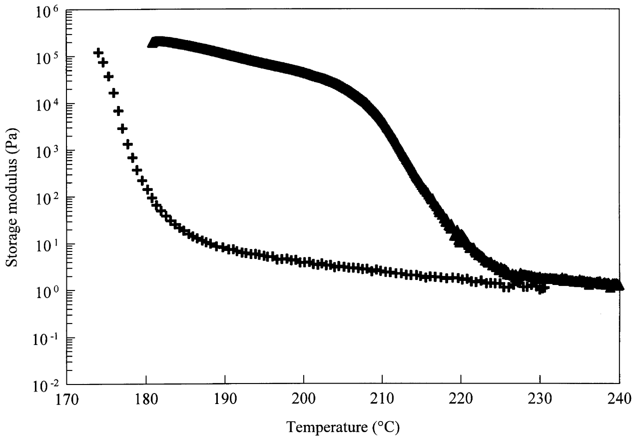

Fig. 3. Storage modulus of the poly(ether-ester) determined at 1 rad/s as a function of temperature with a heating rate of 0.5°C/min (△) and a cooling rate of 0.5°C/min (+).

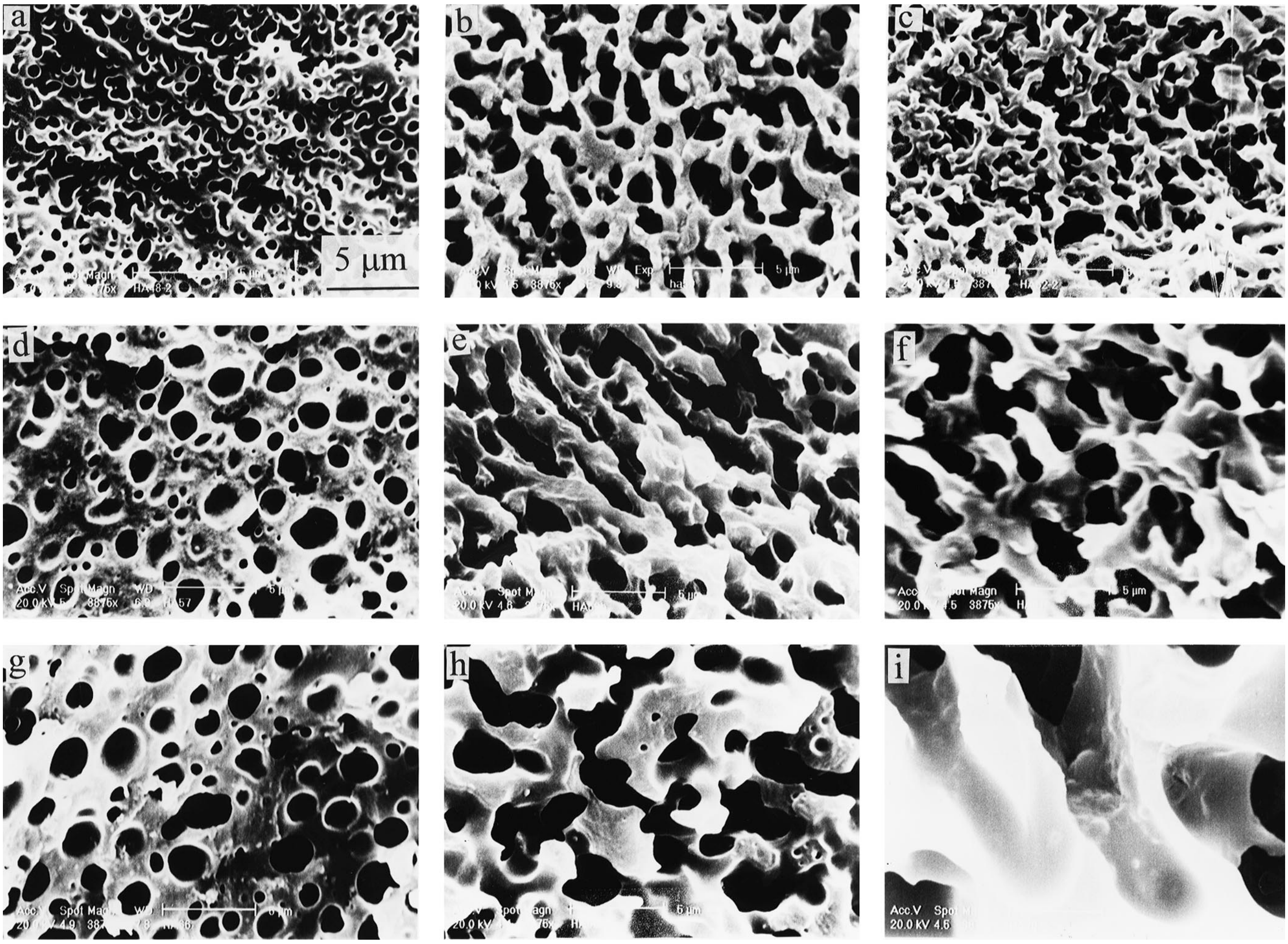

Fig. 4. SEM micrographs of PS/poly(ether-ester) blends processed on a two-roll mill at 200°C (a–c), 210°C (d–f) and 220°C (g–i) with 30 vol% PS, 50 vol% PS and 70 vol% PS, showing the poly(ether-ester) phase after extraction of PS.

the PS phase has been extracted (dark sections). The results of the extraction experiments, showing the percentage PS extracted, for all processing temperatures and the total composition range are given in Table 1. It is evident from the SEM micrographs (Fig. 4(a–c)) and the extraction results that when the blends are processed at 200°C both polymers are continuous in the composition range 30–80 vol% PS. The blend with 10 vol% poly(ether-ester) was no longer self-supporting after the PS phase had been extracted, indicated with a bar in Table 1. SEM analysis of the unextracted blend strongly indicates that the blend with 10 vol% poly(ether-ester) consists of fibres that are not interconnected, or that some transition morphology in between a co-continuous and a droplet/matrix morphology has been formed.

Table 1
Percentage of PS extracted of blends processed on a two-roll mill at the designated temperature and subsequently quenched or annealed for 5 min at the temperature of processing. The samples indicated with (—) were no longer self-supporting after extraction

PS/poly(ether-ester), volume %	$T = 200$°C		$T = 210$°C		$T = 220$°C	
	Quenched	Annealed	Quenched	Annealed	Quenched	Annealed
10/90	30	39	28	47	36	39
20/80	41	20	16	30	18	18
30/70	99	60	14	46	69	48
40/60	100	100	92	52	62	90
50/50	100	100	100	100	100	100
60/40	100	100	100	96	100	97
70/30	100	100	100	—	100	—
80/20	100	—	—	—	—	—
90/10	—	—	—	—	—	—

Table 2
Viscosities of PS N7000 and poly(ether-ester) at processing conditions on a two-roll mill, phase dimensions (from SEM) and the resulting range of co-continuous morphologies as calculated by Eq. (2) as compared to the experimentally found range

Temperature (°C)	Viscosity PS N7000 (Pa.s)	Viscosity poly (ether–ester) (Pa.s)	R_0 poly (ether–ester) (nm)	R_0 PS N7000 (nm)	Co-continuity range (Eq. (2)) (% PS)	Co-continuity range (experiment) (% PS)
200	621	814	250	250	1–99	30–80
210	517	362	400	400	2–99	40–70
220	485	240	900	500	4–99	50–70

When the same blends are processed at 210°C, where the block copolymer becomes less elastic and the number of crosslinks decreases, the range of compositions where co-continuous morphologies are found shifts to 40–70 vol% PS (Fig. 4(d–f)). There is also an increase in the phase size, compared to the blends processed at 200°C. The blends with 20 and 10 vol% poly(ether-ester) are no longer self-supporting after extraction. From SEM analysis of the non-extracted samples it becomes clear that the 10 vol% blend consists of droplets of poly(ether-ester) in a PS matrix and the 20 vol% blend has a transition morphology. At a processing temperature of 220°C, where the poly(ether-ester) shows normal pseudo-plastic behaviour, the range of co-continuous morphologies is limited to 50–70 vol% PS (Fig. 4(g–i)) and again an increase in phase size is evident. The blends with 10 and 20 vol% poly(ether-ester) show clear droplet/matrix morphologies in SEM analysis and fall apart upon extraction.

The formation of co-continuous morphologies, especially at very low volume fractions of the poly(ether-ester) block copolymer must be attributed to stable interconnected elongated structures that have formed during processing. It becomes clear from the aforementioned results that the presence of physical crosslinks in the multiblock copolymer, meaning highly elastic rheological properties and a distinct yield stress, is essential to stabilize these elongated structures.

It is evident that co-continuous morphologies are not only formed at a single concentration, such as a point of phase inversion, but rather over a range of compositions. It is therefore appropriate to compare the results to a model describing a range of co-continuous morphologies as proposed by Willemse et al. [19]. From Fig. 1 the viscosities of both polymers at blending conditions ($\dot{\gamma} = 150\ \mathrm{s}^{-1}$) can be determined, and subsequently the limits of co-continuity can be calculated if the smallest phase dimensions and interfacial tension are known. The interfacial tension between polystyrene and poly(ether-ester) is about 3.3 mN/m, determined with the breaking thread method, and the phase dimensions are obtained from the SEM micrographs. The results for all processing temperatures are given in Table 2. Clearly there is a major discrepancy between the calculated ranges of co-continuity and the ranges found experimentally. This is related to the fact that the model is based on the assumption that the blend, during processing, is constantly subjected to a flow field. This is not the case on the two-roll mill and therefore the blend will undergo, for a large part of the processing time, quiescent conditions which result in relatively large phase domains due to coalescence and retraction. The model is very sensitive to the value of the phase dimensions. To describe the experimentally found range of co-continuous morphologies, at a processing temperature of 220°C, much lower phase dimensions, of 130–200 nm must be taken. For lower processing temperatures the dimensions should decrease to 80 nm in order to obtain agreement with the model predictions.

If the same blends are processed in an extruder equipped with a static mixer, co-continuous morphologies with a two-fold reduction in phase size, when compared to the blends prepared on the two-roll mill, are found. The calculated ranges of co-continuity and the ranges found experimentally for extrusion conditions are given in Table 3. Although there is still some difference between the calculated range of co-continuity and the range found experimentally it is evident that the fit is much better. Therefore it can be concluded that when the blend is constantly subjected to a flow field the model is more in accordance with the experiments. The fit for the blends extruded at 200°C shows a larger discrepancy than the fit for blends extruded at 220°C. This is not too suprising because the model is based on Newtonian fluids and the poly(ether-ester) shows explicit elastic behaviour at this processing temperature which is not accounted for in Eq. (2).

The way of processing also influences the range of co-continuity if the blend is processed at a temperature lower than the ODT of the block copolymer. When the blend is processed at 200°C on the two-roll mill a range of 30–80 vol% PS was found, while this range is limited to

Table 3
Viscosities of PS N7000 and poly(ether-ester) at processing conditions in the extruder, phase dimensions (from SEM) and the resulting range of co-continuous morphologies as calculated by Eq. (2) as compared to the experimentally found range

Temperature (°C)	Viscosity PS N7000 (Pa.s)	Viscosity poly (ether–ester) (Pa.s)	R_0 poly (ether–ester) (nm)	R_0 PS N7000 (nm)	Co-continuity range (Eq. (2)) (% PS)	Co-continuity range (experiment) (% PS)
200	2112	2216	200	200	11–87	40–70
220	800	249	300	250	67–96	50–70

Table 4
Average phase size of a 50 vol% PS/poly(ether-ester) blend, prepared on a two-roll mill, as a function of annealing time and temperature

Annealing time (min)	phase size (μm) at $T = 200$°C	phase size (μm) at $T = 210$°C	phase size (μm) at $T = 220$°C
0	0.8	0.8	0.8
1	1.0	2.0	1.0
3	1.5	4.0	4.0
5	2.0	6.0	7.0
15	2.0	13	30
60	2.0	80	200

40–70 vol% when extruded. This may be the result of hot spots in the extruder where the temperature is higher than the ODT of the poly(ether-ester) and therefore the crosslinks are lost. Another explanation is that the dimensions of the elongated structures become so small that the interfacial forces become larger than the stabilizing forces resulting from the physical crosslinks. 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. Because of the interfacial tension between the two phases the interfacial area will be reduced when the blend is kept at elevated temperatures. To examine the effect of physical crosslinks in the poly(ether-ester) a 50 vol% blend with PS N7000 has been annealed in the temperature range of the block copolymer's ODT. The SEM micrographs for these blends after 0, 5 and 15 min annealing, at all processing temperatures, are shown in Fig. 5. The average phase sizes as a function of temperature and time are given in Table 4.

In all cases the 50 vol% blends stay co-continuous during annealing, but there is a major difference in the change of

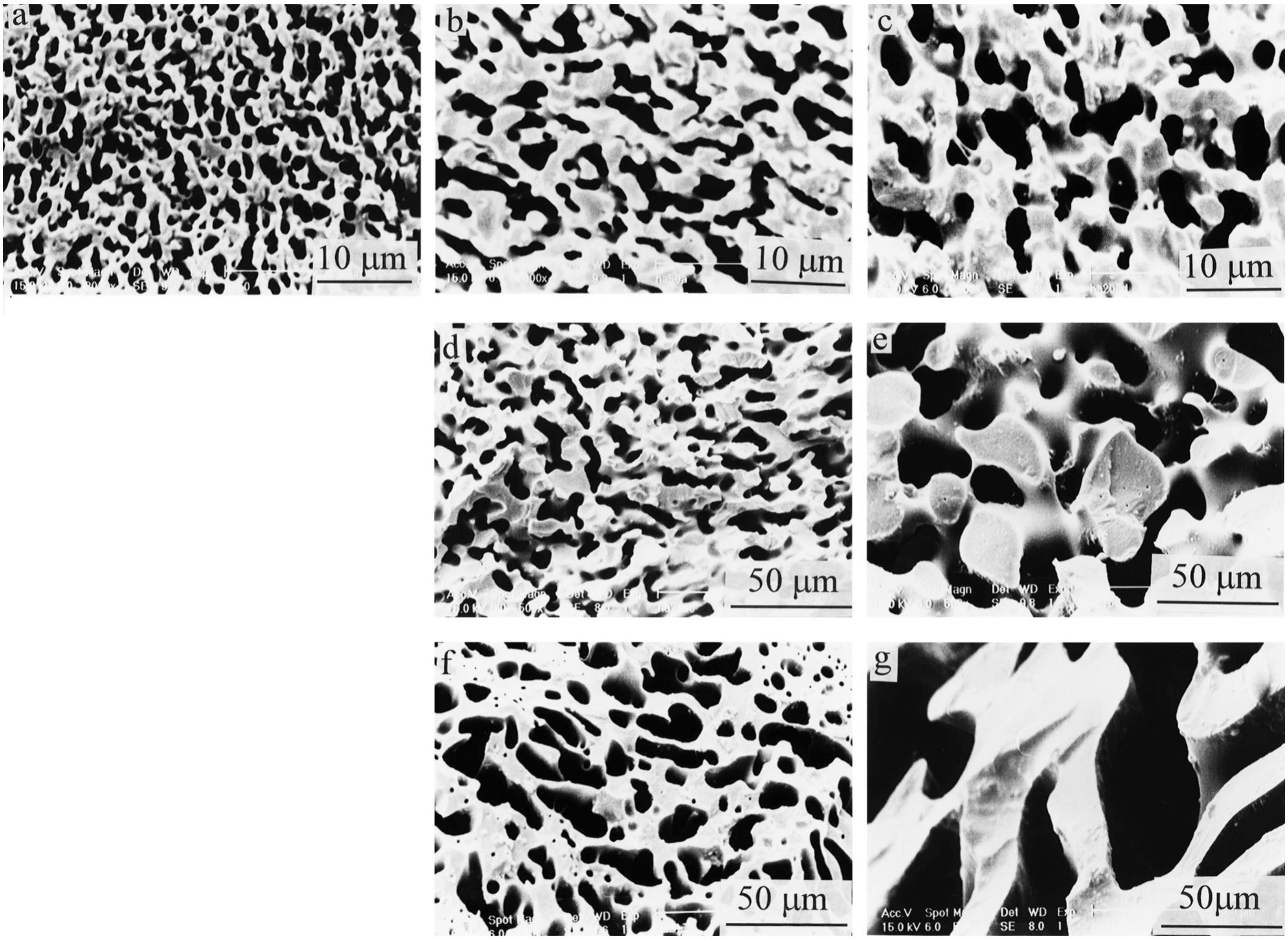

Fig. 5. SEM micrographs of 50 vol% PS/poly(ether-ester) blends that were quenched (a), annealed at 200°C (b, c), 210°C (d, e) and 220°C (f, g) for 0, 5 and 15 min.

phase size. At $T = 220°C$ both polymers show a Newtonian plateau in viscosity at low shear rates and the blend can be considered a mixture of Newtonian fluids during annealing. The increase in phase size is therefore only dependent on the interfacial tension and zero shear rate viscosity, resulting in a continuous increase in phase size with time upon annealing. At an annealing temperature of 210°C the rate of coarsening is not as high as in the experiments at 220°C but the phase sizes still increase in time. In the literature there are some suggestions that physical crosslinks [30,31] or a yield stress [44,45] can prevent coarsening of co-continuous morphologies. It becomes evident from the aforementioned results that flow, in quiescent conditions, is possible despite the presence of a yield stress or physical crosslinks and therefore these phenomena need further investigation. At 200°C the morphology changes from a phase size of 0.8 μm to 2 μm in the first 5 min of annealing. At longer annealing times the co-continuous morphology does not increase in phase size anymore. These results show that coarsening of co-continuous morphologies can be prevented if the number of crosslinks is large enough, meaning that a high elastic modulus or yield stress of the block copolymer stabilizes the morphology.

Although the coarsening of co-continuous morphologies upon annealing can be limited, it is of interest to see if annealing affects the range of co-continuous morphologies. Therefore all blends were annealed for 5 min at the temperature of processing. The results of the extraction experiments on the annealed blends can be found in Table 1. Although it is evident that the composition range of full co-continuous morphologies, annealed at 200°C, is reduced to 40–70 vol% PS, co-continuous morphologies are still present over a wide composition range. Besides that, the increase in phase size, from ~1 to ~2 μm, is limited. The blends annealed at 210 and 220°C only show co-continuous morphologies from 50 to 60 vol% PS. At the other compositions distinct droplet/matrix morphologies are found and annealing results in a six-fold increase in phase size, meaning that at these temperatures non-equilibrium morphologies are not stabilized.

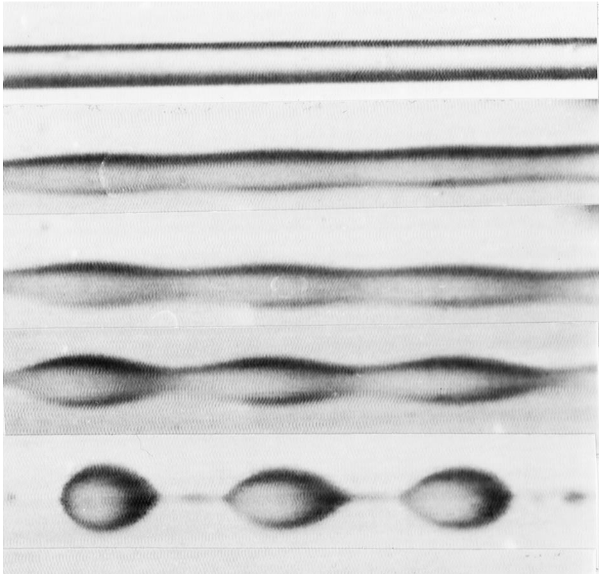

Fig. 6. Breakup process of a poly(ether-ester) thread in a polystyrene (N2000) matrix at 220°C. Photographs taken at 0, 10, 12, 14, 17 and 19 min.

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 structures that do not show breakup, end-pinching or retraction. Therefore these mechanisms for a poly(ether-ester) fibre embedded in a PS matrix have been explicitly examined in the same temperature range as the blending experiments.

A typical example of the breakup behaviour of a poly(ether-ester) thread in a polystyrene matrix at 220°C is illustrated in Fig. 6. At the deformation rates involved both polymers show a Newtonian plateau in viscosity and therefore the system can be described according to Tomotika's theory for Newtonian fluids [26,27]. A reasonably regular sinusoidal distortion is evident after which the thread breaks up in large droplets separated by one wavelength and in between these large 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.

If 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 and coworkers [28,29], may be as important as the classical breakup mechanism. The retraction mechanism, at 220°C, for short poly(ether-ester) fibres embedded in a polystyrene matrix is illustrated in Fig. 7. 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. All fibres with L/R_d values smaller than 4.3, where L is the half length of the initial fibre and R_d the radius of the resulting droplet, show this retraction behaviour and end-pinching is only found for fibres with $L/R_d > 4.3$. The flow behaviour described here is similar to the flow behaviour found for Newtonian fluids by Stone et al.

As was shown before, co-continuous morphologies could only be obtained, at this processing temperature, over a small composition range and the resulting blends were highly unstable in the molten state. For poly(ether-ester) threads of ~100 μm diameter the time-scale for breakup is in the order of a few minutes. The time for breakup, t_b (s), for a viscous thread embedded in a viscous matrix under quiescent conditions can be expressed as Ref. [44]:

$$t_b = \frac{1}{q}\ln\left(\frac{0.82R_0}{\alpha_0}\right) \tag{3}$$

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

$$q = \frac{\sigma}{2\eta_m R_0}\Omega(\lambda, p) \tag{4}$$

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 $\Omega(\lambda,p)$ is a dimensionless growth rate [26]. If a distortion growth rate of $q = 3.9 \times 10^{-3}\ s^{-1}$, taken from experimental results, and a relative initial distortion of $\alpha_0/R_0 = 0.1$ are assumed, the breakup time for a poly(ether-ester) thread of 1 μm is in the order of a few seconds. The time-scales for retraction of a polymer fibre can be expressed as [50,51]:

$$q_r = \frac{\sigma}{\chi R_d \eta_e} \tag{5}$$

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) is an effectiveviscosity that is a function of the matrix viscosity and the fibre viscosity and χ is a hydrodynamic coefficient. Several other authors [52–54] 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, i.e. less than a second, for typical blend dimensions (~1 μm). Although in all blends the matrix polymer (PS N7000) is more viscous, leading to somewhat larger time-scales for breakup and retraction, these experiments show that non-equilibrium morphologies cannot exist for a period of time long enough to be solidified upon quenching or stay stable upon annealing. Therefore co-continuous morphologies blended at 220°C are only found in a limited composition range and are not stable upon annealing.

The breakup, or rather non-breakup, of the poly(ether-ester) thread at 210°C is illustrated in Fig. 8. Even after 8 h the thread embedded in a PS N2000 matrix does not show breakup. The same non-breakup phenomena have been found at a temperature of 200°C. Due to the non-Newtonian behaviour of the poly(ether-ester) (Fig. 1(c)) Tomotika's theory cannot be applied in these cases. Although Palierne and Lequeux [55] extended Tomotika's theory to visco-elastic systems, their theory cannot explain the non-breakup behaviour of the poly(ether-ester). An approximation, proposed by Elmendorp [44,45], to explain the observed phenomena is to use the 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

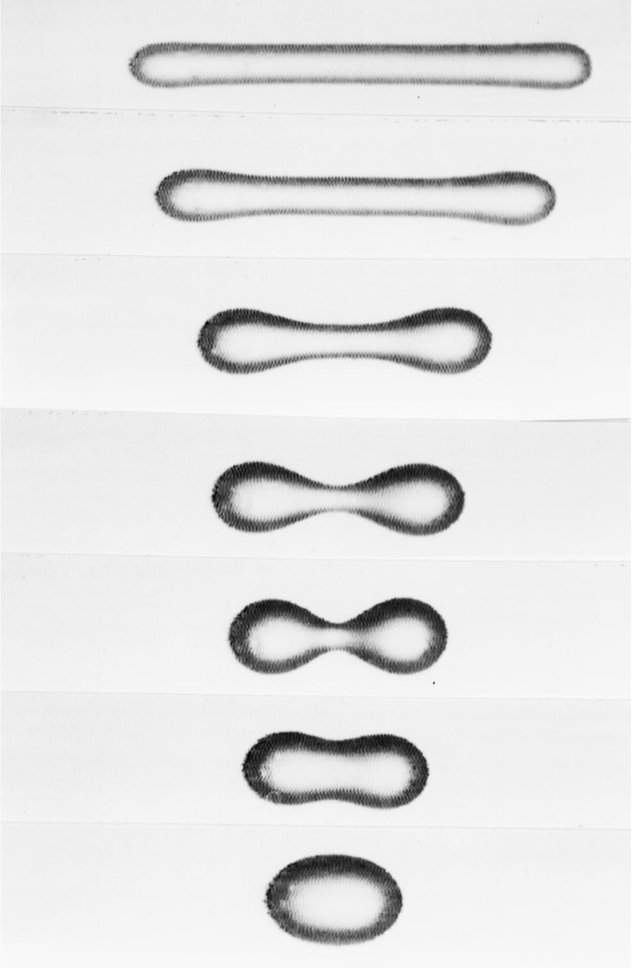

Fig. 7. Retraction process of a poly(ether-ester) thread in a polystyrene matrix (N2000) at 220°C. Photographs taken at 0, 2, 6, 10, 12 and 14 min.

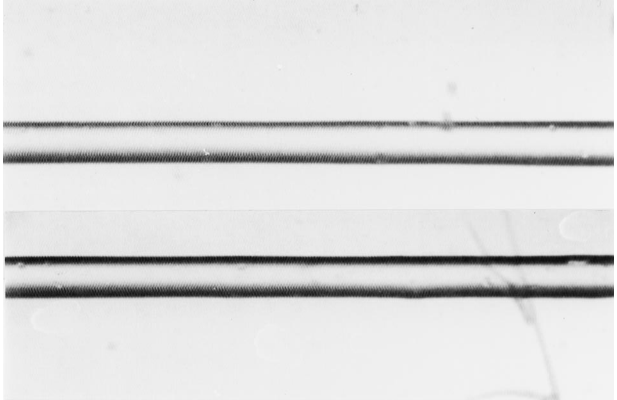

Fig. 8. Non-breakup of a poly(ether-ester) thread in a polystyrene (N2000) matrix at 210°C. Photographs taken at 0 and 8 h.

Table 5
Dominant wavenumber, yield stress obtained from Fig. 2 and calculated pressure differences for three different radii at 200 and 210°C

Temperature (°C)	X_m	Yield stress (Pa)	P_s ($R = 40\ \mu$m) (Pa)	P_s ($R = 0.5\ \mu$m) (Pa)	P_s ($R = 0.2\ \mu$m) (Pa)
200°C	0.12	3800	16.5	1320	3303
210°C	0.24	500	15.8	1264	3160

and minimal radius can be expressed as:

$$P_s = \frac{2\alpha'\sigma}{R_0}\left(\frac{1}{1-1.5\alpha'^2} - X^2\right) \tag{6}$$

where $\alpha' = \alpha/R_0$ is the relative distortion and $X = 2\pi R_0/\lambda$ is the dimensionless wave number. 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 tension between polystyrene and poly(ether-ester) is about 3.3 mN/m, determined with the breaking thread method. For X the value for the dominant wave number (X_m) corresponding to the viscosity ratio at each temperature is used[44], and for α' a value of 0.1 is assumed. The calculated pressure differences for three different radii, X_m and the yield stresses, obtained from Fig. 2, can be seen in Table 5. In the breakup experiments shown in Figs 6, and 8 the thread radius is approximately 40–50 μm. The yield stresses at 210 and 200°C by far exceed the calculated pressure difference if a thread radius of 40 μm is assumed and therefore no breakup should occur according to Elmendorp's approximation. This is in agreement with experimental results that were shown in Figs 6, and 8. At 210°C the calculated pressure difference, if a thread radius of 0.5 μm is assumed, is much larger than the yield stress found, meaning that in blending conditions breakup can occur at 210°C and flow is possible at this temperature. This might explain why co-continuous morphologies are not stable upon annealing at 210°C. The same calculation for 200°C results in a P_s that is smaller than the yield stress, therefore suggesting that breakup in blending conditions, on the two-roll mill, at 200°C is limited and flow is restricted. This might explain why co-continuous morphologies are found at small volume fractions of the poly(ether-ester) and that these morphologies are reasonably stable at this temperature. When the same blends were extruded at 200°C the dimensions could even decrease until 200 nm resulting in a deforming stress that is in the same range as the stabilizing yield stress. It is therefore acceptable that co-continuous morphologies are formed into a more limited range when extruded in comparison to the preparation on the two-roll mill.

A typical example of retraction behaviour of poly(ether-ester) fibres embedded in a polystyrene matrix at 210°C can be seen in Fig. 9. The first part of the retraction mechanism takes place in about 20 min where the ends of the fibre become spherical and are pulled towards the middle of the fibre. After this first relaxation the fibre no longer retracts and keeps its shape for an infinite time. At 200°C the behaviour (Fig. 10) is even more extreme, meaning that the shape of the fibre does not change at all. Even the sharp edges, which results from cutting with the surgeon's knife, do not become more spherical. If the dimensions of the fibre

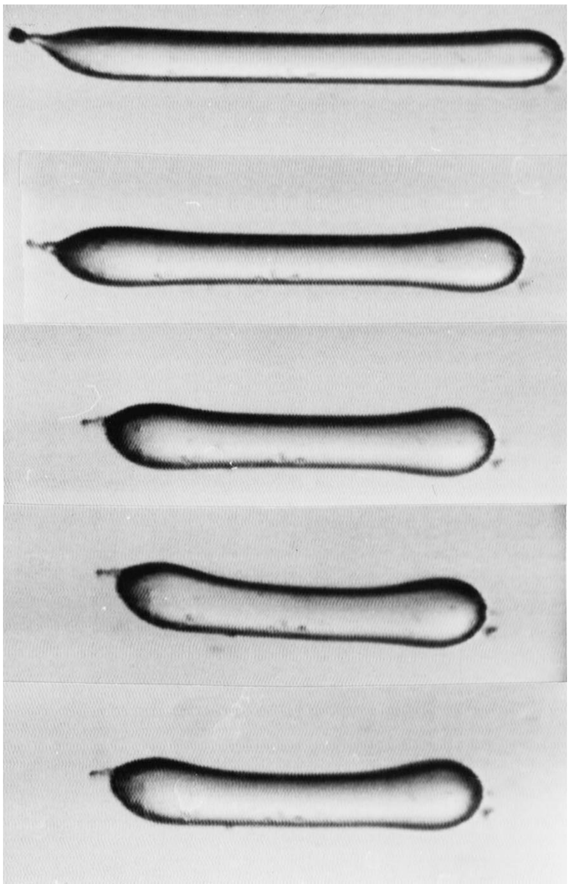

Fig. 9. Retraction process of a poly(ether-ester) thread in a polystyrene matrix (N2000) at 210°C. Photographs taken at 0, 4, 30, 120 and 240 min.

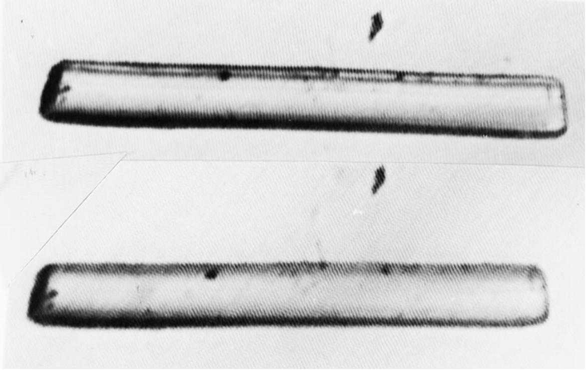

Fig. 10. Retraction process of a poly(ether-ester) thread in a polystyrene matrix (N2000) at 200°C. Photographs taken at 0 and 3 h.

are smaller the driving force for retraction (σ/R) will be larger and therefore the shown retraction behaviour will be less extreme at blending conditions, but it is evident that retraction can be limited or even stopped.

The breakup and retraction experiments clearly show that, dependent on the number of physical crosslinks present in the block copolymer, retraction or breakup can be severely limited or even stopped. Although no exact timescales for breakup and retraction in real blends can be calculated from these experiments, because also other factors such as stabilization through shear can play a role, it is proven that stable elongated structures can exist in polymer blends. Therefore the condition for co-continuous morphologies, especially at low volume fractions, is fulfilled, i.e. the formation of stable elongated structures that do not show breakup or retraction.

4. Conclusions

Co-continuous morphologies are obtained over a wide range of compositions (30–80 vol%) if a poly(ether-ester) block copolymer is blended with PS at a temperature below the block copolymer's ODT. The composition range decreases with increasing temperature resulting in a limited range of co-continuous morphologies if both components show pseudo-plastic behaviour. Annealing at 200°C, under the block copolymer's ODT, hardly influences the size and composition range of the co-continuous morphologies. Annealing at higher temperature results in an increase in phase size and a decrease in composition range of co-continuous morphologies. If crosslinks are present in the block copolymer the breakup and retraction behaviour of poly(ether-ester) threads is severely limited or even stopped, meaning that elongated structures are stable and therefore co-continuous morphologies can be formed. It is shown that the dimensions of the phases and the block copolymer's yield stress can be used to explain the observed phenomena.

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