

On the coarsening of co-continuous morphologies in polymer blends: effect of interfacial tension, viscosity and physical cross-links

Harm Veenstra*, Jaap Van Dam, Abe Posthuma de Boer

Department of Polymer Technology, Faculty of Chemical Technology and Materials Science, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Received 24 April 1998; received in revised form 21 May 1999; accepted 24 June 1999

Abstract

The coarsening of co-continuous morphologies in polymer blends with annealing is studied, demonstrating the effect of interfacial tension, viscosity and also physical cross-links in blends with thermoplastic elastomers. Co-continuous morphologies of 50/50 wt% stay co-continuous with annealing but show a linear increase in phase size with time. The 30/70 wt% blends break up into droplet/matrix morphologies and shows an increase in phase size in the first stage of the coarsening process. A relation has been proposed, using only the interfacial tension and viscosities of both components, to predict the growth rate of coarsening. The relation shows good agreement with the rates found experimentally.

The coarsening process in blends with thermoplastic elastomers is severely slowed down or even stopped when physical cross-links are present in the thermoplastic elastomers. The driving force for coarsening is too small to overcome the stabilizing force due to physical cross-links. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Co-continuous; Coarsening

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 brittle polymers [1–4]. This 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.

It was long believed that co-continuous morphologies are mainly formed close to the point of phase inversion [9–18]. In earlier reports [19–22], 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. This range of volume fractions strongly depends on the processing conditions and the rheological properties of the components [19,22]. An interesting feature of blends with thermoplastic elastomers (TPEs) is that co-continuous morphologies can be obtained over a wide composition range [20–22]. In an earlier paper [22], the formation of such a wide composition range was related to the specific rheological properties of TPEs. TPEs are block copolymers where the blocks are phase separated into micro-domains. These phase-separated domains, also called physical cross-links, are responsible for the unique (rheological) properties of TPEs.

In the region of co-continuity, the morphologies are unstable with annealing [20–29]. Annealing at temperatures where the polymers are in the liquid state not only affect the dimensions of the phase domains, but also the range of volume fractions where co-continuous morphologies are found. Therefore, it is difficult to control these morphologies during further processing such as compression and injection moulding. This change in morphology with annealing,

* Corresponding author. Tel.: +31-15-2781828; fax: +31-15-2787415.

which will be referred to as a coarsening process, is a result of viscous flow driven by the interfacial tension. Because the properties of polymer blends are to a large extent determined by the morphology, a detailed knowledge of the coarsening process upon annealing is desirable.

An interfacial tension driven process that is well known is the breakup of threads through Rayleigh distortions [30]. In Tomotika's theory [31,32] on breakup of viscous Newtonian threads imbedded in a viscous Newtonian matrix, a sinusoidal distortion (α) is imposed upon a thread, which grows exponentially with time:

$$\alpha = \alpha_0 e^{qt} \quad (1)$$

where α_0 (m) is the initial distortion amplitude and $q = \sigma \Omega(\lambda, p) / 2 \eta_m R_0$ (s^{-1}) is the growth rate of the distortion. Here R_0 is the initial thread radius (m), η_m the viscosity of the matrix (Pa s), σ the interfacial tension ($N m^{-1}$) and $\Omega(\lambda, p)$ a dimensionless growth rate which is a known function of λ , the wavelength of the sinusoidal distortion (m) and p the viscosity ratio [31,32]. Although polymer melts most commonly show visco-elastic behaviour, the reports concerning capillary instabilities of polymer threads [22,33,34] are often in accordance with Tomotika's predictions. This can easily be explained by the slowness of the deformation rates, typically in the order of 10^{-3} – $10^{-2} s^{-1}$, during the breakup process. At these small rates, most polymers show a Newtonian plateau in viscosity and therefore visco-elastic phenomena are often not observed in capillary breakup experiments.

Apart from the Rayleigh distortion mechanism, which in principle occurs only for threads or highly extended droplets, other interfacial tension driven processes are reported for moderately extended droplets or short fibres. Stone et al. [35,36] showed that for moderately extended droplets, the main mechanisms to reduce the interface are retraction and end pinching. In the latter case, the spherical ends of the extended drops are pinched off. Retraction is a rather complex flow behaviour, where the ends of the thread become 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. Fibres with an elongational ratio (L/R_d , where L is the half-length of the initial fibre and R_d the radius of the resulting droplet) smaller than a critical elongational ratio (typical order of magnitude is four) show this retraction behaviour. End pinching is found for fibres with an elongational ratio higher than the critical elongational ratio. The time scale for retraction of a polymer fibre is a function of the interfacial tension, viscosity and a droplet or fibre radius [37–41]. For example, Tjahjadi expressed the retraction growth rate (q_r) for an polymer fibre as:

$$q_r = \frac{\sigma}{R_0 \eta_m} \quad (2)$$

Because a co-continuous morphology can be considered as a

three-dimensional (3D) structure that consists of elongated domains that are interconnected, the breakup and retraction mechanisms as described above are very important in the formation and stability of such a morphology [22]. When the elongated domains in a co-continuous morphology show breakup or retraction and the resulting droplets are no longer interconnected, a droplet in matrix morphology will be formed. Stable co-continuous morphologies, especially at low volume fractions, can therefore only be obtained, if the breakup and retraction processes are slowed down or completely stopped.

The objective of this paper is to obtain a detailed knowledge of the coarsening process of co-continuous morphologies upon annealing. Therefore, a number of co-continuous blends, with compositions of 30/70 and 50/50 wt%, have been prepared and subsequently annealed. The coarsening process will be qualitatively and quantitatively related to important parameters in the coarsening process such as interfacial tension, viscosity and physical cross-links in block copolymers.

2. Experimental

2.1. Materials

The polymers used were a polystyrene (PS Hostyrene N7000; Shell), a low-density polyethylene (LDPE Stamyran LD2102; DSM), a polymethyl methacrylate (PMMA MG102; ICI), a polypropylene (PP Stamyran P13E10; DSM), two styrene/(ethylene–butylene) based block copolymers (SEBS Kraton G1650 and SEBS Kraton G1657; Shell) and a poly(ether–ester) multiblock copolymer (Arnitel EM400; DSM). The SEBS G1650 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. 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. [42].

2.2. Rheology

Dynamic shear experiments were performed on a Rheometrics RMS 800 rheometer in the plate–plate configuration with a plate diameter of 25 mm and a gap of 2 mm. The complex viscosity (η^*) was measured at different temperatures in the frequency range of 10^{-2} – 10^2 $rad s^{-1}$ with a strain of 5%. It was made sure that all experiments were done in the linear viscoelastic regime.

2.3. Processing

For the annealing experiments, a number of blends with

Table 1

Blends of pseudo-plastics for the annealing experiments with annealing temperatures (T_a), interfacial tensions (σ) and effective viscosities (η_{30} and η_{50}) for the 30/70 and 50/50 wt% blends

System	T_a (°C)	σ (mN m ⁻¹)	η_{30} (Pa s)	η_{50} (Pa s)
LDPE/PMMA	210	9.0 [43]	11 050	14 750
LDPE/PS	210	5.1 [43]	1 1350	15 250
PP/LDPE	210	0.8 [43]	17 050	13 750
LDPE/PS/5% SEBS	210	1.9 [28]	11 350	15 250
Poly(ether-ester)/PS	220	3.3 [22]	4780	7700
PP/SEBS G1657	240	1.0 [44]	10 900	8160

compositions of 30/70 and 50/50 wt% were 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. The extruded strands were quenched in water. To obtain a LDPE/PS blend with a lower interfacial tension, it was compatibilized with the SEBS G1650 block copolymer. Therefore, the compatibilizer was first mixed with the polystyrene after which the polyethylene was blended in. The amount of compatibilizer added was 5 wt% with respect to the minor phase. All blends have different interfacial tensions and their components' different zero shear rate viscosities. The specifics of the blends can be found in Tables 1 and 2. For the blend viscosities, we took the weight average of the components' zero shear rate viscosities, resulting in an effective viscosity for the 30/70 wt% blend (η_{30}) and the 50/50 wt% blend (η_{50}). All blends show co-continuous morphologies after the first processing step, except for the compatibilized 30/70 wt% PS/LDPE blend which shows a droplet/matrix morphology. The average phase sizes of all blends are in the sub-micron range (0.2–1.0 μ m). All 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 minor phase was extracted with a selective solvent, i.e. 2-butanone to extract PS and PMMA and

Table 2

Blends with thermoplastic elastomers for the annealing experiments with the annealing temperatures (T_a), interfacial tensions (σ) and effective viscosities (η_{50})

System	T_a (°C)	σ (mN m ⁻¹ m)	η_{50} (Pa s)
Poly(ether-ester)/PS	200	3.3 [22]	–
PP/SEBS G1650	200	–	–
PP/SEBS G1657	190	1.2 ^a	29 000

^a Estimate from break-up experiments [44].

iso-octane to extract LDPE and SEBS. 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 of the components can be extracted and the remaining piece is still self-supporting. For the average phase sizes, we determined the midpoint of the ranges of phase sizes found.

3. Results and discussion

3.1. Rheology of the polymers

The viscosity vs. frequency curves for all polymers are shown in Fig. 1. At these temperatures, all polymers show a Newtonian plateau at low frequencies and shear-thinning behaviour at the higher frequencies measured. The curves for PS measured at 200 and 220°C and for PP measured at 190, 200 and 240°C are not shown here, but both polymers also show pseudo-plastic behaviour at these temperatures. From these graphs, the zero shear rate viscosity (η_0) can be determined and subsequently the effective viscosity (η_{30} and η_{50}) can be calculated. The block copolymers show completely different rheological behaviour at lower temperatures. Block copolymers can show phase separation resulting in amorphous micro-domains for the SEBS block copolymers and crystalline micro-domains for the poly(ether-ester) [42]. The viscosity vs. frequency curves for the phase separated block copolymers are shown in Fig. 2. The poly(ether-ester) and SEBS G1650 show shear-thinning behaviour over the complete range of frequencies measured. This is a clear indication that at these temperatures the block copolymers are phase separated into micro-domains [42]. The curve for SEBS G1657 is not as extreme, but the second shear-thinning region between 10⁻¹ and 10⁰ rad s⁻¹, as compared to the curve in Fig. 1, indicates that this block copolymer consists of PS domains in a P(EB) matrix.

3.2. Qualitative analysis of morphological coarsening

Fig. 3 depicts the morphology of the 50/50 wt% PP/LDPE blend after 0, 5, 15 and 60 min of annealing at 210°C. The SEM micrographs show the PP matrix (grey sections) that is left after the PE phase has been extracted (dark sections). From extraction experiments and SEM analysis, it is evident that a co-continuous morphology has formed directly after extrusion (0 min). When the blend is annealed, a significant increase in phase sizes is observed with increasing annealing time, but the blend remains co-continuous. This conclusion is sustained by the extraction experiments where 100% of the LDPE can be extracted and the remaining piece stays self-supporting, after all annealing times. The 3D structure consists of elongated domains that are interconnected. The elongational ratio (L/R_d) of these domains is too small to show capillary breakup. To reduce the number of branch points in the 3D structure upon

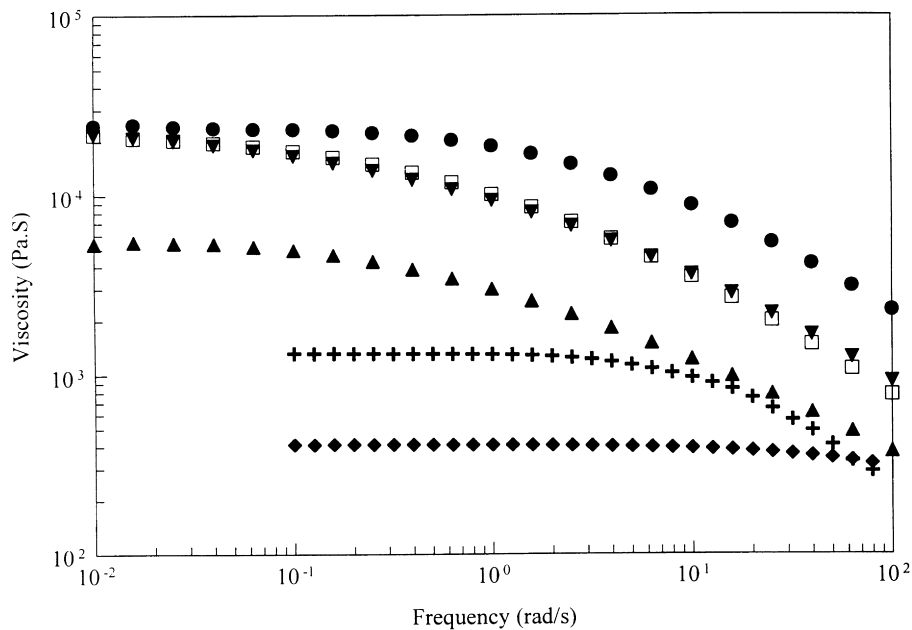


Fig. 1. Viscosity as a function of frequency for PMMA (●), PS (□), PP (▼), LDPE (▲) determined at 210°C, SEBS G1657 (+) determined at 240°C and poly(ether-ester) (◆) determined at 220°C.

annealing some of the elongated domains have to be split into two, but at this high concentration the phases stay interconnected, and therefore, the blend reduces its interface mainly by a continuous retraction process. Breakup of the co-continuous morphology is therefore prevented, and an increase of phase size with time is found.

The same coarsening process upon annealing, i.e. co-continuity is maintained but the phase sizes are increasing, has been found for all other 50/50 wt% blends. Although the coarsening process may be the same for all blends, the rate

of this process is very different for each blend investigated. In Fig. 4, the average phase sizes are plotted as a function of annealing time. At these temperatures, all polymers show a Newtonian plateau in viscosity at low shear rates and all blends can be considered as mixtures of Newtonian fluids during annealing. The rate of the process is therefore determined by the interfacial tension and the zero shear rate viscosities.

In Fig. 5, the morphology of the 30/70 wt% LDPE/PP blend after 0, 5, 15 and 40 min annealing at 210°C is

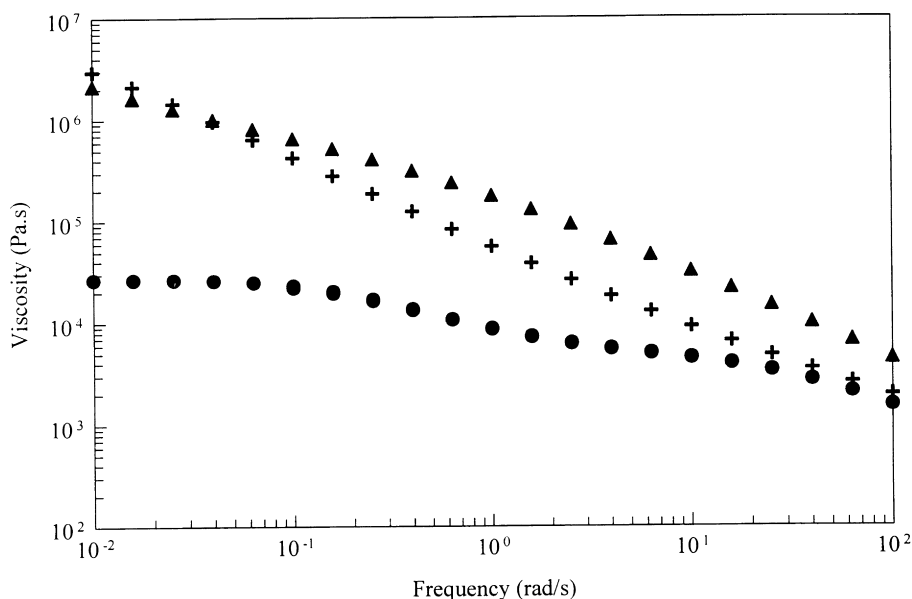


Fig. 2. Viscosity as a function of frequency for SEBS G1650 (▲), poly(ether-ester) (+) determined at 200°C and SEBS G1657 (●) determined at 190°C.

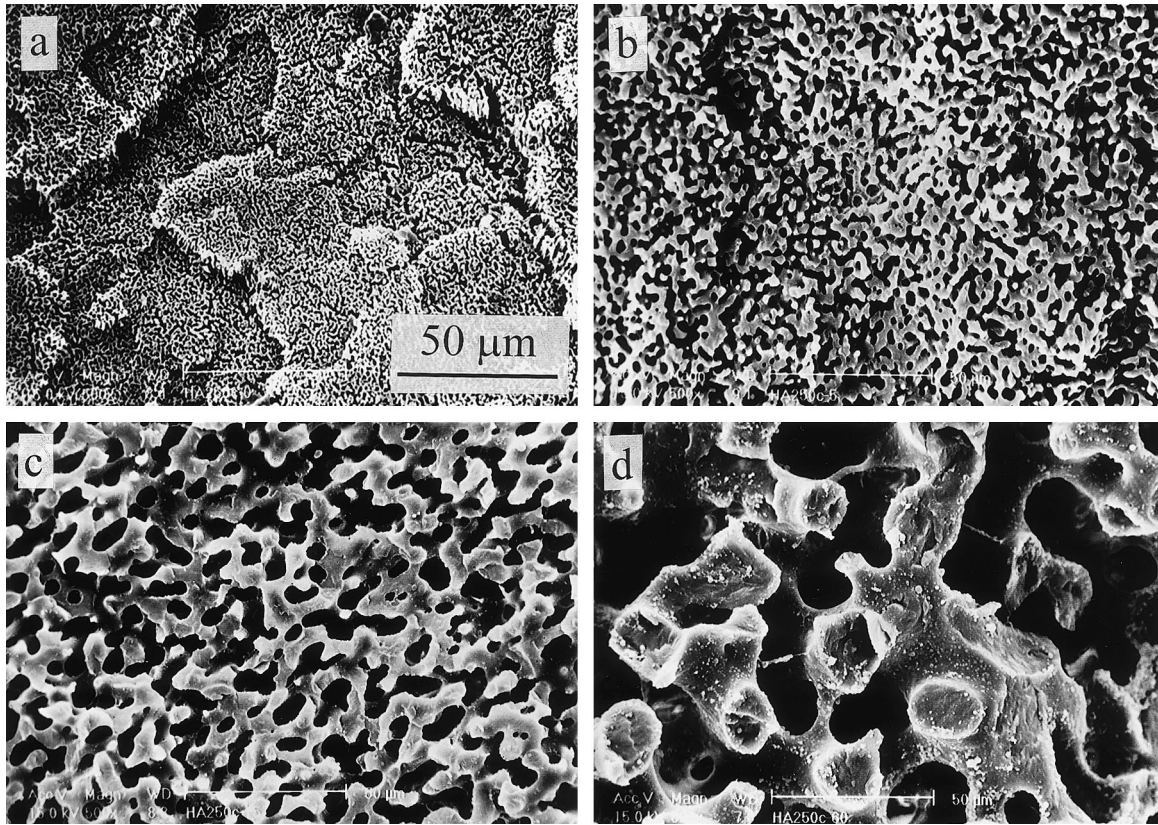


Fig. 3. SEM micrographs of a 50/50 wt% PP /LDPE blend annealed at 210°C for: (a) 0; (b) 5; (c) 15; and (d) 60 min.

depicted. The SEM micrographs show that a co-continuous morphology has been formed directly after extrusion (0 min). This is sustained by extraction experiments where 100% of the LDPE could be extracted (Table 3). As the blend is annealed, an increase in average phase sizes is

observed up to an annealing time of 15 min. At longer annealing times, no significant changes were found any more. The morphology of the blend changes from a co-continuous to a droplet in matrix morphology as can be concluded from SEM analysis and extraction. Not only

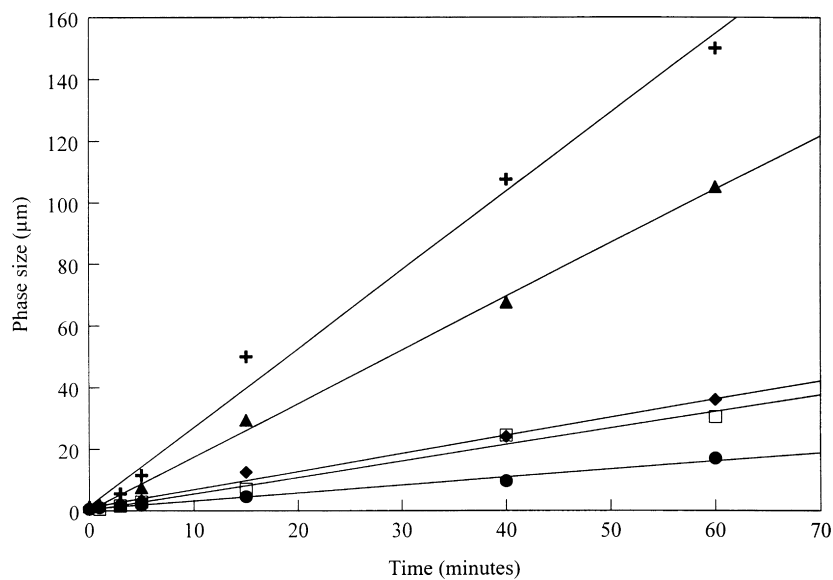


Fig. 4. Phase sizes of 50/50 wt% blends as function of annealing time for LDPE/PMMA (+), LDPE/PS (▲), LDPE/PS/SEBS (◆), LDPE/PP (●) at 210°C and PP/SEBS G1657 (□) at 240°C.

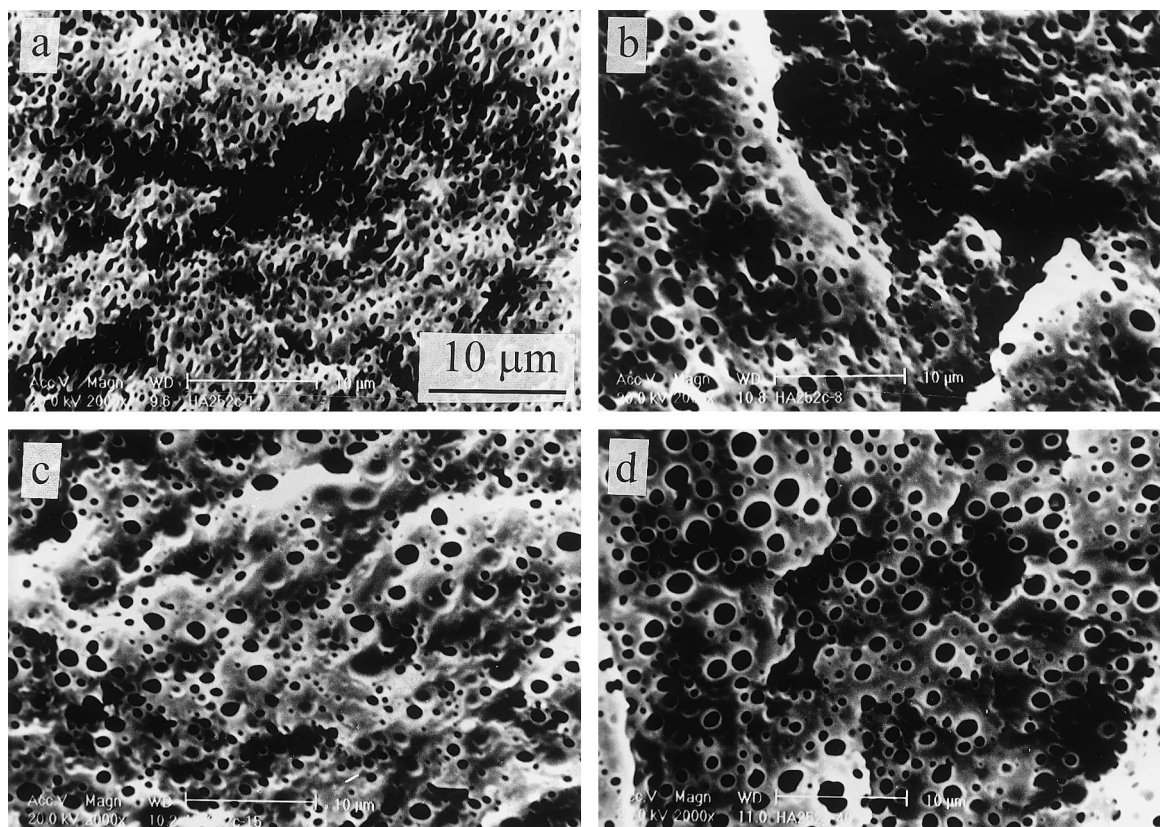


Fig. 5. SEM micrographs of a 30/70 wt% PP/LDPE blend annealed at 210°C for: (a) 0; (b) 5; (c) 15; and (d) 40 min.

does the average phase size increase initially upon annealing but also a major increase in the range of phase sizes is found (Table 4). This is the result of the complexity of the coarsening process at this composition. Part of the blend will only show retraction or end-pinching upon annealing leading to a two-fold increase in phase size. This process results in the lower limit of phase sizes indicated in Table 4. A major part of the phase domains show a larger increase in phase sizes than the typical two-fold increase for retraction, breakup and end-pinching, which must be the result of another coarsening process. This is sustained by the time scale of the coarsening process. A typical time scale for breakup or retraction for isolated polymer fibres of 1 μm thickness is in the order of seconds while the total coarsening process takes place within 10–15 min.

The percolation threshold for droplets is 16 vol% while

this value will be even smaller for slightly elongated structures. The blends with 30 wt% of the minor component will therefore stay partly interconnected, even after the first retraction. This interconnectivity will lead to continuous retraction behaviour, comparable to the coarsening process in the 50/50 wt% blends, until droplets are formed. When these droplets are no longer interconnected their phase sizes no longer increase. Coarsening via coalescence of non-interconnected droplets will hardly take place because of the high viscosity of the polymers.

All 30/70 wt% blends show the same coarsening process upon annealing in the major part of the samples, i.e. a change from co-continuous to droplet/matrix morphology and an increase in phase sizes in the first 15 min of annealing. The average phase sizes vs. annealing time are shown in Fig. 6 (not all blends are shown for sake of clarity). The

Table 3

Extraction results (%) for all 30/70 wt% blends that were annealed for 0, 1, 3, 5, 15, 40 and 60 min

System	(0 min)	(1 min)	(3 min)	(5 min)	(15 min)	(40 min)	(60 min)
LDPE/PMMA	100	92	82	75	75	72	70
LDPE/PS	100	74	32	53	34	10	9
PP/LDPE	100	100	75	54	29	22	28
LDPE/PS/5% SEBS	26	11	5	4	1	4	5
Poly(ether-ester)/PS	100	90	85	74	77	75	69
PP/SEBS G1657	100	100	51	40	45	45	52

Table 4
Range of phase sizes (μm) for all 30/70 wt% blends that were annealed for 0, 1, 3, 5, 15, 40 and 60 min

System	(0 min)	(1 min)	(3 min)	(5 min)	(15 min)	(40 min)	(60 min)
LDPE/PMMA	0.7–1.3	0.5–1.5	1.5–6.5	2.0–10	2.0–8.4	2.0–10	2.0–10
LDPE/PS	0.6–1.3	0.9–2.5	1.5–7.0	1.5–9.0	1.5–11	1.5–11	1.5–12
PP/LDPE	0.2–0.8	0.3–0.8	0.5–1.3	0.5–1.6	0.4–1.5	0.5–1.6	0.5–1.6
LDPE/PS/5% SEBS	0.3–0.9	0.5–1.1	0.5–2.3	0.5–4.1	0.5–3.8	0.5–4.6	0.5–4.6
Poly(ether-ester)/PS	0.5–0.8	0.5–0.9	0.8–3.0	1.0–5.3	1.0–3.8	1.1–7.4	1.0–8.0
PP/SEBS G1657	0.2–0.3	0.3–0.6	0.3–0.9	0.3–1.2	0.3–0.8	0.3–1.6	0.4–1.7

difference between the blends is the rate of the process, which is related to the interfacial tension and zero shear rate viscosities, and the final phase sizes after annealing. Besides the major coarsening process, as described above, some blends also show coarsening similar to the process described for the 50/50 wt% blends. This is the result of the percolation of phase domains that always occurs if the concentration is higher than the percolation threshold for droplets. This latter process which takes place in a minor part of the blend results also in somewhat high extraction results (Table 3).

3.3. Quantitative analysis of morphological coarsening

The coarsening process of a co-continuous morphology is similar to breakup [22,31–34] and retraction [35,36] of isolated polymer fibres in a polymer matrix, i.e. the process is interfacial tension driven. Similar to the growth rate for retraction (Eq. (2)) and growth rate for breakup, the rate of the coarsening process is therefore proportional to the interfacial tension and inversely proportional to the viscosity of the system. Since the coarsening process occurs simultaneously in both blend components, the viscosity of the system is determined by the viscosities of both components,

i.e. by an effective viscosity (η_e) as defined in the experimental section. The rate of coarsening (dR/dt) can now be expressed as:

$$\frac{dR}{dt} = c \frac{\sigma}{\eta_e} \quad (3)$$

where dR/dt is the average thickness of the network strands changing with time, η_e the effective viscosity that depends on the weight fraction of the blends (η_{50} for 50/50 wt% blends and η_{30} for 30/70 wt% blends) and c is a dimensionless factor.

The values for the interfacial tensions and effective viscosities (η_e) for the 30/70 wt% and 50/50 wt% blends can be found in Tables 1 and 2. The values for the growth rate according to Eq. (3) can now be calculated and compared to the values found experimentally (Table 5). For the 50/50 wt% blends, the experimental growth rates for all blends were obtained by a linear curve fit through all points in Fig. 4. A value of $c = 0.07$ was chosen for the calculations to obtain an agreement with experimental data. For the 30/70 wt% blends, a linear curve fit was made through the points obtained in the first 5 min of annealing (Fig. 6), i.e. before the co-continuous morphologies breakup into

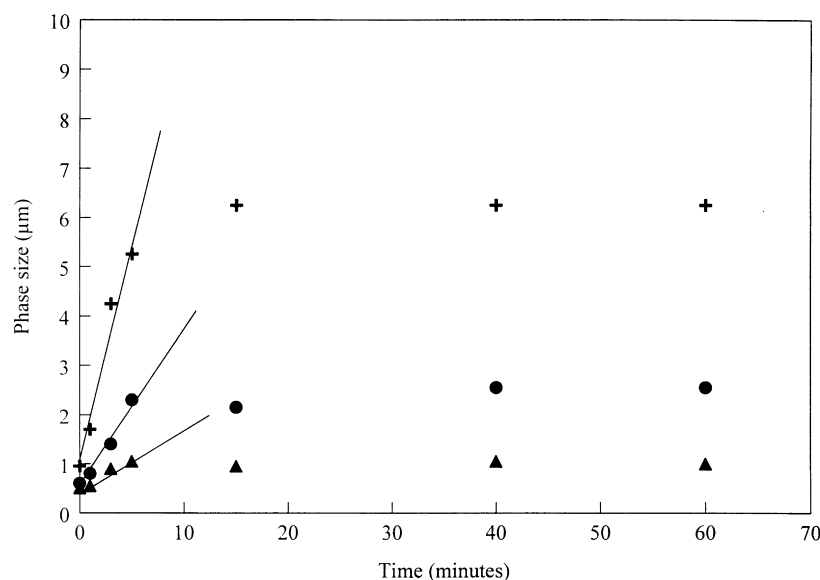


Fig. 6. Phase sizes of 30/70 wt% blends as function of annealing time for LDPE/PS (+), LDPE/PP (▲) and LDPE/PS/SEBS (●) at 210°C.

Table 5

Rates of coarsening (m s^{-1}) determined experimentally (dr/dt (exp)) as compared to calculated values (dr/dt) according to relation (3), for 50/50 and 30/70 wt % blends

System	50/50 (wt%)		30/70 (wt%)	
	dr/dt (exp)	dr/dt	dr/dt (exp)	dr/dt
LDPE/PMMA	4.3×10^{-8}	4.3×10^{-8}	2.1×10^{-8}	2.4×10^{-8}
LDPE/PS	2.9×10^{-8}	2.3×10^{-8}	1.5×10^{-8}	1.3×10^{-8}
PP/LDPE	4.3×10^{-9}	4.1×10^{-9}	2.0×10^{-9}	1.4×10^{-9}
LDPE/PS/5% SEBS	9.8×10^{-9}	8.7×10^{-9}	5.7×10^{-9}	5.0×10^{-9}
Poly(ether–ester)/PS	3.3×10^{-8}	3.0×10^{-8}	1.1×10^{-8}	2.0×10^{-8}
PP/SEBS G1657	8.9×10^{-9}	8.6×10^{-9}	1.7×10^{-9}	2.7×10^{-9}

droplet/matrix morphologies, and $c = 0.03$ was used for the calculations.

The calculated values for the growth rate of the 50/50 wt% blends agree very well with the experimental values. Considering the errors associated with the determination of interfacial tensions, viscosities and phase sizes, the excellent agreement for all blends with a single value for c is most satisfying. For the 30/70 wt% blends, the agreement is still very good but the deviations are somewhat larger than those for the 50/50 wt% blends. This can be explained by the limited number of points through which the lines were fitted to obtain the growth rates, resulting in a larger error.

These results are surprising, considering that the change in domain size for breakup and retraction processes are not linear with time (Eq. (1)), which is the result of the change of shapes during the course of these processes. The rate of coarsening of the co-continuous structure remains constant despite the change in shape of the interconnected phase network. The constant c appears to be independent of the nature of the polymers and to depend only on their volume fraction. Although the constant coarsening rate seems

surprising to a similar result, i.e. a coarsening rate that is linearly proportional to the interfacial tension and inversely proportional to the viscosity of the system, was found for the later stages of spinodal decomposition in binary mixtures [45].

The results of this analysis show that the growth rate of phase sizes of co-continuous morphologies can be predicted if the interfacial tension and the zero-shear viscosities of both components are known.

3.4. Morphological stability of blends with thermoplastic elastomers

In Fig. 7, the phase sizes vs. annealing time for the 50/50 wt% blends with TPEs are shown. The PS/poly(ether–ester) blend and the PP/SEBS G1650 blend show a two-fold increase in phase size in the first 5 min of annealing after which the co-continuous morphologies become stable. This is a completely different behaviour as has been found for the pseudo-plastic 50/50 wt% blends (Fig. 4). Indeed, the very high viscosities of the block copolymers should reduce the coarsening rates in these blends, based on Eq. (3), but it does not explain why the blends do not show any coarsening at all after the first 5 min of annealing. In earlier papers [22,44], we have shown that physical cross-links or a yield stress has a profound effect on the formation and stability of co-continuous morphologies. In the blends mentioned above, the driving force for coarsening, i.e. the interfacial tension, is apparently too small to overcome the stabilizing force due to physical cross-links or a yield stress. It also becomes clear from Fig. 7 that the presence of physical cross-links does not always stabilize co-continuous morphologies. Although the SEBS G1657 is phase separated in amorphous domains at the temperature of annealing, the blend with PP still shows a linear increase of phase sizes upon annealing. However, the

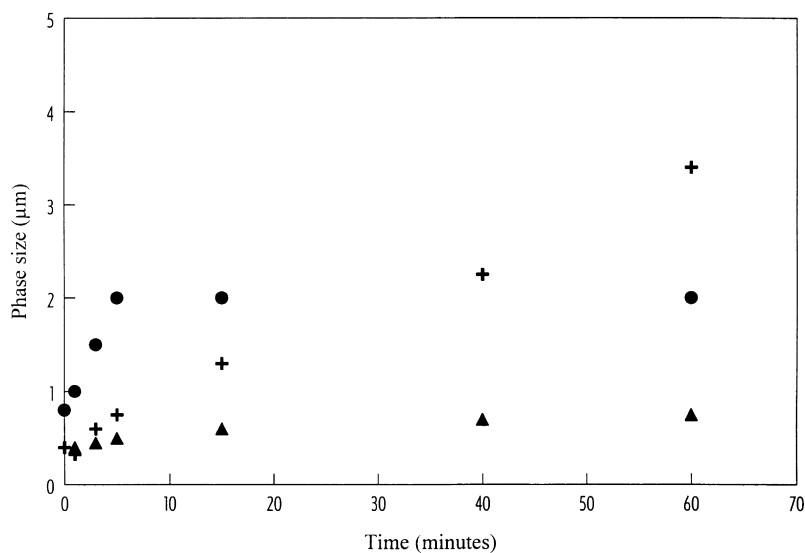


Fig. 7. Phase sizes of 50/50 wt% blends as function of annealing time for PP/SEBS 1650 (▲), PS/poly(ether–ester) (●) at 200°C and PP/SEBS G1657 (+) at 190°C.

rate of coarsening is three times slower than predicted by Eq. (3), indicating that the physical cross-links slow down the process.

4. Conclusions

Co-continuous morphologies with a composition of 50/50 wt% stay co-continuous upon annealing but show a linear increase in phase size. Blends of 30/70 wt% show breakup into droplet/matrix morphologies and an increase in phase size in the first stage of annealing. The rate of coarsening of these co-continuous morphologies can be described with a simple relation using only the interfacial tension and the viscosities of both components. The coarsening of blends with thermoplastic elastomers can be severely slowed down or even completely stopped when physical cross-links are present in the thermoplastic elastomers.

Acknowledgements

The authors would like to thank Ben Norder for the rheological experiments.

References

- [1] Paul DR, Newman S. *Polymer blends*, 1/2. New York: Academic Press, 1978.
- [2] Borggreve RJM, Gaymans RJ, Schuijjer J. *Polymer* 1989;30:71.
- [3] van der Sanden MCM. PhD thesis, Eindhoven University of Technology, The Netherlands, 1993.
- [4] Joziassé CAP, Topp MDC, Veenstra H, Grijpma DW, Pennings AJ. *Polym Bull* 1994;33:599.
- [5] Verhoogt H, Langelaan HC, van Dam J, Posthuma A. de Boer. *Polym Engng Sci* 1993;33:754.
- [6] Machiels AGC, Denys KFJ, van Dam J, Posthuma A. de Boer. *Polym Engng Sci* 1996;36:2451.
- [7] Machiels AGC, Denys KFJ, van Dam J, Posthuma A. de Boer. *Polym Engng Sci* 1997;37:59.
- [8] Nir MB, Ram A, Miltz J. *Polym Engng Sci* 1995;35:1878.
- [9] Avgeropoulos GN, Weissert FC, Biddison PH, Bohm GGA. *Rubber Chem Technol* 1976;49:93.
- [10] Paul DR, Barlow JW. *Macromol Sci, Rev Macromol Chem* 1980;C18:109.
- [11] Jordhamo GM, Manson JA, Sperling LH. *Polym Engng Sci* 1986;26:507.
- [12] Miles IS, Zurek A. *Polym Engng Sci* 1988;28:796.
- [13] Metelkhin VI, Blekht VS. *Kolloid Z* 1984;46:476.
- [14] Utracki LA. *J Rheol* 1991;35:1615.
- [15] Favis BD, Chalifoux JP. *Polymer* 1988;29:1761.
- [16] Valenza A, Demma GB, Acierno D. *Polym Networks Blends* 1993;3:15.
- [17] Ho RM, Wu CH, Su AC. *Polym Engng Sci* 1990;30:511.
- [18] de Roover B, Devaux J, Legras R. *Polym Sci Part A: Polym Chem* 1997;35:917.
- [19] Willemsse RC, Posthuma de Boer A, van Dam J, Gotsis AD. *Polymer* 1998;39:5879.
- [20] Verhoogt H. PhD thesis, Delft University of Technology, The Netherlands, 1992.
- [21] Verhoogt H, van Dam J, Posthuma A. de Boer. *Adv Chem Ser* 1994;239:333.
- [22] Veenstra H, van Dam J, Posthuma A. de Boer. *Polymer* 1999;40:1119.
- [23] McMasters LP. *Adv Chem Ser* 1975;142:43.
- [24] Quintens D, Groeninckx G, Guest M, Aerts L. *Polym Engng Sci* 1990;30:1484.
- [25] Harrats C, Blacher S, Fayt R, Jerome R, Teyssie Ph. *J Polym Sci Part B: Polym Phys* 1995;33:801.
- [26] Andradi LN, Hellmann GP. *Polym Engng Sci* 1995;35:693.
- [27] Li L, Chen L, Bruin P, Winnik MA. *Polym Sci Part B: Polym Phys* 1997;35:979.
- [28] Mekhilef N, Favis BD, Carreau PJ. *Polym Sci Part B: Polym Phys* 1997;35:293.
- [29] Gergen WP, Lutz RG, Davison S. In: Legge NR, editor. *Thermoplastic elastomers. A comprehensive review*, Munich: Hanser, 1986. p. 507, Chap. 14.
- [30] Rayleigh Lord. *Proc R Soc* 1879;29:45.
- [31] Tomotika S. *Proc R Soc* 1935;A150:322.
- [32] Tomotika S. *Proc R Soc* 1936;A153:302.
- [33] Elmendorp JJ. *Polym Engng Sci* 1986;26:418.
- [34] Elemans PHM, Janssen JMH, Meijer HEH. *J Rheol* 1990;34:1311.
- [35] Stone HA, Bentley BJ, Leal LG. *J Fluid Mech* 1986;173:131.
- [36] Stone HA, Leal LG. *Fluid Mech* 1989;198:399.
- [37] Carriere CJ, Cohen A, Arends CB. *J Rheol* 1989;33:681.
- [38] Cohen A, Carriere CJ. *Rheol Acta* 1989;28:223.
- [39] Tjahjadi M, Ottino JM, Stone HA. *AIChE J* 1994;40:385.
- [40] Luciani A, Champagne MF, Utracki LA. *Polym Sci Part B: Polym Phys* 1997;35:1393.
- [41] Sigillo I, di L, anto S, Guido S, Grizzuti N. *Polym Engng Sci* 1997;37:1540.
- [42] Veenstra H, Hoogvliet RM, Norder B, Posthuma A. de Boer. *J Polym Sci Part B: Polym Phys* 1998;36:1795.
- [43] Wu S. *Polymer interface and adhesion*, New York: Marcel Dekker, 1982.
- [44] Veenstra H, van Lent BJJ, van Dam J, Posthuma de Boer A. *Polymer* 1999;40:666.
- [45] Siggia E. *Phys Rev* 1979;A20:595.