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Stability of co-continuous polystyrene/poly(ether–ester) blends in shear flow

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Abstract

Co-continuous morphologies in a blend of poly(ether–ester) and polystyrene break up into a droplet/matrix morphology when subjected to a shear flow in a rheometer with a cone–plate configuration and are therefore not stable under shear. It is shown that the capillary number at these flow conditions is too small to maintain stable extended structures that are necessary for a co-continuous morphology. Co-continuity at such flow conditions is limited to the point of phase inversion, contrary to the range of co-continuity usually found after extrusion.

Keywords: Co-continuous morphology; Blends; Stability

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 (droplets [1–4] and fibers [5–7]), stratified [8] and co-continuous morphologies. In co-continuous morphologies both components are fully interpenetrated throughout the sample. Therefore an interesting feature of these morphologies is that both components, in all directions, can fully contribute to the properties of the blend.

In a number of articles [9–13] we have shown that co-continuous morphologies are not only found at a single volume fraction, such as a point of phase inversion, but can be obtained over a range of volume fractions. In particular in blends with thermoplastic elastomers (TPEs) co-continuous morphologies can be obtained over a wide composition range [12,13]. This range of co-continuity strongly depends on the processing conditions, interfacial tension and the rheological properties of the components.

The intrinsic instability of co-continuous morphologies during further processing, such as compression and injection moulding, is still one of the main problems. In earlier articles [14,15] the coarsening, in quiescent conditions, of co-continuous morphologies upon annealing was reported, demonstrating the effect of interfacial tension, viscosity and also of physical crosslinks in blends with thermoplastic elastomers. It was shown that co-continuous morphologies of 50/50 wt% stay co-continuous upon annealing but will show a linear increase in phase size with time. However, 30/70 wt% co-continuous blends break up into a droplet/matrix morphology. It was also shown that the coarsening process in blends with thermoplastic elastomers is severely slowed down or even stopped when physical crosslinks are present in the thermoplastic elastomers. A proper knowledge of the formation and stability of co-continuous morphologies [12–14] enabled us to adapt the processing conditions in such a way that at a single volume fraction, either co-continuous or dispersed morphologies could be obtained [16].

Although the results from annealing experiments in quiescent conditions are applicable for compression moulding they cannot be used for processing conditions where shear is applied, such as injection moulding or twin-screw extrusion, where blends are subjected to a large amounts of shear. The effect of shear flow on the stability of co-continuous blends is largely unknown and therefore requires further investigation.

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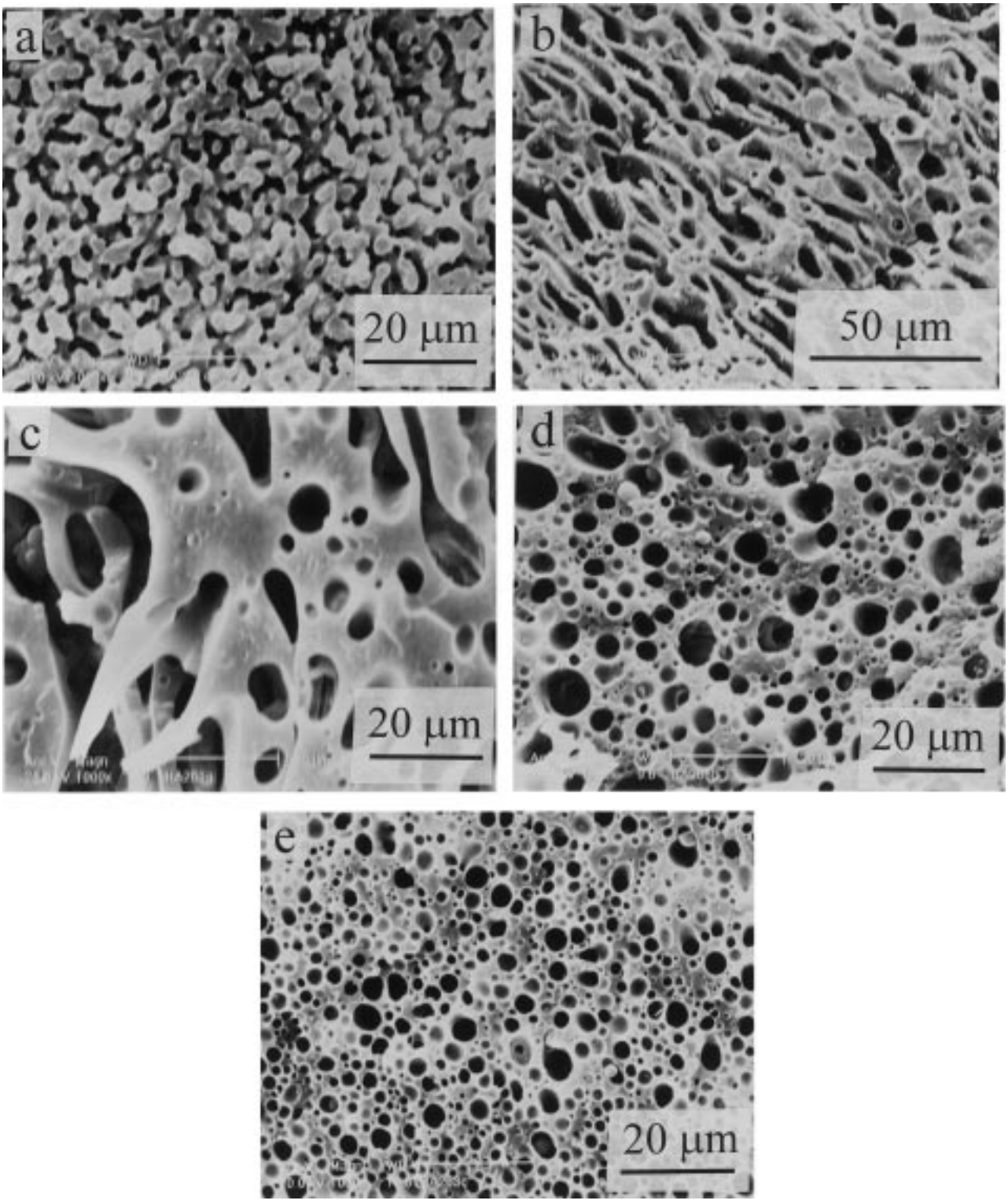

Fig. 1. SEM micrographs of 50/50 vol% poly(ether–ester)/PS blends (a) directly after extrusion (b) mounted on rheometer (c) sheared at 30 s^{-1} for 180 s.u., (d) sheared at 30 s^{-1} for 600 s.u. (e) sheared at 30 s^{-1} for 1200 s.u.

The objective of this article is to demonstrate the effect of shear flow on the stability of co-continuous blends. Therefore co-ontinuous blends of polystyrene and poly(ether–ester) have been subjected to shear flows with different shear rates and subsequently the resulting morphology was examined. The change in morphology will be related to the micro-rheological processes that play a role in polymer blending.

Table 1
Percentage of PS extracted of 50/50 PS/ poly(ether–ester) blends after 0, 180, 600 and 1200 s.u. of shear for three different shear rates. The standard deviation is never more than 2%

Shear rate (s^{-1})	0 s.u.	180 s.u.	600 s.u.	1200 s.u.
0.3	98	97	84	67
3.0	98	91	97	81
30	98	92	74	78

2. Experimental

2.1. Materials

The polymers that were used are polystyrene (PS Hostyrene N2000; Shell) and poly(ether–ester) (Arnitel EM400; DSM), which is a multiblock copolymer, consisting of 40 wt% hard, crystalline poly(tetra methylene terephthalate) segments and 60 wt% soft, amorphous poly(tetra methylene oxyde) segments. The melting and crystallization characteristics of this polymer as well as the rheological properties are described in Ref. [17].

2.2. Processing

All blends (50, 60 and 70 vol% PS) have been prepared on a 20 mm Collin laboratory extruder equipped with a transport screw in series with a static mixer containing 10 Ross ISG 15 mm diameter mixing elements. Each element contains four channels with a radius of 0.135 cm. The blends were extruded at 230°C and subsequently the extruded strands were quenched in water. Samples for the shear experiments were obtained by compression moulding.

2.3. Shear experiments

The samples were sheared at 230°C on a Rheometrics RMS 800 rheometer in the cone–plate configuration with a plate diameter of 25 mm and a gap of 2 mm. The mounting and squeezing of the samples was standardized to make sure that the thermal history of all samples was the same. Samples were sheared for 180, 600 or 1200 strain units (s.u.) at a shear rate of 0.3, 3.0 or 30 s^{-1} and subsequently frozen in with liquid nitrogen.

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 seven days at room temperature, with 2-butanone as the solvent. The combination of extraction experiments, using at least three samples, 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. The SEM was also used to determine the range of droplet sizes.

Table 2
Viscosities (η), minimum droplet sizes (R_d) and calculated capillary numbers (Ca) for 50/50 PS/poly(ether–ester) blends

Shear rate (s^{-1})	η_{ps} (Pa.s)	$\eta_{poly(ether-ester)}$ (Pa.s)	R_d (μm)	Ca	Ca_{crit}
0.3	465	275	3.5	0.1	0.7
3.0	435	275	0.9	0.2	0.6
30	310	265	0.5	1.2	0.5

3. Results and discussion

The morphology of a 50/50 vol% PS/poly(ether–ester) blend obtained after extrusion and the same blend after it was mounted on the rheometer are depicted in Fig. 1(a) and (b). Fig. 1(c)–(e) show the same blend after it has been sheared at a shear rate of 30 s^{-1} for 180, 600 and 1200 s.u. The SEM micrographs show the poly(ether–ester) matrix (grey sections) that is left after the PS phase has been extracted. The results of the extraction experiments, showing the percentage PS extracted, for all shear experiments with the 50/50 vol% blends are shown in Table 1. The SEM-micrographs in Fig. 1 and the extraction results shown in Table 1 make clear that the blend still shows a co-continuous morphology after the sample had been mounted. After 180 s.u. at a shear rate of 30 s^{-1} at 230°C the blend still seems partly co-continuous or some intermediate morphology was formed, but when the blend is sheared for a longer time the co-continuous morphology clearly changes into a droplet/matrix morphology. Similar results are found for all shear rates measured. The only difference is the final droplet sizes, i.e. the droplet sizes decrease with increasing shear rate.

When the viscosities of the components (η), droplet radius (R_d) and the interfacial tension (σ) are known [12] the capillary number ($Ca = \eta_m \dot{\gamma} R_d/\sigma$) can be calculated, using the lowest value for R_d in the range of droplet sizes found. For the calculation of the critical capillary number (Ca_{crit}) we used the equation as proposed by De Bruyn [18]. The results for all shear rates can be found in Table 2. It is evident that the capillary numbers are too small to obtain extended structures, i.e. the capillary numbers are smaller than or only twice the value of the critical capillary number. Co-continuity can only be obtained when the minor component consists of structures with an extended shape [10–12]. At these conditions only dispersed morphologies can be obtained. An estimate of the capillary number in the extruder, where the shear rate is around 30 s^{-1}, resulted in a value of around 2.4, which is almost five times of the critical capillary number. Besides that, the flow in an extruder is more chaotic than between the cone and plate in the rheometer, which favors random orientation of extended structures. Therefore the conditions in the extruders are such that a co-continuous blend is obtained.

The same shear expriments were done for blends with 60 and 70 vol% PS. When the 60 vol% blends are extracted,

after the shear experiments, the samples disintegrate partly into powder, meaning that droplets of poly(ether–ester) in the PS matrix have formed. Therefore no SEM-micrographs could be obtained, except for the blend that was sheared at 30 s^{-1}. These micrographs show PS droplets, co-continuous morphologies and even poly(ether–ester) droplets at low strain units. Apparently 60 vol% is close to the point of phase inversion. If the point of phase inversion is calculated according to the relation by Miles and Zurek [19] a value of around 60 vol% is indeed obtained. When the 70 vol% blends are sheared and subsequently extracted they all fall apart, meaning that a dispersion of poly(ether–ester) in a PS matrix has formed at all shear rates.

These experiments make clear that co-continuous morphologies in poly(ether–ester)/PS blends are not stable when sheared at 230°C and that co-continuity seems to be limited to the point of phase inversion, contrary to the range of co-continuity found after extrusion. These results seem to suggest that co-continuity cannot be obtained in conditions where large amounts of shear are applied, such as in twin-screw extrusion and injection moulding. However, when the flow conditions are such that a high value for the capillary number is obtained, co-continuous blends could be stable in shear flow. Another possibility to obtain stable co-continuous blends in shear is to use a physically crosslinked thermoplastic elastomer as one of the components. The results described in this article are limited to a co-continuous blend where the components show simple viscous flow behaviour. To obtain a more general insight into the stability of co-continuous blends in shear flow, further investigations are necessary.

4. Conclusions

Co-continuous morphologies of poly(ether–ester) and PS that are subjected to a shear flow break up into droplet matrix morphology and are therefore not stable. The capillary number is too small to maintain extended structures. Consequently, at these flow conditions co-continuous morphologies are limited to the point of phase inversion, contrary to the range of co-continuity usually found after extrusion.

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