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Co-continuous morphologies in polymer blends:stability

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Abstract

A critical volume fraction of the minor component within the major component can be distinguished above which the co-continuous morphology in a polymer blend remains stable during annealing of the blend. Below this volume fraction breakup leads to a transition of the co-continuous structure to a dispersed one. This critical composition can be understood by depicting the co-continuous structure as an assembly of fibres randomly oriented at their maximum packing density. These fibres have 'coalesced' at their cross-over points. The length of the filament between two cross-over points decreases with increasing volume fraction of the minor phase. At a certain length the dominant wavelength of the sinusoidal disturbances is larger than the length between two cross-over points and the disturbances will not grow further. Consequently, the filament cannot break up. The critical volume fraction above which breakup of the co-continuous structure during annealing is not possible, is found to be around 30 vol% of the minor phase. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blend; Co-continuous morphology; Stability

1. Introduction

Blending of polymers usually leads to heterogeneous morphologies with 'tailor-made' properties. The type of the morphology and its phase dimensions determine these properties. The morphology of an immiscible polymer blend can be unstable leading to a coarsening and/or a change of the morphology if it is not frozen in fast [1], e.g. fibres of polymer A in a matrix of polymer B may break up and droplets are formed. In this paper the stability of a co-continuous morphology in a quiescent molten medium is studied. Verhoogt [2] found that blends of 20% SEBS (a styrene–ethylene/butylene block copolymer) in PEE (a polyetherester) with a co-continuous morphology, broke up on annealing leading to a dispersion, whereas blends with 30 and 50% SEBS in PEE which also exhibited a co-continuous morphology, did not break-up and the co-continuous morphology was preserved. The phase dimensions, however, increased. Similar results were found by Quintens et al. [3] in blends of PC (polycarbonate) and SAN (styrene acrylonitrile). A transition from a co-continuous structure to dispersed phase structure occurred in the 70/30 PC/SAN blend with increasing annealing time. Coarsening of the phase dimensions in the 60/40 PC/SAN blends was found, whereas the co-continuous morphology was preserved on annealing. From the above it appears that a critical volume fraction can be distinguished where the co-continuous morphology can be preserved. In this paper a theoretical consideration is presented which predicts the existence of a critical volume fraction of the minor phase above which the co-continuous morphology is stable.

2. Theory

In this study only polymer blends with fully co-continuous structures are considered where both phases form single continuous interpenetrating structures. For low volume fractions of either component a fully continuous structure can exist only if it is made up of extended structures which was already discussed in a previous paper [4]. The continuous minor phase is depicted as an assembly of fibres randomly oriented and at their maximum packing density inside the matrix (major component). At this packing density all the fibres have touched each other and have 'coalesced' at their cross-over points. The maximum packing density ($\phi_{\max}$) of randomly oriented fibres depends on their aspect ratio L/B, where L is the length and B is the diameter of the fibres [5]:

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

The filaments between two cross-over points have a certain length which increases with increasing length of the fibres,

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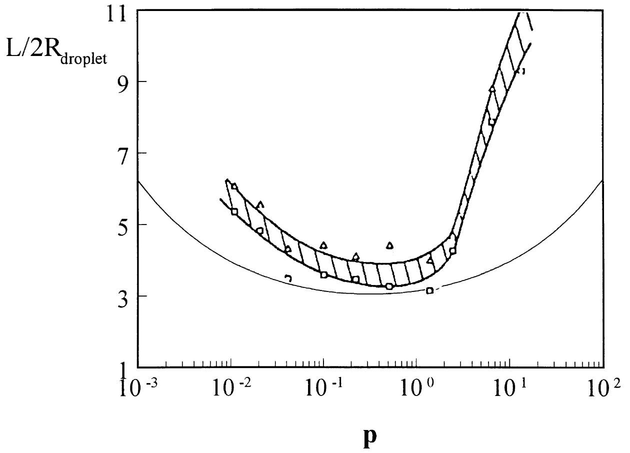

Fig. 1. Critical elongation ratio, $L/2R_{droplet}$, necessary to ensure breakup found experimentally [6] as a function of the viscosity ratio, p, compared with a sketch of the calculated one (full line represent, Eq. (3)). Triangles denote the smallest $L/2R_{droplet}$ for which a droplet was observed to breakup. Squares denote the largest $L/2R_{droplet}$ for which a droplet relaxed back to a sphere. The shaded region denotes the uncertainty in the critical elongation ratio [6].

i.e. with decreasing volume fraction. If the co-continuous morphology breaks up, then these filaments should breakup. Stone et al. [6] reported that break-up of fibres (via sinusoidal distortions) only occurs in the case of highly extended fibres. For moderately extended fibres, end pinching or retraction occurs. A critical length of the fibres above which breakup can occur is shown in Fig. 1 as a function of the viscosity ratio, p, which is the ratio of the viscosity of the dispersed phase (η_d) and the viscosity of the continuous phase (η_c). The existence of such a critical length can easily be understood using the theory for breakup of extended fibres. From calculations of the surface area of the sinusoidally disturbances it follows that, if the wavelength of the disturbance, λ is larger than the circumference, πB, the interfacial area decreases when the amplitude of the disturbance increases [7]. The disturbances grow exponentially with time and the growth rate is proportional to the dimensionless growth rate, $\Omega_{\lambda,p}$, which is calculated with the theory of Tomotika [8]. This $\Omega_{\lambda,p}$ function shows a maximum, Ω_m, for a certain λ_m, which is the dominant wavelength where the disturbance will grow fastest, and it is shown in Fig. 2. The dominant wavelength which is usually expressed as a dominant wave number, $X_m = \pi B/\lambda_m$, is also shown in Fig. 2.

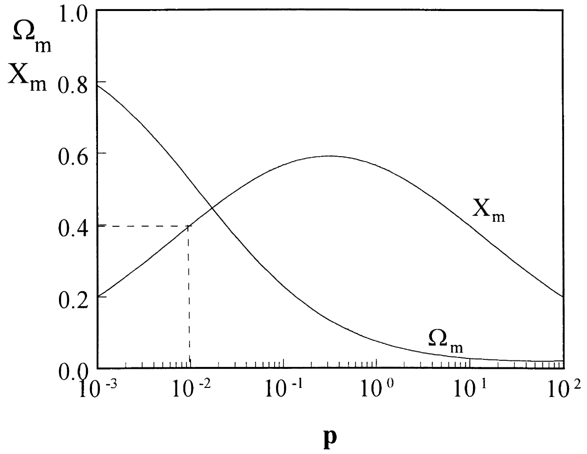

Fig. 2. Theoretical values of the wave number, X_m, and the dimensionless growth rate $\Omega_{m,p}$ as a function of the viscosity ratio, p. This theory predicts $X_m = 0.4$ for $p = (\eta_{PS}/\eta_{PE}) = 0.01$ as shown in this plot (- - -).

It is asserted here that the length of a fibre should exceed this dominant wavelength for breakup. At a shorter length this dominant wavelength cannot exist and the growth of a disturbance is much slower. The critical aspect ratio, $(L/B)_{cr}$, below which a fibre will not breakup is given by:

$$\left(\frac{L}{B}\right)_{cr} = \left(\frac{\lambda_m}{B}\right) = \frac{\pi}{X_m(p)} \qquad (2)$$

Stone et al. [6] reported the length of the deformed droplet divided by the initial diameter of the undeformed droplet, $2R_0$, as shown in Fig. 1. If the deformed droplet is an ellipsoid then $L/2R_{droplet} = (B/2R_{droplet})^{-2}$. The parameter $L/2R_{droplet}$ as a function of the aspect ratio L/B is given by:

$$\frac{L}{2R_{droplet}} = \left(\frac{L}{B}\right)^{2/3} = \left(\frac{\pi}{X_m(p)}\right)^{2/3} \qquad (3)$$

The critical value of $L/2R_{droplet}$ calculated with Eq. (3) is also shown in Fig. 1. It can be seen that the results of Stone et al. [6] can be described qualitatively up to $p = 1$, above which some deviation can be seen because $\Omega_{\lambda,p}$ will become almost 0. The absolute values of $L/2R_{droplet}$ reported by Stone et al. [6] are approximately a factor of 1.5 higher than the one calculated with Eq. (3).

The results of Stone et al. [6] can be explained qualitatively and will be applied together with Eq. (1) to explain the critical volume fraction in a polymer blend above which the co-continuous morphology does not break up. The critical aspect ratio found by Stone et al. [6] is expected to correspond to the aspect ratio of the filament between two cross-over points, as can be found in the assembly of randomly oriented fibres. The maximum aspect ratio in this assembly corresponds to the one given in Eq. (1). In that case the fibre is touched by other fibres at its end points.

3. Experimental

Blends of 15, 27 and 35 vol% polystyrene (PS; Hostyrene N2000, Shell) in polyethylene (PE; Stamylan LD 2100TN00, DSM) are studied. The ratio of the zero-shear viscosities of this blend system (η_{PS}/η_{PE}) at 200°C is 0.01 [4]. A Collin single-screw extruder equipped with a transport screw ($D = 20$ mm, $L/D = 20$) was used feeding PS and PE at 200°C to a static mixer which contains 10 static mixing elements (type Ross ISG; 15 mm diameter). The blends were quenched in water.

The extruded blends were annealed at 200°C in a compression moulding apparatus (Fontijne press). Different

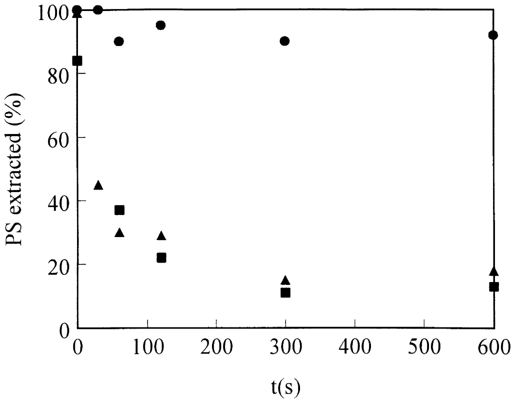

Fig. 3. Fraction of PS extracted from the PE/PS blends as a function of annealing time; (■), (▲) and (●) represent the blends with 15, 27 and 35 vol% PS in PE, respectively.

annealing times of 0, 0.5, 1, 2, 5 and 10 min were used. After annealing the samples were quenched in water.

Both the extruded and the annealed strands were broken in liquid nitrogen and extraction of the PS phase was performed in a Soxhlet extraction apparatus with 2-butanone over 3 days. This was sufficient for complete removal of the soluble fraction. In the case of co-continuity, 100% of the PS phase can be extracted [9]. If fibres or the co-continuous morphology break up leading to a dispersion, less PS can be extracted. A scanning electron microscope (Philips XL 20) was used to study the morphology after extraction.

4. Results and discussion

The blend with 15 vol% PS in PE showed a fibre/matrix morphology. The fibres broke up during annealing, which is proved by the results of the extraction experiments shown in Fig. 3. Before annealing, about 80% PS could be extracted due to the fibrillar morphology. During annealing the fraction of extractable PS decreased, because droplets are formed.

The blends with 27 and 35 vol% PS in PE showed a co-continuous morphology, as can be concluded from the extraction experiments shown in Fig. 3 at $t = 0$ s. Some SEM pictures are shown in Fig. 4, representing the morphology perpendicular to the flow direction. The type of morphology in the blend with 27 vol% PS in PE changed during annealing, as can be seen in Fig. 4a,b. The co-continuous structure broke up in the same way as the fibrillar morphology (15 vol% PS) and a dispersion was formed. Less PS could be extracted, as can be concluded from Fig. 3. The co-continuous structure in the blend with 35 vol% PS in PE did not break up, as can be concluded from Fig. 3 and Fig. 4c,d. Annealing of this blend led to a coarser structure, as shown in Fig. 4d.

From the results described above, it appeared that a critical volume fraction between 27 and 35 vol% PS exists, above which the co-continuous morphology does not break up. This volume fraction, around 30 vol%, was also found by Verhoogt [2] and Quintens et al. [3]. It was asserted above that this critical volume fraction corresponds to the aspect ratio of the filament between two cross-over points. This critical aspect ratio can be calculated with Eq. (2). The required parameter, X_m at $\eta_{PS}/\eta_{PE} = 0.01$, can be deduced from Fig. 2. Solving Eq. (2) for $X_m = 0.4$ gives a critical aspect ratio of 8. The values of $L/2R_{droplet}$ calculated with Eq. (2) are a factor of 1.5 lower than the ones found by Stone et al. [6]. Consequently, the aspect ratio estimated with Eq. (2) is a factor of $(1.5)^{3/2}$ lower. By taking this factor into account the critical aspect ratio now becomes approximately 14 ($8 \times (1.5)^{3/2}$) and the corresponding critical volume fraction calculated with Eq. (1) is 35%, which

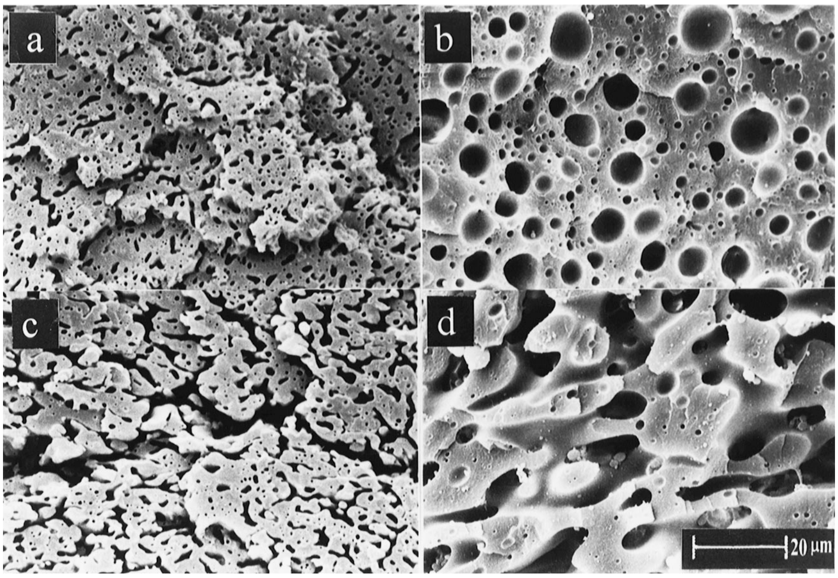

Fig. 4. Scanning electron micrographs of blends with 27 and 35 vol% PS. (a,b) The morphology of the blend with 27 vol% PS before and after 10 min annealing, respectively; (c,d) the morphology of the blend with 35 vol% PS before and after annealing, respectively.

was also found experimentally. The co-continuous morphology in the blend with 35 vol% PS did not break up. The aspect ratio between two cross-over points will exceed its critical value at lower volume fractions of the minor phase and breakup will occur during annealing, as was indeed found experimentally by annealing the blend with 27 vol% PS in PE.

It is difficult to measure this aspect ratio experimentally, as can be concluded from Fig. 4a,c. By extracting the PE phase, the PS network can be made visible. However, extraction of the PE phase is not possible without damaging the PS phase [4].

5. Conclusions

A critical composition can be distinguished above which the co-continuous structure in a polymer blend does not break up. This composition can be predicted by depicting the co-continuous structure as an assembly of fibres and it can be related to the aspect ratio of the filament between the points where the fibres have touched. If the length of this filament is smaller than the dominant wave length of a sinusoidal disturbance, then this filament will not break up. As such the co-continuous structure is inherently stable against breakup within a certain composition range.

It is to be expected that there is a critical volume fraction for every immiscible blend system above which the co-continuous morphology does not break up on annealing. This volume fraction is a function of the viscosity ratio which will be discussed in a subsequent paper.

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