



Phase separation morphology of spin-coated polymer blend thin films

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Abstract

We present the results of a study of the morphology of phase separation in thin films of two different polymer blend systems: polystyrene/polyisoprene and polystyrene/poly(methyl methacrylate). For each blend system, the two polymer components are dissolved in a common solvent. Spin coating of the ternary solutions (polymer blend/solvent) is used to confine the blends to a thin film geometry and to produce phase separation because of rapid evaporation of the solvent (solvent quench). As a quantitative measure of the phase separation morphology the average domain area of the minority component is measured as a function of the polystyrene mass fraction. For both blend systems we identify a small range of composition corresponding to a large increase in the average domain area. We show that the strong dependence of the average domain area on spin speed allows control over the quench time of the polymer blend thin films.

1. Introduction

The technological importance of polymer blends has motivated studies which have produced a well-developed understanding of phase separation in bulk polymer blends [1]. If the blend is confined to a thin film geometry [2-10], such that the surface area to volume ratio is large, surface effects may dominate, and the phase separation behaviour may be different from that for bulk samples.

Typically, the polymer blend is quenched in temperature from the stable one-phase region of the phase diagram into the metastable or unstable regions, corresponding to nucleation and growth [11] and spinodal decomposition [11,12] respectively. The temperature quench results in phase separation of the polymer blend. Studies of the phase separation morphology can be used to elucidate aspects of the phase diagram of polymer blends. For example, both experimental [13-15] and theoretical [2,16,17] studies have shown that a bicontinuous morphology is usually obtained for a critical

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quench into the unstable region of the phase diagram. While the temperature quench method is well suited to the study of two-component systems which have similar glass transition temperatures T_g , it cannot be used if the components have large differences in T_g . For the latter case the temperature required to ensure that both polymers are in the melt phase may be high enough to result in degradation or even decomposition of the lower T_g component. This difficulty can be avoided by using blends in which both components have low molecular weights M_w , with correspondingly low values of T_g ; however it does not allow for the study of technologically important high molecular weight polymers. Alternatively, phase separation in blends containing high M_w polymers can be studied by dissolving the polymers in a common solvent and then allowing the solvent in the ternary mixture to evaporate (solvent quench). Evaporation of the solvent results in phase separation of the two polymer components. In Ref. [18], the phase separation process which occurs as the total polymer concentration in a ternary mixture increases is compared to the quenching of the temperature of a binary polymer blend.

This paper focusses on phase separation in two ternary systems: polystyrene (PS)/polyisoprene (PI)/toluene and PS/poly(methyl methacrylate) (PMMA)/methyl ethyl ketone (MEK). The PI, PS and PMMA polymers have glass transition temperatures of -70°C , 100°C and 105°C , respectively. The PS/PI blend is difficult to study as a binary blend because the PI degrades at temperatures above the PS glass transition. Therefore, the PS/PI blend is ideally suited to solvent quenching rather than temperature quenching to achieve phase separation.

The phase separation of spin-coated PS/PI and PS/PMMA blends is studied as a function of the PS mass fraction ϕ_m . The average domain area is used as a quantitative measure of the observed morphology.

2. Experimental

2.1. Materials and sample preparation

Two ternary systems (polymer blend/solvent) were studied: PS/PI/toluene and PS/PMMA/methyl ethyl ketone (MEK). For both ternary systems, the solvents were good solvents for both polymer components. The polymers [19] had molecular weights $\bar{M}_w = 760\,000$ (PS), $\bar{M}_w = 1\,220\,500$ (PMMA) and $\bar{M}_w = 410\,000$ (PI) and polydispersities $\bar{M}_w/\bar{M}_n = 1.10$ (PS), $\bar{M}_w/\bar{M}_n = 1.39$ (PMMA) and $\bar{M}_w/\bar{M}_n = 1.06$ (PI). The total polymer concentration was fixed for both systems at $C = 2.00\%$ while the mass fraction was varied between $0.35 < \phi_m < 0.77$ for the PS/PI system and $0.35 < \phi_m < 0.61$ for the PS/PMMA system.

Spin coating [20] was used to obtain confinement of the blend to a thin film geometry and also to achieve a solvent quench of the ternary systems. Small substrates ($1\text{ cm} \times 1\text{ cm}$) of Si(001) with the native oxide layer (Si-SiO_x) were used. Thin films were prepared by placing a droplet of the solution onto a spinning substrate.

The experiments described in this paper are of two different types: (1) spin-coating blend solutions with fixed spin speed $\omega = 3000$ rpm for different values of the PS mass fraction ϕ_m ; and (2) spin-coating blend solutions with fixed $\phi_m = 0.63$ for different values of the spin speed $700 \text{ rpm} < \omega < 7000 \text{ rpm}$. The spin-coating time, as estimated from the observation of changes in the film colour during deposition, ranged from ~ 0.5 s for $\omega = 7000$ rpm to ~ 10 s for $\omega = 700$ rpm.

2.2. Data analysis

The phase-separated films were studied using an optical metallurgical microscope. The microscope was fitted with a CCD camera which was interfaced through a frame grabber to a PC in order to obtain digital images. There was no need for staining the films to enhance the optical contrast of one of the components, since the difference in the index of refraction ($\Delta n = 0.07$ for PS/PI and $\Delta n = 0.10$ for PS/PMMA) ensured that the two phases had different colours. Colour filters were used in some cases to increase the contrast. This method was sufficient for all films used in the present study although the image quality is poor for very thin films ($h \sim 350 \text{ \AA}$) [18]. The characteristic domain size was generally greater than $3 \mu\text{m}$, so that optical microscopy was sufficient for all morphology measurements.

The phases of the phase-separated films were identified unambiguously by selectively removing one of the polymer components. This was done by rinsing the film with a solvent for only one of the polymer components. All measurements were carried out at the centre of the spincoated films to minimize the effect of shear [21] on the morphology. For the PS/PI system this proved to be unnecessary since the radial dependence of the morphology was negligible. However, the morphology of the PS/PMMA system was affected more strongly by shear, which resulted in domains that were slightly elongated in the radial direction near the edge of the films. To avoid the elongated domain patterns, measurements of the morphology were performed near the centre of rotation of the films.

The average domain area was measured for both the PS/PI and PS/PMMA blends as a function of the mass fraction. Measurements of other quantities such as shape factor suffer from greater errors due to digitization. The minimum number of domains included in the image analysis was 150, and typically the number of domains was 400. Multiple images were taken of the films if this requirement could not be met for a single image. This requirement was relaxed for compositions within ± 0.02 of the bicontinuous morphology composition $\phi_{m,b}$, for which the individual domain areas were very large, and the number of domains was correspondingly small.

3. Results and discussion

The spin-coating process used to study phase separation can be most easily understood in terms of the schematic phase diagram shown in Fig. 1. A polymer blend

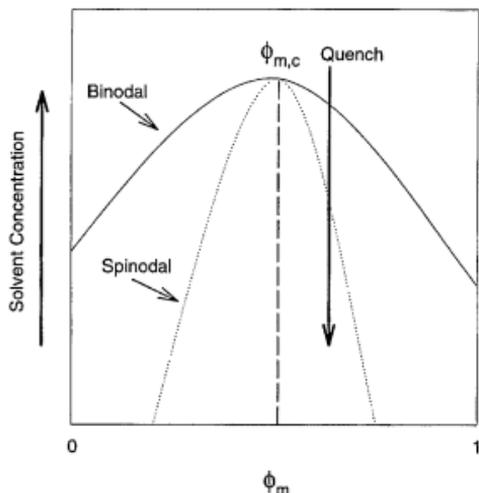


Fig. 1. Schematic ternary phase diagram of a two polymer/solvent system.

solution with low polymer concentration (typically several percent polymer content by mass) is dropped onto the spinning substrate. During the initial stages of the spin-coating process most of the solution is cast off leaving a thin layer on the substrate. As the layer thins due to fluid flow, the evaporation of the solvent becomes important. The effect of evaporation is to increase the polymer concentration which dramatically increases the viscosity of the polymer solution and slows the shear thinning of the film. Phase separation of the polymer blend occurs during these later stages of the spin-coating process. This process produces a rapid quench of the polymer blend, which 'freezes in' a nonequilibrium phase separation morphology. Since essentially all of the solvent has evaporated, the final composition of the polymer blend lies on the ϕ_m axis of the schematic phase diagram in Fig. 1.

Typical morphologies are shown for the PS/PI system in Fig. 2. Small, circular PS-rich domains are observed for $\phi_m = 0.40$ in a matrix of the PI-rich phase (Fig. 2(a)). As the mass fraction is increased the PI-rich domains grow until the bicontinuous morphology is obtained for $\phi_m = \phi_{m,b} = 0.45 \pm 0.02$ (Fig. 2(b)). Further increases in ϕ_m result in the formation of noncircular PI-rich domains in a PS-rich matrix, as shown in Fig. 2(c) for $\phi_m = 0.61$. The absence of optical fringes in the optical microscope images indicates that the domains are quite flat. The curvature of the surfaces of the domains is small since the in-plane extent of the domains was typically a factor of 50 greater than the thickness ($h \sim 1000 \text{ \AA}$) of the films, indicating that two-dimensional morphologies are observed.

In Fig. 3, the average domain area is plotted as a function of ϕ_m for the PS/PI and PS/PMMA systems on Si-SiO_x substrates. For the PS/PI system, the

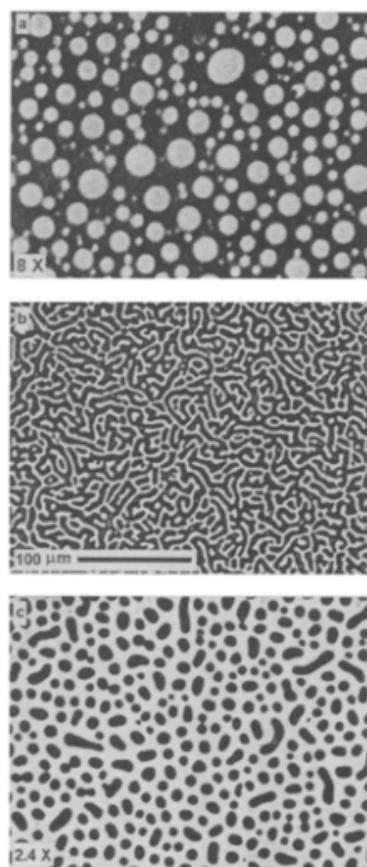


Fig. 2. Morphology images for 1000 Å thick PS/PI blend films on Si-SiO₂ substrates. The ϕ_m values are (a) 0.40, (b) 0.45, and (c) 0.61.

bicontinuous morphology is observed only within an extremely narrow range of the mass fraction (± 0.02) as evidenced by a large increase in the average domain area within this small range. The observation of the bicontinuous morphology has been used to study substrate [18] and viscosity [9,22] effects on the morphology. It is worth noting that the bicontinuous morphology was obtained repeatably for different polymer blend solutions with the same value of the mass fraction $\phi_m = 0.45$. Since the morphology is very sensitive to changes in mass fraction near $\phi_m = 0.45$, this indicates that the observed polymer blend morphologies are very reproducible. We

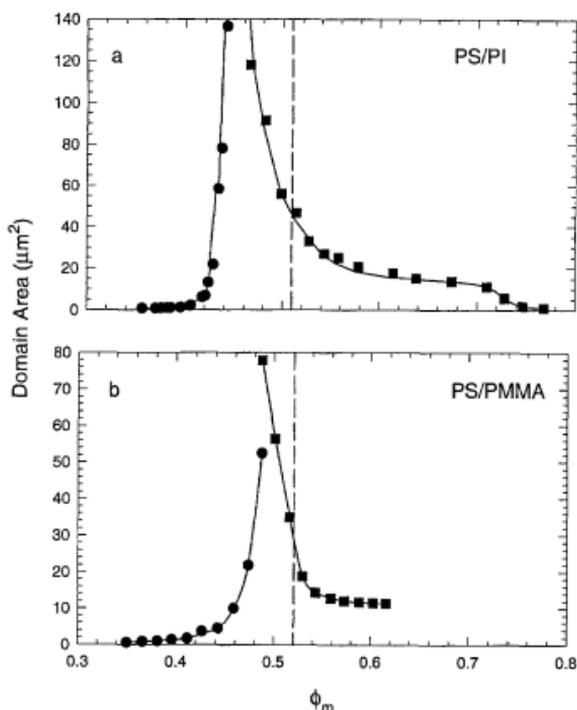


Fig. 3. Average domain area versus PS mass fraction for (a) PS/PI blend films and (b) PS/PMMA blend films on Si-SiO_x. The curves are intended to guide the eye. The vertical dashed lines correspond to $\phi_m = \phi_{m,c}$.

have applied the same image analysis to the PS/PMMA system, for which we observe the bicontinuous morphology for mass fraction values near $\phi_m = 0.48$ (see Fig. 3(b)).

For the two systems studied, the values of the critical composition ($\phi_{m,c}$) as calculated using Flory–Huggins theory for binary polymer blends [23] are indicated for both the PS/PI and PS/PMMA systems in Fig. 3. Differences between the $\phi_{m,c}$ and $\phi_{m,b}$ values are observed for both blends: for the PS/PI system, $\phi_{m,b} = 0.45 \pm 0.02$ and $\phi_{m,c} = 0.51$, and for the PS/PMMA system, $\phi_{m,b} = 0.48 \pm 0.02$ and $\phi_{m,c} = 0.52$. These differences between $\phi_{m,b}$ and $\phi_{m,c}$ could possibly be due to differences in the viscosities of the components during the spin-coating process [22, 9] or due to the formation of thin homopolymer layers near the film–air and film–substrate interfaces because of the polymer–substrate and polymer–air interactions [3, 4, 6].

For the PS/PI system, as ϕ_m is increased above $\phi_m = 0.71 \pm 0.05$ a sharp decrease in the average domain areas is observed (Fig. 3(a)). For mass fractions larger than

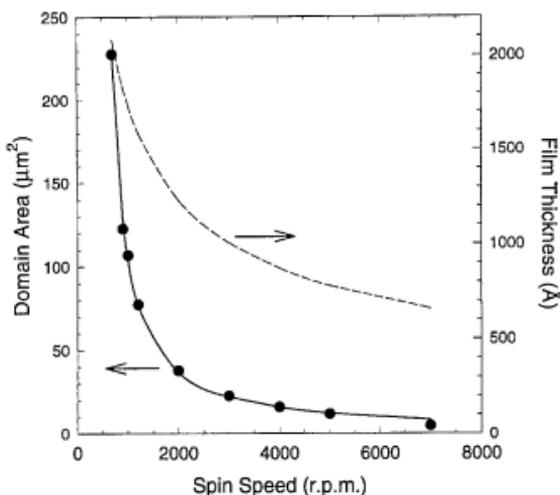


Fig. 4. Average domain area and film thickness as a function of the spin speed during spin coating.

$\phi_m = 0.71$ there are few small phase-separated domains that are likely caused by nucleation and growth in the metastable region of the phase diagram [18].

The dependence of the domain area on the spin speed used in the deposition of the films was also investigated for the PS/PI system for $\phi_m = 0.63$ and an initial total polymer concentration of $C = 2.00\%$. The measured average domain area is plotted as a function of the spin speed in Fig. 4. There is an increase of a factor of 45 in the domain area as the spin speed ω is decreased from 7000 to 700 rpm. The solid line joining the data points in Fig. 4 corresponds to a least-squares fit of the domain area $A(\omega)$ to the empirical form

$$A(\omega) = \frac{\alpha}{\omega^n - \beta},$$

where ω is the spin speed in rpm and α , β and n are fit parameters: $\alpha = 6 \times 10^4 \pm 50\%$; $\beta = 500 \pm 50\%$; and $n = 1.1 \pm 10\%$. Although the fit is rather insensitive to the α and β parameters, it is evident that the average domain area varies as ω^{-1} to a very good approximation. The average domain area varies much more strongly with spin speed than does the film thickness (also shown in Fig. 4) which has a $\omega^{-1/2}$ dependence, as measured for spin-coated PS films [24]. The strong spin speed dependence of the average domain area is likely due the corresponding spin speed dependence of the solvent quench time during the spin-coating process. Therefore, by changing the spin speed one can change the solvent quench time for the polymer blend.

4. Summary and conclusions

The morphology of phase separation was studied as a function of the PS mass fraction ϕ_m for PS/PI and PS/PMMA blend thin films. To create the films, two different ternary polymer blend/solvent systems were used: PS/PI/toluene and PS/PMMA/MEK. Spin coating was used to confine the blends to a thin film geometry, and to quench the blends at room temperature by rapid evaporation of the solvent. The average domain area was used as a quantitative measure of the morphology. The bicontinuous morphology was observed within a very narrow range (~ 0.02) of the PS mass fraction for both polymer blends. We observed that the average domain area is a strong function of the spin speed, which allows control of the solvent quench time in the spin-coating process.

Acknowledgements

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