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Phase inversion and viscoelastic properties of phase-separated polymer blends

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Summary

The morphologies and viscoelastic properties of the phase-separated poly(styrene-co-maleic anhydride)/poly(methyl methacrylate) bends have been investigated using TEM and rotational rheometry. Various rheological criteria based on the viscoelastic properties of the blends have been used to evaluate the phase inversion. By correlating the rheological results to data from morphological analysis by TEM, it is found that the maximum of the storage modulus and the viscosity at low shear rate are most suitable for determining the phase-inversion composition of the present phase-separated polymer blends. While the data from the maximum of the shear viscosity at high shear rate and from the shear-thinning extent proposed by Ziegler et al. slightly deviate from that from TEM micrograph, which indicates that shear-induced structure lie. Moreover, the prediction using various rheological models, as the viscosity ratio of the two coexisting phases is substituted for that of the pure components, is in nearly good agreement with that from TEM observation.

Introduction

Blending of different polymers most leads to multi-phase systems with various morphologies. Of these morphologies, the co-continuous morphology is particularly of interest because the blend with such morphology exhibit typically specific mechanical properties[1, 2]. The type of morphology is often formed in a certain concentration range around the phase-inversion concentration in which two phases switch their functions, so it is of importance to determine and to predict the phase inversion for tailoring of polymer blend. Many studies have been focused on exploring phase inversion phenomenon of immiscible polymer blend, and a lot of criteria have been established for predicting the phase inversion by rheology[3-9]. Of these criteria, some semi-empirical methods are based on viscosities of the blend components. Paul et al.[3] proposed the phase-inversion point (ϕ_I) is related to the zero shear viscosity ratio (p): using the following expression:

$$\phi_{I,1}/\phi_{I,2} = \eta_{0,1}/\eta_{0,2} \equiv p \tag{1}$$

Miles et al.[4] argued that the point of phase inversion should more precisely be related to the effective viscosity ratio.

$$\phi_{I,1}/\phi_{I,2} = \eta_1(\dot{\gamma})/\eta_2(\dot{\gamma}) \equiv p_{eff} \qquad (2)$$

These two equations imply that the viscosity ratio of the two components determines the phase-inversion point, and they have been demonstrated to be only valid for the blends with a viscosity ratio near unity[4, 10-12], but invalid for the ones that exhibit viscoelastic asymmetry between the melt components[5, 13].

Utracki[5] derived a model being valid for blends with viscosity ratio different from unity. He proposed the addition of polymer 1 to polymer 2 or vice versa, leads to an increase in the respective blend viscosities, and the blend viscosity reaches a maximum at the point of phase inversion. Thus, the phase-inversion concentration can be determined by this maximum.

Ziegler et al.[7] found the shear thinning behavior can also reflect the morphology of the blend in a characteristic manner, and thus may also serve as a tool to detect changes in morphology with the blend composition.

In contrast, Bourry et al.[6] tried to correlate the elasticity of the blend components, instead of the viscosity ratio, with the appearance of phase inversion. Their criterion based on the elasticity ratio is valid for the system they investigated, however, its usefulness has not been proven for another system[14].

Steinmann et al.[9] investigated the rheological properties of a series of two-phase polymer blends in the phase inversion region, and found the criterion based on the maximum of the storage modulus is most robust and most suitable for predicting the phase inversion.

Jeon et al.[15] investigated the effect of phase inversion on the domain morphology and rheological properties of two different blends of low-vinyl polybutadiene/low-vinyl polyisoprene and low-vinylpolybutadiene/high-vinyl polyisoprene, and found that the phase-inversion composition coincides with a discontinuity in the shear viscosity and dynamic storage modulus.

The analyses of phase inversion have been mainly focused on the immiscible polymer blends so far; however, little work has been done on predicting co-continuity development in the phase-separated conditions of the partially miscible blend. In general, the morphology of the phase-separated blend is strongly determined by the mechanism by which the phase separation occurs[16]. When a blend of a given composition sees a change of temperature that forces it from the single-phase region to enter the metastable region in the temperature-composition phase diagram, the phase separation occurs via slow nucleation followed by growth of the phase-separated domains, and the resulting morphology is often the droplet-matrix one. On the other hand, when the system is forced to jump from the single-phase region into the unstable region, the phase separates via instantaneous spinodal decomposition, and the resulting morphology is a co-continuous one. The associated rheological properties are often characteristic[17] and thus should be theoretically applied for determining phase inversion.

Jeon and Hobbie [18, 19] investigated shear viscosity of phase-separating polymer blends with viscous asymmetry, and found that shear viscosity always display a discontinuity when phase inversion occurs, which in turn can be used for determining phase-inversion composition. Such work is heuristic for characterizing by rheology the blend structure; however, different from completely immiscible polymer blend, as pointed out by Han et al.[20], partially miscible polymer blends subjected to an external shear flow often exhibit complex phase behavior: homogeneous or heterogeneous depending on weak or strong externally applied shear. Therefore, shear-induced change has to be considered before shear viscosity being applied for characterizing phase inversion.

In our previous studies[21, 22], we investigated phase behavior and its viscoelastic responses of the partially miscible poly(styrene-co-maleic anhydride) (SMA) /poly(methyl methacrylate) (PMMA) blend, and found the viscoelastic properties are sensitive to phase separation, in addition, the phase-separated blends with a droplet-matrix morphology or co-continuous one show characteristic viscoelastic properties. Thus, the criteria mentioned above should theoretically be also suitable for the presented phase-separated systems. It is noted that the two phases resulted from phase separation are not two pure-constituent phases but two phases of a certain composition, which are different from the two phases of an immiscible polymer blend. Therefore, those criteria should be retested in the phase-separated systems. The aim of the present work is to relate rheology to phase inversion in phase-separated polymer blends.

Experimental Section

Materials

SMA containing 12 wt% of maleic anhydride (M_w=159,200, M_w/M_n=1.7), was supplied by SINOPEC Shanghai Research Institute of Petrochemical Technology (Shanghai, China). PMMA G66 (M_w=72,400, M_w/M_n=2.0) was obtained from BASF (Ludwigshafen, Germany). The weight-average molecular weight and polydispersity were determined by gel permeation chromatography (GPC) (Perkin Elmer Series 200).

Samples

Homogeneous blends of SMA/PMMA were prepared by melt blending on a Haake Rheocord 99 with a Rheomix 60 mixer at 175°C and 40 rpm. The mixing continued until a constant torque was reached, which took about 12 min.

Phase-separated blends were obtained by annealing their homogeneous counterparts at 220°C for one hour. In order to avoid water absorption, the blend constituents and their blends were stored in a vacuum oven at 90°C before being used.

Morphology

The phase-separated samples were rapidly quenched to a temperature lower than the glass transition temperature by liquid nitrogen and then sectioned into thin films approximately 90 nm thick with a low-temperature LKB 2088 ultramicrotome with a diamond knife. The ultrathin films were attached to a copper grid and stained with 1% aqueous OsO_4 for 12 hours to increase the contrast between the two phases. Morphologies were observed with a HITACHI H-860 transmission electron microscope (TEM). The light areas in the resulting micrographs corresponded to the PMMA-rich phase, whereas the dark areas were related to the SMA-rich phase.

Rheology

A Bohlin Genemi 200HR rheometer was utilized for oscillatory-shear and steady-shear measurements, which were carried out with 25mm diameter fixtures and a 1mm and 0.15mm gap thickness for parallel-plate and cone-and-plate geometry, respectively. The temperature was controlled to 220°C. Oscillatory shear measurements at various frequencies (0.01-100rad/s) in a constant-strain mode at a strain of 0.05 in the linear viscoelastic regime and steady shear measurements were performed at a shear rate range of 0.01-10s^{-1}.

Results and Discussion

Phase diagram of the SMA/PMMA blend

The phase-separation temperatures of the SMA/PMMA blends were determined by turbidity and small angle light scattering[23]. Figure 1 shows the phase diagram calculated using Flory-Huggins model by assuming that the Flory-Huggins parameter, χ, depends only on temperature, i.e., $\chi=A+B/T$[24], in which the volume fractions were calculated from the weight fractions assuming a vanishing excess mixing volume. According to Figure 1, once phase separation takes place, a blend of an arbitrary composition (ϕ) always separates into two phases with composition of $\phi_1=0.095$ and $\phi_2=0.85$ at 220°C (where ϕ denotes the SMA volume fraction), and the volume fractions (x_1, x_2) of the two coexisting phases after quench to this temperature can be given from this figure using the lever rule[25]:

$$x_1 = (\phi_2 - \phi)/(\phi_2 - \phi_1) \tag{3}$$

$$x_2 = (\phi - \phi_1)/(\phi_2 - \phi_1) \tag{4}$$

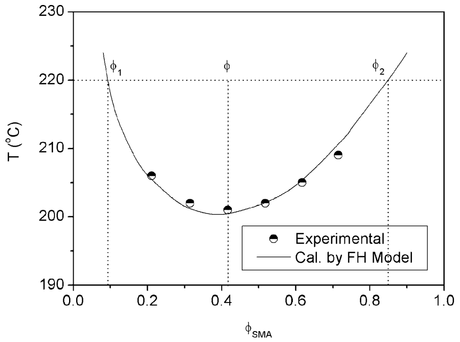

Figure 1 The measured phase diagram of the SMA/PMMA blend

Phase inversion

Figure 2 shows TEM micrographs of the phase-separated SMA/PMMA blends under quiescent conditions at 220°C. Although the phase interface in the present phase-separated blends is not so sharper as that of typical immiscible blend reported in the literatures, the resulting morphologies can still be distinguished each other.

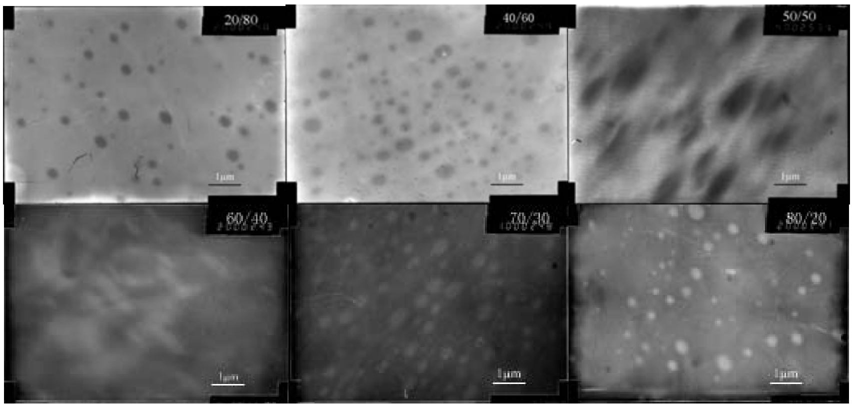

Figure 2 TEM images of the phase-separated SMA/PMMA blends

The darker SMA-rich droplets appear at $w<0.5$, while the lighter PMMA-rich droplets at $w>0.6$ (where w denotes the weight fraction of SMA in the blend). The dispersed phases appear as droplets over a wide range of compositions ($w<0.5$ and $w>0.6$), while the co-continuous morphologies doesn't appear a certain concentration but a composition range ($0.5<w<0.6$). It can be seen, phase inversion occurs around $w=0.5\sim0.6$.

Dynamic storage moduli of the phase-separated blends

Figure 3 shows the dynamic storage moduli of the phase-separated SMA/PMMA blends of different compositions and their pure components at 220°C. Compared with their pure components, the phase-separated blends exhibit enhanced elasticity; one can see that the dynamic storage moduli are sensitive to the morphologies resulted from phase separation. Therefore, the criteria based on the maximum of the storage modulus established by Steinmann et al.[9] for determining the phase-inversion composition should be available for the present system.

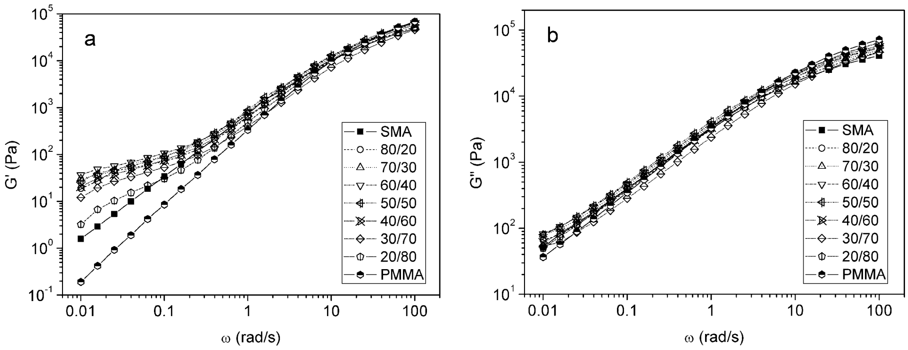

Figure 3 The dynamic storage moduli of the phase-separated SMA/PMMA blends and their pure components at 220°C

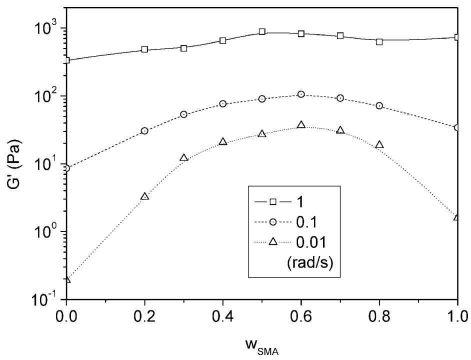

Figure 4 The composition dependence of the dynamic storage modulus of the phase-separated SMA/PMMA blends and their pure components at 220°C
(The lines are drawn to guide the eye.)

Figure 4 shows the composition dependence of the dynamic moduli of the phase-separated SMA/PMMA blends and their pure components at three frequencies of 0.01, 0.1 and 1rad/s at 220°C. One can see that the storage moduli gradually increase with increasing SMA weight fraction, corresponding to an increase in the concentration of the SMA-rich droplets, reach the maximum at w=0.6 and then decrease continuously for w >0.6, corresponding to that the dispersed phase is inverted from SMA-rich to PMMA-rich. Compared with the TEM micrographs shown in Figure 2, we can conclude that phase-inversion composition determined from the maximum of G' agrees well with that obtained by direct morphology observation. In addition, we also test the composition dependence of G' at higher frequencies above 1 rad/s; however, we do not observe any obvious discontinuity in the present case.

In contrast to those of G', the compositional dependence of the loss modulus at different frequencies, for clarity purpose, which is not presented here, is consistent with a log-additive mixing rule, and does not exhibit any peak or discontinuity.

Steady shear viscosities of the phase-separated blends

In general, the viscosity of a phase-separated blend contains an excess shear viscosity term that arises from the presence of domain interfaces[26], and thus the viscosity should be somewhat sensitive to change in morphology. Figure 5 shows the steady shear viscosities of the phase-separated blends and their pure constituent components at 220°C at a shear rate ranged of 0.01-10s^{-1}. Compared with their pure components, the phase-separated blends display enhanced viscosity especially at low shear rates, which agrees well with the prediction by Onuki[27]. Further, the shear viscosity curves of the phase-separated blends at this temperature, obviously different from those of the pure components, exhibit a clear intermediate plateau. This suggests the possibility of shear-induced remixing in these ranges, but this is evidence is not conclusive. Nakatani et al.[28] studied the phase separation of a deuterated polystyrene/poly(vinyl methyl ether) blend with the critical composition in steady shear flow by SANS, and suggested a shear-induced homogenization can sometimes be inferred from a plateau region in the middle shear range. However, shear-induced structure is complex even for completed immiscible polymer blends as investigated by

Hobbie et al.[29]; and it is more complex for partially miscible ones since shear flow can not only induce change in the shape of phase domains but also cause apparent shifts in the phase boundaries according to Han et al.[20]. We don't focus on shear-induced structure in detail here, since it goes beyond the present issue.

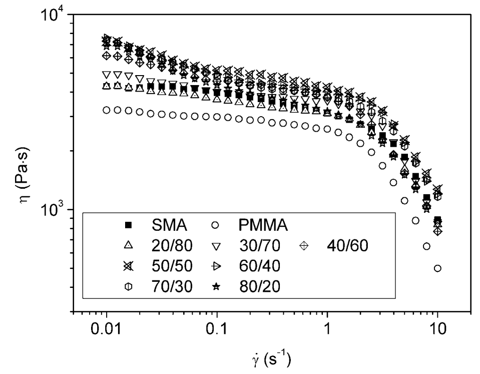

Figure 5 The steady-shear viscosities of the phase-separated SMA/PMMA blends and their pure components at 220°C

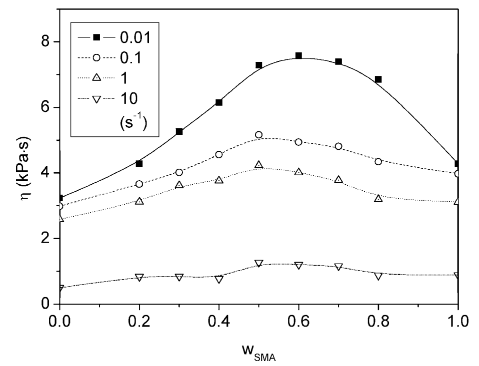

Figure 6 The composition dependence of the viscosities of the the phase-separated SMA/PMMA blends and their pure components at 220°C
(The lines are drawn to guide the eye.)

Figure 6 illustrates the composition dependence of shear viscosities of the phase-separated blends at three shear rates of 0.01, 0.1, 1 and 10s^{-1} at 220°C. From this figure, at a shear rate of 0.01s^{-1}, one can observe a continuous increase in the blend viscosity as the SMA-weight fraction increases from 0 to 0.6, while the blend viscosity decreases systematically for *w*>0.6, suggesting that the continuous phase is inverted from PMMA-rich to SMA-rich, which agrees well the observation by TEM micrographs shown in Figure 2. However, the results from the same criterion for the shear rates of 0.1, 1 and 10 s^{-1} slightly deviates from the direct morphology observation, as discussed above, which should be a result of shear-induced structure. This is needed to be verified by more experimental work.

Shear thinning behavior of the phase-separated blends

Ziegler et al.[7], investigated viscosities and morphologies of the two-phase systems consisting of poly(dimethyl siloxane) and poly(dimethyl siloxane-ran-methyl phenyl-siloxane), and found the sensitivity of viscosity towards shear, i.e., the extent of shear thinning which is quantified in terms of $-(\partial \ln\eta / \partial \ln\dot{\gamma}) = d^*$, can also reflect the morphology of the blends in a characteristic manner. Therefore, their method can be used as a tool to detect changes in morphology with composition. With this idea in mind, we carried out the similar procedure. The result obtained is depicted as a function of the composition in Figure 7.

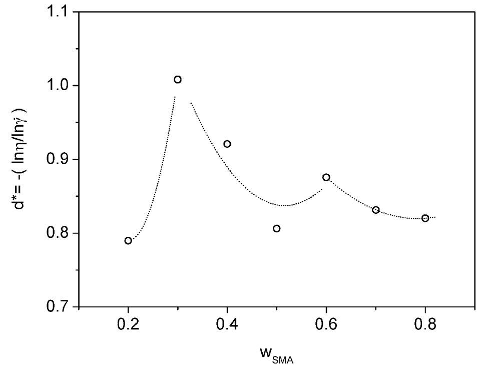

Figure 7 The extent of shear thinning of the phase-separated SMA/PMMA blends at 220°C (The dot lines are drawn to guide the eye.)

From Figure 7, one can see that three clearly separated regions in this figure. The extent of shear thinning rises to a summit at *w*=0.3, subsequently descends to the bottom at *w*=0.5, and then rises again to a second summit at *w*=0.6. According to the criterion presented by Ziegler et al.[7], the summit and the minimum marks the entrance into a region of co-continuity and phase inversion, respectively. Compared with the TEM micrographs shown in Figure 2, it can be seen that the determination base on this criterion also slightly deviates from the direct morphology. As mentioned above, that should be also a result of shear-induced structure.

Prediction of phase-inversion composition

As mentioned above, the two phases resulted from phase separation are not two pure-constituent phases but two respective phases of a certain composition. Therefore, the viscosities of the two coexisting phases should be used instead of those of the pure components for predicting phase-inversion composition in the phase-separated blends. However, due to be close to phase boundary, the viscosities of the two coexisting phases can not be experimentally obtained, so they are approximately define by the linear logarithmic additivity[30]

$$\log\eta_{mix} = \sum \phi_i \log\eta_i \qquad (5)$$

where η_{mix} and η_i are the viscosity of the phase and the two blend components, respectively; ϕ_i is the volume fraction in each phase of the two blend components, which can be obtained from the equilibrium composition of the two coexisting phases. According to Equation (5) and the phase diagram shown in Figure 1, we can calculate the viscosities of the PMMA-rich phase and SMA-rich phase at 220°C. Thus we can use Equation (2) to predict phase-inversion composition. The predicted phase-inversion concentration using Equation (2) is 0.64 and then the result denoted by the total SMA-volume fraction in the blend derived by Equation (3) is 0.57, which is in reasonably good agreement with the phase-inversion composition determined from TEM microscopy and rheometry. We conclude that the viscous criterion is still suitable for the partially miscible blend as the viscosity ratio of the blend components is substituted by that of the two coexisting phases.

Utracki[5] proposed that the blend viscosities increase from both sides with increasing content of second blend component and can be described by the model developed by Krieger et al.[31]:

$$\eta_{blend} = \eta_{matrix}(1-\phi/\phi_{\max})^{-[\eta]\phi_{\max}} \qquad (\mathbf{6})$$

where [η] is the intrinsic viscosity, ϕ is the volume fraction of the second blend component, and ϕ_{max} is the volume fraction at maximum sphere packing density. These blend viscosities should be equal at the point of phase inversion. For the isoviscous point, Equation (5) gives

$$p_{eff} = \frac{\eta_1}{\eta_2} = \left(\frac{\phi_{\max}-\phi_{I,1}}{\phi_{\max}-\phi_{I,2}}\right)^{-[\eta]\phi_{\max}} \qquad (\mathbf{7})$$

For polymer blends, ϕ_{max} is assumed to be equal to 1-ϕ_c, in which ϕ_c is the critical volume fraction for percolation[32] and amounts to 0.16. According to Utracki[5], the optimum value of [η] is 1.9. Thus the phase-inversion concentration can be determined by Equation (7). The predicted result denoted by the total SMA volume fraction in the blend derived by Equation (3) is 0.52, which is also in nearly good agreement with our TEM micrograph observation.

Conclusions

We have investigated phase inversion and viscoelastic properties of phase-separated SMA/PMMA blends, and found dynamic storage modulus and shear viscosity reaches a maximum at the point of phase inversion, while the extent of shear thinning displays a wide concentration range around the point of phase inversion. The phase-inversion composition determined from the maximum of dynamic storage modulus and shear viscosity at low shear rate agrees well with that from TEM micrograph. However, the data from the maximum of the shear viscosity at high shear rate and from the shear-thinning extent proposed by Ziegler et al. slightly deviate from that from TEM micrograph, which is possibly a result of shear-induced structure. That is needed to be verified in future. The prediction using various rheological models, as the viscosity ratio of the two coexisting phases is substituted for that of the pure components, is in nearly good agreement with that from TEM observation.

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