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Influence of Block Copolymer on Droplet Breakup and Coalescence in Model Immiscible Polymer Blends

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ABSTRACT: Shear-induced droplet breakup and coalescence were investigated by optical microscopy. Model polymer blends comprising 5% poly(propylene oxide) (PPO) dispersed in a poly(ethylene oxide) (PEO) matrix were studied in situ. Addition of 0.1% or 1.0% of PEO-*b*-PPO-*b*-PEO triblock copolymers facilitated breakup and inhibited coalescence. The steady-state droplet size produced by breakup was reduced only slightly by addition of 0.1% copolymer and more substantially by addition of 1%. However, the kinetics of coalescence were suppressed effectively even when 0.1% of copolymer was added, and only marginal additional gains in suppressing coalescence were achieved by addition of more copolymer. Analysis of coalescence kinetics shows that in these systems the copolymer acts to reduce the efficiency of both droplet collision and film drainage and/or rupture.

Introduction

Copolymers are used to emulsify immiscible polymer blends, because the mechanical and optical properties of immiscible polymers generally improve with a decrease of the dispersed phase droplet size.[1] However, the mechanism of emulsification is not known precisely. The traditional view has been that the copolymer significantly reduces the surface tension. This interpretation invokes the Taylor equation,[2,3] which defines the steady-state droplet size during shearing in terms of a balance between the shear forces which act to deform a droplet and the surface tension which acts to restore spherical shape:

$$D = \frac{2\nu \mathrm{Ca}_{\mathrm{crit}}}{\eta_{\mathrm{m}}\dot{\gamma}} \qquad (1)$$

where η_{m} is the matrix phase viscosity, $\dot{\gamma}$ is the applied shear rate, D is the droplet diameter, and ν is the interfacial tension between the two phases. The critical capillary number, $\mathrm{Ca}_{\mathrm{crit}}$, is approximately 0.5 and depends on the viscosity ratio.

More recently, the potential role of a block copolymer additive in the inhibition of coalescence has been suggested.[4−7] Coalescence is possible when the droplet size is less than the steady-state droplet size given by eq 1. A distribution of droplet sizes is created by breakup,[8,9] so that coalescence of the smaller ones may occur during steady shear. Moreover, in industrial practice, the flow rate within a mixer is inhomogeneous, so that small droplets are produced in regions of high deformation rates and coalescence can occur in the regions of more gentle flow within the mixer.[6] Frequently, it would be advantageous to use an appropriate additive, so that the desired phase size is established by breakup at high shear, and coalescence is prevented at subsequent slower shear.

Several research groups have investigated the breakup and coalescence processes in compatibilized immiscible blends. Beck Tan et al. investigated the effect of graft copolymers in the suppression of coalescence in a batch mixer through reactive compatibilization of polystyrene and an amorphous polyamide.[5] Their results indicate that the average droplet diameter is decreased to a much greater degree in blends with high dispersed-phase concentration than in systems with correspondingly low dispersed-phase concentration and that this reduction in size is due primarily to a suppression of coalescence and not to a reduction in the interfacial tension.[5] Macosko et al. also conclude that the interface need not be saturated in order for coalescence to be impeded.[4] Kim et al.[10] were able to directly visualize the block copolymer at the interface of PCHMA/PMMA-*b*-PS/SAN blends by selective staining of the PS segment of the block copolymer. In the wet-brush limit, they found that the ratio of swelling of the block copolymer by the respective phases strongly influences both the fraction of bcp that migrates to the interface during melt blending and the degree to which the rate of coalescence is suppressed.[10] Investigations of coalescence in binary uncompatibilized polymer blends have also been carried out (e.g., see refs 11 and 12).

The purpose of this investigation is to quantify and compare the effects of block copolymer on the reduction of the dispersed-phase morphology during breakup and coalescence processes. Furthermore, we aim to determine the relative efficiency of various block copolymers in controlling the disperse phase morphology by adjusting molecular parameters in a controlled fashion.

Experimental Section

Two homopolymers were used for this investigation. Poly(ethylene glycol), a form of poly(ethylene oxide), PEO, that is hydroxyl terminated at both chain ends was obtained from Polysciences, having an average molecular weight of 10 000 and a melt viscosity of 25P at 90 °C. The distribution though not monodisperse is relatively narrow, i.e., $M_{\mathrm{w}}/M_{\mathrm{n}} \sim 1.1$. Poly(propylene glycol), the hydroxyl-terminated form of poly(propylene oxide), PPO, having a molecular weight of 12 200 and a melt viscosity of 5.0P at 90 °C, was obtained from Arco Chemical. These materials were advantageous for in-situ optical microscopy for several reasons: their relatively low melt viscosities produced a convenient combination of droplet size and shear rate; experiments could be conducted at relatively low temperature; and their indices of refraction were sufficiently different from one another that phase contrast

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images could be obtained by optical microscopy. The systems investigated were Newtonian over the entire range of shear rates examined (up to 800 s^{-1}). PEO was chosen as the continuous phase, because it wets the quartz substrate more effectively than the PPO. This choice is also desirable because the viscosity of the dispersed phase is then less than that of the continuous phase. The weight fraction of PPO was 5%.

Poly(ethylene glycol-*b*-propylene oxide-*b*-ethylene glycol) ($EO_\alpha PO_\beta EO_\alpha$) triblock copolymers (Pluronic P105 ($EO_{37}PO_{56}$-EO_{37}) and F127 ($EO_{100}PO_{65}EO_{100}$); from BASF) were incorporated as compatibilizers into the blend system. Pluronic P105 contains 50 wt % propylene oxide, while F127 contains only 30 wt %. Their average molecular weights are 6500 and 12 600, respectively. Their polydispersity index (M_w/M_n) as specified by BASF is approximately 1.4.[13] Each of these copolymers is an isotropic fluid at the temperature utilized in the shearing experiments (90 °C). In the compatibilized ternary blends, the compositions were chosen so that the total concentration of propylene oxide segments (homopolymer and copolymer) in each system was 5 wt %.

The blend systems were investigated under steady shear conditions. A Linkam Scientific Instruments CSS-450 Cambridge shearing cell was mounted upon an Olympus BX-60 optical microscope, which was operated in phase contrast transmission mode, using a 20× long-working-distance phase-contrast objective. The temperature of the specimen was controlled at 90 ± 0.2 °C. The shearing cell consists of two quartz parallel plates with an adjustable gap, which was set to 50 μm, so that all droplets would be contained in the depth of field, i.e., in focus. In addition, the experiments were conducted so that average droplet diameters typically did not exceed 25 μm or $^1/_2$ of the gap width. This upper limit on the average droplet size allows for the droplets to flow over one another but does not eliminate hydrodynamic interactions with the quartz windows. The upper (smaller) plate has a radius of 15 mm. The observation window is fixed at a radius of 7.5 mm. The total sample volume was approximately 35 μL. To facilitate accurate blend preparation, a larger volume was weighed into a Petri dish. This mixture was melted and stirred until a uniform whitish appearance was obtained.

Droplet breakup under steady shear was investigated at progressively faster shear rates. Video images (having resolution 0.81 μm/pixel) were recorded after cessation of a prescribed amount of shear strain (e.g., 2000 units) using a CCD camera. Although the image was acquired immediately after cessation of shear, the droplets were stable without coalescence in the quiescent state for hours. All coalescence observed in this study was shear-induced (see below). The droplet size distribution was determined by image analysis using the Danielson operator,[14] which approximates the edge between a droplet and the surrounding phase as a circle. Droplets having a diameter of at least 2 pixels were included in the calculation. Number and volume average droplet diameters were calculated:

$$D_n = \frac{\sum_{i=1}^{n} n_i D_i}{\sum_{i=1}^{n} n_i}; \quad D_v = \frac{\sum_{i=1}^{n} n_i D_i^4}{\sum_{i=1}^{n} n_i D_i^3} \tag{2}$$

The total number of droplets for each calculation was approximately 500−2000.

Coalescence was investigated by first establishing a small relatively narrow droplet size distribution by shearing the mixture at a rapid rate (e.g., at 200 s^{-1} for the experiments described in Figure 1) and then shearing at a lower rate so as to induce coalescence. For large reductions in shear rate (at least a factor of 10), the droplets produced by the previous shear are sufficiently small that they are spherical during flow at the slower rate. Therefore, to facilitate analysis of coalescence kinetics (as in Figure 4), a sequence of video images was obtained during flow.

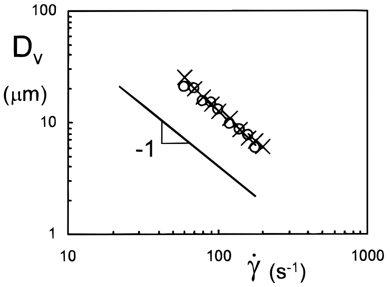

Figure 1. Breakup (× symbols) and coalescence (circles) behavior in the binary homopolymer blend (PPO 5%/PEO) as a function of shear rate. To obtain the coalescence data, the mixture was sheared first at 200 s^{-1} for 2000 units of strain and then for an additional 2000 units of strain at a lower rate, as indicated by the abscissa.

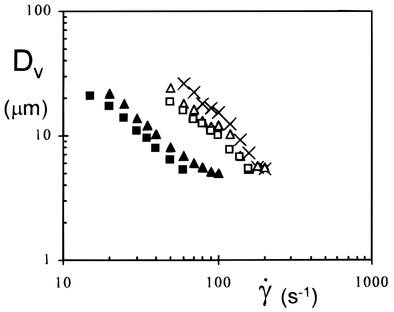

Figure 2. Steady-state volume average droplet size vs shear rate for various mixtures. The × symbols represent the binary homopolymer blend (PPO 5%/PEO) (data replotted from Figure 1). Open and filled symbols represent 0.1% and 1% block copolymer concentration, respectively. Mixtures containing P105 and F127 are represented by triangles and squares, respectively.

Results

When the binary homopolymer system was sheared, the steady-state volume-averaged droplet size was achieved during breakup in less than 100 units of shear strain. These steady-state sizes are approximately inversely proportional to the applied shear rate (Figure 1), as predicted by Taylor.[2,3] Although somewhat slower than the kinetics of breakup, the kinetics of coalescence in this binary system are quite rapid, and the droplets grow toward the steady-state breakup values, which are substantially reached after approximately 1000 units of steady shear strain and fully attained at 2000 strain units (Figure 1).

Copolymers were added, and their effect on breakup and coalescence was investigated. When the breakup curves for blends containing P105 and F127 copolymers at bulk concentrations of 0.1% and 1.0% are plotted against the breakup curve of the uncompatibilized blend, a reduction in droplet size is apparent (Figure 2), suggesting a corresponding decrease in interfacial tension. Addition of 0.1% copolymer has little influence on the steady-state droplet size produced by breakup. Therefore, the amount of copolymer adsorbed to the interface is relatively small. Substantially more significant decreases in droplet size are observed when the block copolymer concentration is much greater (i.e., 1%).

The effect of block copolymer concentration on the coalescence behavior, however, is diametrically opposite. The coalescence behavior is highly sensitive to small concentrations (0.1%) of compatibilizer (Figure 3), and when copolymer is present, even in small amounts, the average droplet size grows much more slowly than in

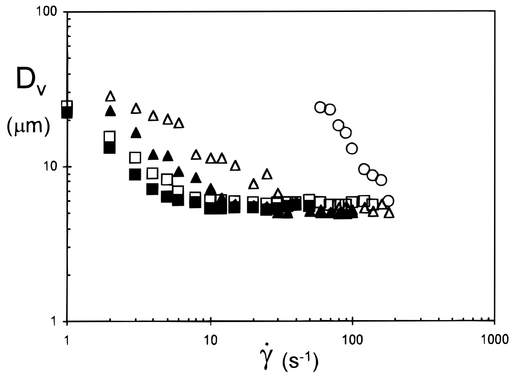

Figure 3. Coalescence behavior (after shearing first 2000 units at a rapid rate (i.e., 100 or 200 s^{-1}) and then 2000 units at a lower rate, as indicated by the abscissa) for various blend systems, illustrating the effect of copolymer type and concentration. Symbols represent mixtures as defined in Figures 1 and 2.

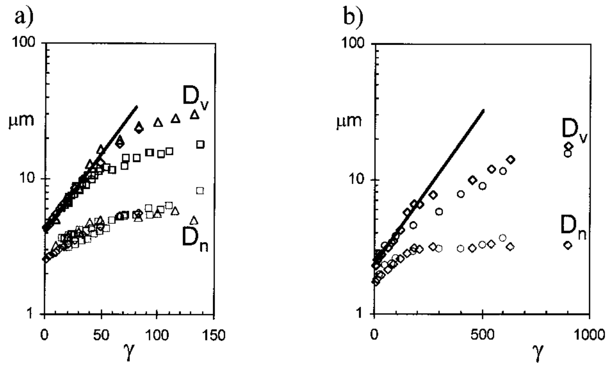

Figure 4. Weight- and number-average droplet sizes as a function of applied shear strain after a sudden reduction in shear rate. The previous shear condition was 300 s^{-1} for 60 s. (a) A binary mixture of 5% PPO in PEO, sheared at 0.3, 3, and 30 s^{-1}, as represented by diamonds, triangles, and squares, respectively. (b) A ternary mixture containing 0.1% F127, sheared at 0.3 and 1 s^{-1}, as represented by diamonds and circles, respectively. Note the much expanded scale of the abscissa.

the mixture without copolymer. Surprisingly, mixtures having much more copolymer (i.e., 1.0 wt %) exhibit droplets that are only slightly smaller after 2000 units of shear strain than those in the 0.1% copolymer mixture (Figure 3). For either mixture, the coalescence rate is especially small when the step down ratio ($\dot{\gamma}_{\mathrm{prior}}/\dot{\gamma}$) is small; the droplets are essentially the same size as that produced by the previous breakup shear at 100 s^{-1}, even after 2000 units of shear strain at the lower rate (Figure 3).

Insight into the origin of the slower coalescence in the presence of copolymer can be obtained through analysis of the coalescence kinetics. Therefore, a binary homopolymer mixture and a ternary mixture containing 0.1% F127 were sheared rapidly (at 300 s^{-1}) for approximately 1 min to establish a fine dispersion of small droplets. The rate was decreased suddenly, and the average droplet size was measured as a function of applied shear strain (Figure 4). A time-lapse video was obtained, with the delay between frames appropriately adjusted.

As demonstrated earlier (Figure 2), the addition of 0.1% F127 causes a measurable decrease in the steady-state droplet size at any given shear rate. Therefore, the initial average droplet size of the ternary system (Figure 4b) is smaller (i.e., $D_v = 2.4$ µm) than that of the binary system (4.1 µm, Figure 4a). At first, the volume average droplet size grows approximately according to an exponential growth law, regardless of shear rate. After the droplets become sufficiently large, the growth rate slows. At faster shear rates, the departure from exponential growth occurs at smaller droplet size. This behavior is consistent with coalescence theory, which considers multiple steps leading to coalescence: droplet collision[6,7,15,16] followed by drainage[17] and rupture[18] of a thin film of the matrix fluid separating two droplets after they have been pressed together. The earliest theory for coalescence rate considered only droplet collision, while ignoring hydrodynamic interactions between droplets:[15]

$$dD/d\gamma = D\phi(4/\pi)(2 - 2^{2/3}) \qquad (3)$$

The theory was made more realistic[19−21] by incorporating a coalescence efficiency $\epsilon = EP_dP_r$ as a prefactor on the right-hand side of eq 3, where the individual terms E, P_d, and P_r represent the collision efficiency and the probability of drainage and rupture, respectively. Experimentally, ϵ is derived from the slope of log(D) vs shear strain (Figure 4). If ϵ is constant, then the droplet size grows exponentially with applied shear. Analysis of the D_v data, as plotted in Figure 4, indicates that ϵ is indeed constant at very small strains (or droplet sizes[22]) for which it equals 1.1 and 0.22 for the binary and ternary systems, respectively. We note that these values of the coalescence efficiency are influenced by polydispersity of droplet size, because the apparent coalescence efficiency at small strains for the number-average droplet size is substantially smaller (Figure 4). As a result of the slower growth rate for D_n, the polydispersity increases.[6] It is clear in comparing parts a and b of Figure 4 that the addition of copolymer dramatically decreases the rate of coalescence during the initially exponential growth phase. After this initial period, ϵ continuously decreases, exponential growth in the volume average is no longer observed, and growth of both the number and volume averages slows considerably. As expected from film drainage theory,[17] the droplet size at which the coalescence efficiency begins to decrease reduces with increasing shear rate. The small amount of copolymer present in the mixture has a major effect on the coalescence rate, both reducing the initial coalescence efficiency by approximately a factor of 5 and reducing the droplet size at which the coalescence efficiency begins to decrease.

The individual contributions of E, P_d, and P_r to ϵ can be identified by comparing results under different experimental conditions such as shear rate, droplet size, and concentration. For example, E is predicted to be independent of average droplet size and of shear rate,[16] whereas P_r, when less than unity, decreases with increasing shear rate,[23] and P_d, when less than unity, decreases sharply with increasing droplet size and somewhat less strongly with increasing shear rate.[17] The rupture probability appears to be independent of droplet size.[23] Noting that the initial exponential growth in droplet size is independent of shear rate and of droplet size (Figure 4), hence we identify $P_r \approx P_d \approx 1$, so that $\epsilon \approx E$ during this period. We also note that during this initial stage the droplets are approximately an order of magnitude smaller than the spacing between the quartz plates ($D_v \sim 3-8$ µm) and are numerous ($\sim 10^9$/cm^3), so that the hydrodynamic interactions between droplets are more significant than those between a droplet and the wall.[24] Since E is associated with hydrodynamic interaction, a reduction in E with addition of copolymer suggests that the copolymer adsorbed to the droplet interface resists fluid convection within the droplet (as previously demonstrated in mixtures containing small molecule surfactants[25−28]), thereby reducing the frequency of droplet collisions as theoretically proposed.[6,7] The copolymer also appears to inhibit film drainage, because the droplet size at which ϵ begins to decrease is smaller (Figure 4b) than for the mixture without copolymer (Figure 4a). The latter effect is likely to depend on copolymer solubility.[29] Future experiments will investigate ϵ under diverse experimental conditions. At present, we emphasize that the experiments summarized in Figure 4 demonstrate that small amounts of copolymer (i.e., at a level, 0.1%, which only weakly influences the breakup behavior) strongly inhibit droplet coalescence by increasing the hydrodynamic interaction between droplets and perhaps also delaying film drainage and/or film rupture.

Conclusions

Droplet breakup and coalescence processes in model ternary blends of two homopolymers and a copolymer compatibilizer were studied. As expected, a relatively large amount of copolymer adsorbed to the interface is required to modify the breakup behavior. Most strikingly, a very small amount of copolymer adsorbed to the interface is dramatically effective in suppressing coalescence. Kinetic analysis suggests that the block copolymer both reduces the efficiency of droplet collisions and slows film drainage and/or rupture.

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