

Effect of Marangoni Stresses on the Deformation and Coalescence in Compatibilized Immiscible Polymer Blends

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The effect of physical compatibilization on the deformation and coalescence of droplets in immiscible polymer blends is discussed. Evidence is provided for the existence of concentration gradients in block copolymers along the interface during deformation. This causes complex changes in droplet shapes during deformation and relaxation. These concentration gradients also result in Marangoni stresses, which stabilize the droplets against deformation and breakup. Coalescence experiments have been performed, varying both the compatibilizer concentration and the shear rate. Existing coalescence models have been evaluated. An empirical extension of Chesters' partially mobile interface model is presented, that treats the effects of Marangoni stresses on the coalescence process as a higher effective viscosity ratio.

1 INTRODUCTION

The blending of polymers provides a powerful route for producing materials with improved performance/cost ratio (1). Two-phase blends are preferred, but these require compatibilization in order to obtain a suitable combination of mechanical properties. This can be achieved primarily by either adding premade block copolymer or by in-situ formation of a graft copolymer at the interface (2). Originally, it was believed that the addition of a block copolymer merely reduced interfacial tension (3). Such a reduction would facilitate the breaking-up of the dispersed phase into much finer droplets, thus improving the mechanical properties of the blend. Reduction in interfacial tension upon adding compatibilizer is indeed expected on theoretical grounds (4, 5) and has been observed experimentally by various authors (e.g. 6). This long-standing idea has recently been questioned by several experimental studies, postulating that prevention of coalescence rather than the decrease in interfacial tension is the main consequence of compatibilization

(e.g. 7–10). To date, the precise action of the compatibilizer in the coalescence process remains unclear. Some authors invoke Marangoni stresses as being responsible for the stabilizing action (e.g. 11, 12). It is then assumed that, when two droplets approach, squeezing flow in the intermediate matrix fluid results in a concentration gradient of block copolymer along the interface. The resulting gradient in interfacial tension, i.e. a Marangoni stress, immobilizes the interface, thus retarding the drainage of the film and thereby suppressing coalescence. Another explanation is suggested by Sundararaj and Macosko (7). These authors assume that coalescence suppression arises mainly from the steric repulsive force between the droplets as a result of compression of the block copolymer chains at the surface of the approaching droplets.

In order to elucidate the role of block copolymers on the various structural changes in compatibilized blends, more systematic studies of the morphological processes in blends are indicated. Such an approach has been applied successfully in the case of uncompatibilized blends (see e.g. the review by Tucker and Moldenaers (13)). However, as pointed out in a review on the rheology and dynamics of compatibilized blends (14), experimental studies on compatibilized blends focusing on the various structural phenomena during flow are still fairly scarce. Recently, Velankar *et al.* (15) demonstrated that in a PIB/PDMS blend,

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compatibilized by the corresponding block copolymer, the steady shear capillary number strongly increased upon addition of compatibilizer. It was postulated that concentration gradients caused Marangoni stresses along the interface, which resisted droplet deformation and breakup. These results are in line with simulations by Stone and Leal (16) and by Li and Pozrikidis (17).

In order to elucidate the role of the compatibilizer, we will concentrate on two morphological processes. First, deformation of droplets during a stepwise increase in shear rate will be briefly discussed. Second, results from a systematic study on coalescence will be reported, in which relevant parameters such as block copolymer concentration and shear rate have been varied.

2 MATERIALS AND METHODS

The model blend used in this study is composed of 1% polyisobutene (PIB, Parapol 1300) from Exxon Chemicals, $M_w = 1300$, $\eta = 113$ Pa.s at 23°C) in polydimethylsiloxane (PDMS, Rhodorsil V100000 from Rhodia Chemicals, $M_w = 145000$, $\eta = 107$ Pa.s at 23°C). Both components are nearly Newtonian with hardly any measurable elasticity under the present experimental conditions. The interfacial tension of the uncompatibilized blend is 3 mN/m (18).

A diblock copolymer of PIB-PDMS, procured from Polymer Source, was used as a compatibilizer. The structural characteristics are: $M_{w,PIB} = 6150$, $M_{w,PDMS} = 8000$, polydispersity 1.3 as provided by the manufacturer. The low molecular weights of the two blocks imply that there are no entanglements between the blocks and the constituent phases of the blend.

Samples have been prepared by first mixing the required amount of block copolymer into the dispersed

phase and then blending this phase into the matrix. The amount of block copolymer is quoted as a weight fraction of the dispersed phase rather than of the total sample. For example, a 2% compatibilized blend has overall 0.2 % by weight of block copolymer based on the global blend composition. Blends with 0–10% compatibilizer were studied. The addition of a block copolymer in these small amounts was measured to have a negligible effect on the viscoelastic properties of the bulk phases. The materials and the blend preparation procedures are the same as those used by Velankar *et al.* (2000). The sole difference is the much lower volume fraction used here in order to facilitate microscopic observations of individual droplets.

The blend morphologies, resulting from the various shear histories, have been investigated microscopically. A Linkam Scientific Instruments CSS-450 shearing cell was mounted on a Leitz Laborlux 12 PolS optical microscope; the shearing cell consists of two quartz plates with an adjustable gap, which was kept at 500 micrometers. The temperature of the sample was controlled at 23°C. For the coalescence study, typically over a hundred droplets have been analyzed by means of an image analysis program (Scion Image, Scion Corporation).

3 RESULTS AND DISCUSSION

3.1 Deformation of Droplets

First, the effect of block copolymer on the deformation of droplets will be discussed. Three concentrations of block copolymer have been selected: 0%, 2% and 10%, the 0%-case serving as a reference. *Figure 1* shows the deformation of droplets in the different systems after shearing at 10 s^{-1} for 2 s. The pictures were taken just after the flow was stopped. The uncompatibilized droplets are deformed into ellipsoids or even

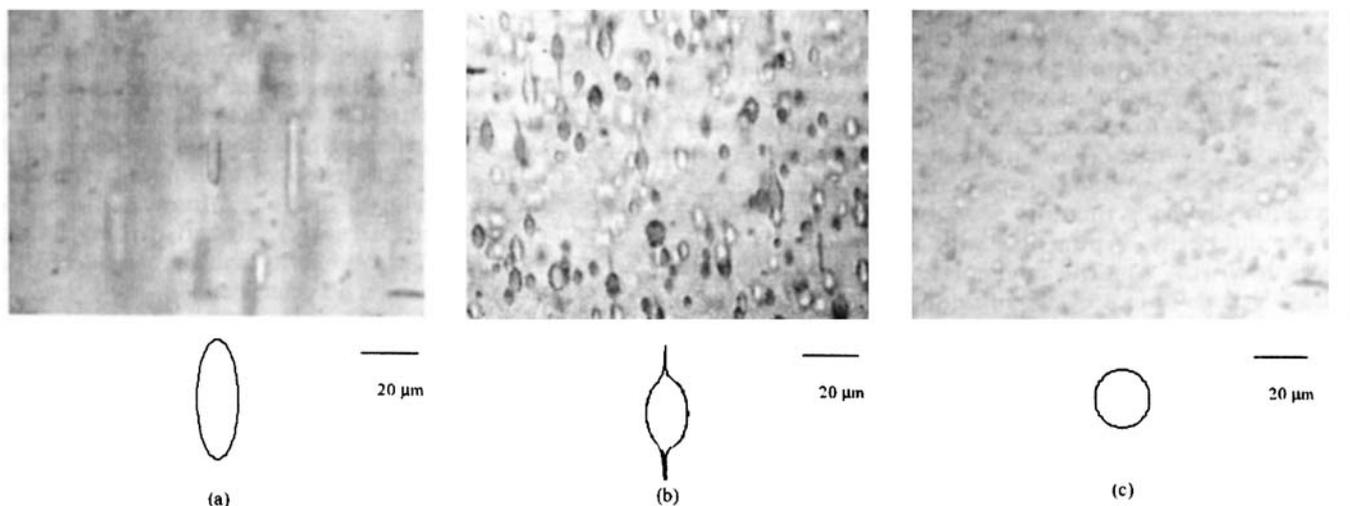


Fig. 1. Microscopic images of droplet deformation after shearing for 2 s at 10 s^{-1} . a) uncompatibilized droplets; b) 2% compatibilizer, c) 10% compatibilizer.

fibrils as reported in earlier studies (e.g. the recent review by Tucker and Moldenaers (13)). With 2% compatibilizer, however, some of the droplets show a particular shape: during the deformation stage, they produce pointed ends. When the same flow field is applied to the system with 10% compatibilizer, it can be observed that the droplets are smaller and remain nearly undeformed.

These observations can be compared with the expected effects of surfactants on droplet deformation. When a flow field is applied to a droplet with block copolymer on its surface, the copolymer will be swept around by surface convection. This convective flux creates gradients in interfacial coverage and hence in interfacial tension. The importance of these gradients can be estimated by calculating a surface Peclet number Pe_s , defined as (Pawar and Stebe (19)):

$$Pe_s = \frac{\dot{\gamma}R^2}{D_s}, \quad (1)$$

in which $\dot{\gamma}$ is the applied shear rate, R the radius of the droplet and D_s the surface diffusivity of the surfactant molecule. At large Pe_s , strong gradients in interfacial coverage may develop, whereas at low Pe_s , the interfacial tension is expected to remain nearly uniform over the surface of the droplet. In the former case, accumulation of block copolymer at the drop tips will reduce the interfacial tension locally, leading to a higher local curvature to balance the pressure jump across the interface. As a result, drop tips tend to stretch further than in a drop without block copolymer at the same hydrodynamic conditions. This situation is clearly observed for the system containing 2% compatibilizer (Fig. 1b).

With 10% compatibilizer, neither stretched tips nor deformation is observed (Fig. 1c). Two possible mechanisms can be given for the change in behavior. First, when a drop deforms, its surface area increases. Assuming small Pe_s and no exchange of block copolymer between the surface and the bulk, the mean surface concentration of the block copolymer is thus reduced, increasing the interfacial tension over the entire drop with respect to the undeformed case. An increased interfacial tension will make the droplets more resistant to deformation. To evaluate this mechanism, the magnitude of Pe_s in the present system must be estimated. Since the diblock copolymer is unentangled, its diffusivity along the drop surface is at most equal to the diffusivity of pure PIB with MW = 6150 (the block MW) (15, 20). The monomeric friction factor of PDMS is four orders of magnitude lower than that of PIB, and hence is expected to have a negligible effect on the diffusivity of the block copolymer. Hence the upper limit for D_s is given by the Rouse theory (21):

$$D_s = \frac{RT}{N\zeta N_{avo}} \quad (2)$$

where R and T are respectively the gas constant and the temperature, ζ is the monomeric friction coefficient

of PIB (4.5×10^{-8} kg/s (21)), N the number of monomers in each PIB block and N_{avo} Avogadro's number. The upper limit for D_s is then calculated to be $\sim 10^{-15}$ m²/s. This low value of the diffusivity implies rather high values of Pe_s , even for small droplets, ruling out an overall dilution as a mechanism to explain the results of Fig. 1.

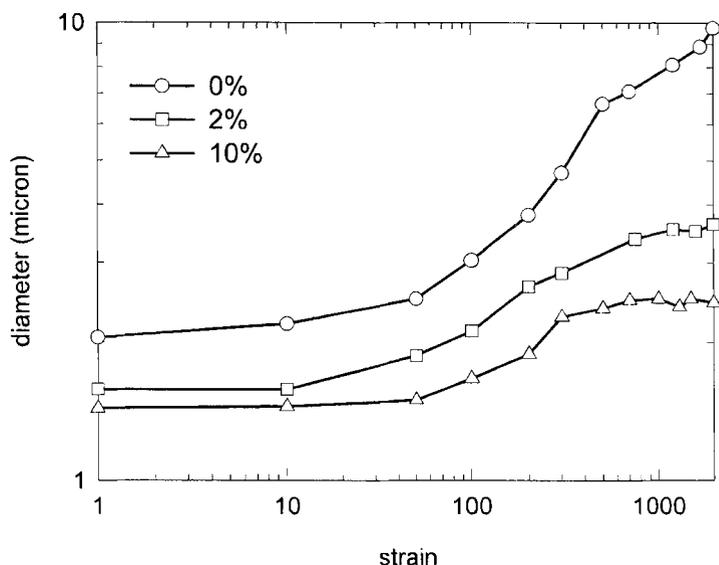
Having eliminated overall dilution as a significant factor, Marangoni stresses remain the most likely explanation for the observed droplet behavior. The gradient in interfacial tension, resulting from the applied flow field, induces a Marangoni stress along the drop surface. When the Marangoni stress is sufficiently large, droplet deformation can be prevented altogether as it greatly exceeds the applied hydrodynamic stress. The magnitude of the Marangoni stresses strongly depends on the surface coverage. As noted by several authors (e.g. the review by Koning *et al.* (2)), the decrease in interfacial tension for small surface concentrations is rather moderate but becomes more important at higher coverages. Hence, for small coverages the generated gradient in interfacial tension is small in the initial stages of droplet deformation, allowing surface concentration gradients to develop without interference from Marangoni stresses. The surface convective flux remains large, thus promoting tip stretching as seen in the system with 2% compatibilizer. When the hydrodynamic stress is removed, the concentration gradient is still present. If the deformation of the stretched tips is not too large, Marangoni stresses support their shape relaxation and the droplet relaxes without breakup. It is observed microscopically that the central portion of the droplets relaxes first; subsequently, the tips retract also, reconstructing the original droplet. At higher concentrations of block copolymer, the interfacial tension becomes increasingly sensitive to small gradients of concentrations. The resulting Marangoni stresses are therefore strong enough to immobilize the interface and to strongly inhibit deformation. This behavior can indeed be observed for the system containing 10% compatibilizer (Fig. 1c).

The results discussed above suggest that gradients in interfacial tension develop along the drop surfaces and lend support to the idea that Marangoni stresses act on droplet surfaces when droplets are deformed by shear. The stabilizing effect of Marangoni stresses is qualitatively similar to that of an increased drop viscosity, an effect already pointed out by Li and Pozrikidis (17). This similarity will be considered further in the discussion on coalescence.

3.2 Coalescence Under Flow

In the coalescence experiments, the applied shear history consisted of first shearing at 5 s^{-1} until steady state is achieved. Subsequently the shear rate was reduced to induce coalescence. The evolution of the number averaged drop diameter for a decrease from 5 to 0.5 s^{-1} is shown in Fig. 2. It can be seen that the uncompatibilized blend did not reach steady state

Fig. 2. Effect of compatibilizer concentration on the evolution of the droplet diameter after a step-down in shear rate from 5 s^{-1} to 0.5 s^{-1} .



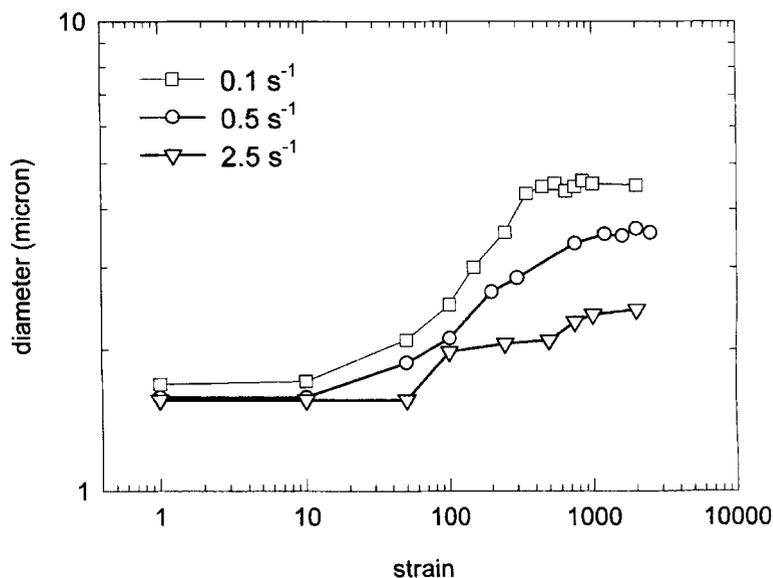
even after 1000 strain units. This is not surprising considering the low frequency of droplet collisions with only 1% dispersed phase (22). Vinckier et al. (22) have shown that for dilute uncompatibilized blends, the steady state droplet size after coalescence corresponds closely to the diameter at critical conditions for breakup, i.e. to that given by the critical capillary number (0.5 in this case). For the PIB-PDMS blend under investigation, this would result in a steady droplet size, around $56 \mu\text{m}$, at a shear rate of 0.5 s^{-1} . In Fig. 2, it can be observed that the block copolymer significantly reduces the mean drop size, even at 2% compatibilization, the effect becoming of course more pronounced at higher compatibilizer concentrations. Moreover, the higher the compatibilizer loading, the faster the droplet size reaches a steady state level. This is consistent with the observation of the data

of Velankar et al. (15) that the capillary number reaches a steady state faster upon addition of compatibilizer. Figure 2 also shows that the compatibilizer levels used here do not suppress coalescence completely, and hence shearing at a given shear rate for a sufficiently long time results in a well-defined morphology.

The effect of shear rate on coalescence has been studied for a 2% compatibilized blend (Fig. 3). When the shear rate is large (e.g. 2.5 s^{-1}), coalescence still occurs, but very slowly. For lower shear rates, the increase in drop size due to coalescence is more pronounced but is found to stop at smaller values of the strain, consistent with experimental observations by Lyu et al. (23).

The effect of compatibilization on the final droplet size under shear is quantified in Fig. 4, where the

Fig. 3. Effect of shear rate on coalescence in a 2% compatibilized blend after preshearing at 5 s^{-1} .



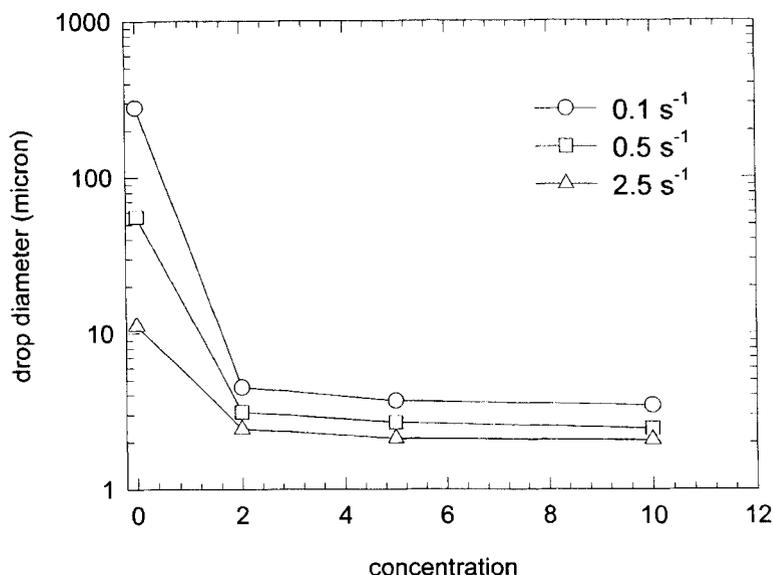


Fig. 4. Effect of compatibilizer on final droplet size after shearing (data for the uncompatibilized blend are calculated from the critical capillary number).

number average diameter is given as a function of compatibilizer concentration for different shear rates. The values at 0% compatibilization are not the experimentally observed diameters. They are calculated on the basis of the critical capillary number, which, as mentioned above, is expected to be a good approximation of the steady state droplet size. Adding 1% to 2% compatibilizer, calculated on the dispersed phase only, has a drastic impact on the droplet size during flow. The effect seems to be more pronounced at low shear rates. Higher concentrations of compatibilizer further reduce the droplet size, but only very gradually. The increase in interfacial area with increasing compatibilizer concentration, due to the decrease in droplet size, is less than proportional to this concentration in the present experiment. Hence, assuming that all the block copolymer remains on the interface, the corresponding interfacial concentration of the block copolymer should be increased also. Based on the mean drop size in Fig. 4, total saturation is apparently not achieved at 10% compatibilization. The concentration effects are not very sensitive to shear rate, considering the nearly constant shape of the curves for different shear rates.

If a mere reduction in interfacial tension were the only consequence of added block copolymer, the droplet size under shear should be determined by the critical capillary number for breakup, i.e. it should scale with the interfacial tension. Since the mean drop size of the 10% compatibilized blend is about 10 times smaller than that of the uncompatibilized blend, this would require values of the interfacial tension of e.g. 0.3 mN/m for the 10% compatibilized blend. Such a drastic reduction of interfacial tension is possible in low molecular weight surfactant systems but quite

unlikely in polymer mixtures (4, 23). This is consistent with recent results by Velankar *et al.* (15). These authors measured directly the capillary number Ca for different block copolymer concentrations. The data did not superimpose, although the use of Ca already covered the reduced interfacial tension.

The complex problem of flow-induced coalescence can be approached by decoupling the flow into sub-processes. Usually the flow is split up in an external flow and a flow in the intermediate region between droplets (24). The external flow is the macroscopic flow field, which brings the droplets together and hence governs the collision frequency, the contact force, and the interaction time. The drainage of the fluid film between colliding droplets constitutes the intermediate flow. Whether coalescence will occur or not is determined by the collision probability and by the drainage probability.

The drop collision can be accounted for by using a collision frequency C . For monodisperse spheres, following their undisturbed streamlines in simple shear flow, the collision frequency per unit volume is given by the Smoluchowski equation:

$$C = \frac{2}{3} \dot{\gamma} D^3 n^2 \quad (3)$$

D being the diameter of the droplets and n the number of droplets per unit volume. For a collision to result in coalescence, the matrix film between the droplets has to be drained during the collision. The required drainage time depends on the interfacial mobility, which affects the flow pattern between the colliding droplets. Models for fully mobile, partially mobile, and immobile interfaces have been suggested (see, for example, the review by Chesters (24)).

The drainage probability P_{drain} can be expressed as:

$$P_{drain} = \exp\left(-\frac{t_{drain}}{t_{int}}\right) \quad (4)$$

where t_{int} is the interaction time during collision and t_{drain} the drainage time. Drainage probabilities for partially mobile and immobile interfaces are given by:

$$P_{drain, PMI} = \exp\left[-0.07655\left(\frac{\eta_m \dot{\gamma}}{\Gamma}\right)^{3/2} D^{5/2} \frac{p}{h_c}\right] \quad (5)$$

$$P_{drain, IMI} = \exp\left[-0.14\left(\frac{\dot{\gamma}}{\Gamma}\right)^2 D^4 \frac{\eta_m}{h_c^2}\right] \quad (6)$$

in which η_m is the matrix viscosity and p the viscosity ratio of the blend. The parameter h_c is the critical distance between the droplets at which coalescence suddenly occurs as a result of film rupture.

Based on these arguments, an expression for the evolution of the rate of change of the specific interfacial area Q can be written:

$$\frac{DQ}{Dt} = C(t) \cdot P_{drain} \cdot \Delta S(t) \quad (7)$$

in which $C(t)$ is the collision frequency and $\Delta S(t)$ the change in interfacial area due to a single coalescence event. Combining Eq 7 and Eq 5 or 6, and expressing Q , $\Delta S(t)$ and $n(t)$ in terms of volume fraction of the disperse phase ϕ and the droplet diameter, result in the following differential equation for the evolution of droplet size:

$$\left(\frac{dD}{dt}\right)_{PMI} = 0.525 \phi \dot{\gamma} D \exp\left[-(m.D)^{5/2} \dot{\gamma}^{3/2}\right] \quad (8)$$

with m given by:

$$m = 0.358 \cdot \left(\frac{p}{h_c}\right)^{2/5} \left(\frac{\eta_m}{\Gamma}\right)^{3/5} \quad (9)$$

in the case of the partially mobile interface and by:

$$\left(\frac{dD}{dt}\right)_{IMI} = 0.525 \phi \dot{\gamma} D \exp\left[-(k.D)^4 \dot{\gamma}^2\right] \quad (10)$$

for an immobile interface where k is given by:

$$k = 0.612 \cdot \left(\frac{\eta_m}{\Gamma^2 h_c^2}\right)^{1/4} \quad (11)$$

The equation for the partially mobile interface model has been used to fit the coalescence data of the uncompatibilized blend, using h_c as a fitting parameter. This model has been selected since, at a viscosity ratio of 1, this theory gives a better description than the PMI or immobile interface models for the types of blends under consideration (25). As can be seen in Fig. 5, a value of $h_c = 14$ nm yields a good prediction of the experimental data at different step-down ratios with literature values (22).

In Fig. 6 experimental coalescence data on a 2% compatibilized blend are compared with the predictions of various coalescence models. The PMI model (Eqs 8 and 9) has been used with the same value of h_c as in the uncompatibilized case. This is consistent with a recent study by Valkovska *et al.* (2001), in which it was suggested that in the concentration regions of practical importance no strong dependence of h_c on the surfactant concentration should be expected. The agreement between the model and the data is

Fig. 5. Coalescence in the uncompatibilized blend: application of the PMI model.

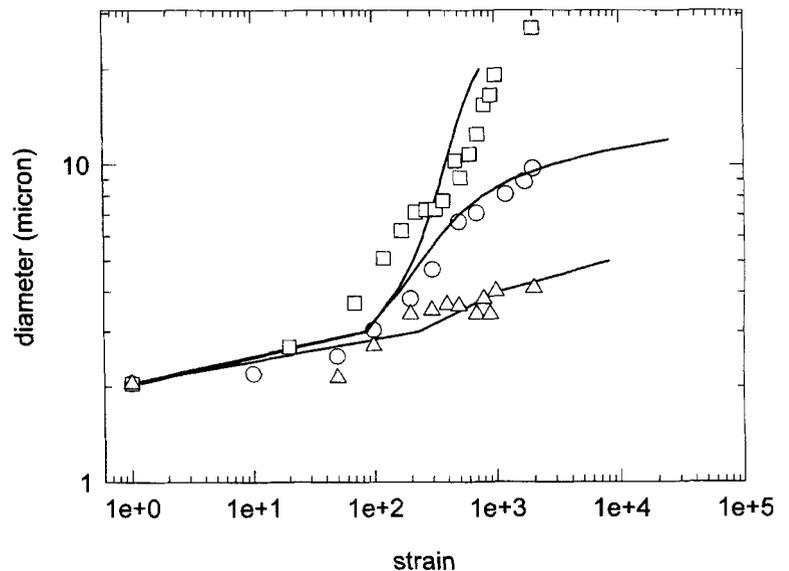
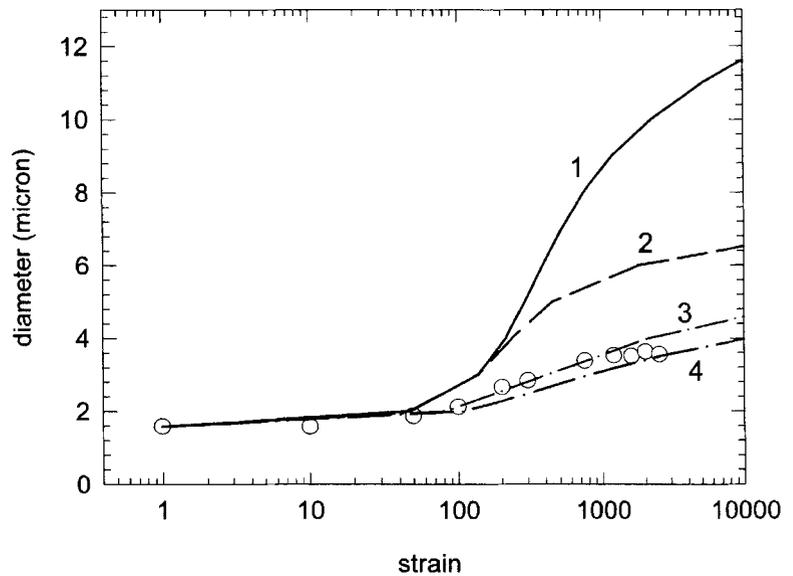


Fig. 6. Coalescence in a blend containing 2% compatibilizer: comparison with the PMI and IMI models (coalescence at 0.5 s^{-1}). 1: PMI- $h_c = 14 \text{ nm}$, 2: IMI- $h_c = 14 \text{ nm}$, 3: PMI- $h_c = 1 \text{ nm}$, 4: PMI- $\Gamma = 0.1 \text{ mN/m}$.



poor. A better agreement can be obtained by adjusting h_c . As can be seen in Fig. 6, however, unrealistically low values of h_c must be used to fit the data. Chesters suggested that the immobile interface model might be relevant for systems containing surface active species (24). Figure 6 shows the comparison between the IMI model and the experimental data on a blend containing 2% compatibilizer. It can again be seen that the agreement is not satisfactory. The same conclusions can be drawn for other concentrations.

The lack of interfacial tension data for the compatibilized systems greatly hinders quantitative analysis of the data. The fits shown in Fig. 6 are all based on the interfacial tension of the uncompatibilized blend. A better fit can be obtained by varying this interfacial tension. However, as observed in Fig. 6 (thick line, $h_c = 14 \text{ nm}$), unrealistically low values of the interfacial tension for this compatibilizer concentration (2%) must be used to obtain a better agreement between experiment and model. Adjusting both h_c and interfacial tension at the same time also resulted in unphysical values of the interfacial tension.

Coalescence in the presence of compatibilizers is complicated by the development of a nonuniform surfactant concentration on the interface. Governed by a diffusion-convection balance it causes a gradient in interfacial tension, which in turn induces to Marangoni effects. Chesters and Bazhlekov (12) solved this problem numerically. When diffusion of the compatibilizer is negligible, the rate of film drainage was found to change from that characteristic for PMI to one that is more reminiscent of IMI.

The results of section 3.1 suggest that concentration gradients are indeed present in our compatibilized system during droplet deformation. It was mentioned that the resulting Marangoni stresses are qualitatively similar to droplets with a higher effective viscosity. In order to use this argument in the discussion of the

coalescence models, the expression for the drainage probability of the partial mobile interface theory is slightly modified. This model is chosen since it is the only one that contains the viscosity ratio p explicitly (see Eq 5). The viscosity ratio is now written as Fp , F being a scaling factor accounting for the higher effective viscosity in case of Marangoni stress. A similar argument was used by Velankar *et al.*, who shifted Cap-curves for various compatibilizer concentrations by using an effective viscosity ratio (26). The resulting expression for the drainage probability is given by:

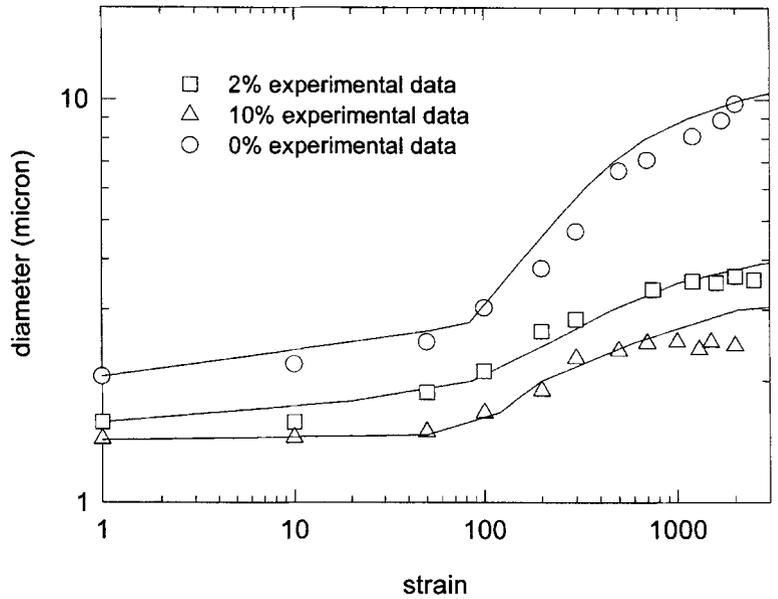
$$P_{\text{drain,PMI}} = \exp\left[-0.07655\left(\frac{\eta_m \dot{\gamma}}{\Gamma}\right)^{3/2} D^{5/2} \frac{Fp}{h_c}\right] \quad (12)$$

Keeping the same values of h_c and interfacial tension as for the uncompatibilized blend, F can be used as a fitting factor to describe the experimental coalescence data. The results for the 0%, 2% and 10% compatibilized blend are shown in Fig. 7. For the 0%-sample, the scaling factor is 1.

It can be seen that this empirically modified drainage probability provides a reasonable fit for the experimental observations. The resulting scaling factors for different step-down ratios in shear rate and for different compatibilizer concentrations are given in Fig. 8. Here it can be seen that F increases with compatibilizer concentration but levels off at high concentrations where the saturation concentration is reached. Moreover, the higher the step-down ratio, the higher the effective viscosity of the droplets. The values of F reported in Fig. 8 have been calculated with the interfacial tension of the uncompatibilized system. Using the real values for Γ would reduce the values of F without changing the general picture, as the decrease in Γ would not completely compensate the rise in F .

The trends observed in Fig. 8 are consistent with a coalescence model by Milner and Xi (11). These authors considered the work done in sweeping the block

Fig. 7. Comparison experimental coalescence data with modified PMI model for different compatibilizer concentrations (coalescence at 0.5 s^{-1}).



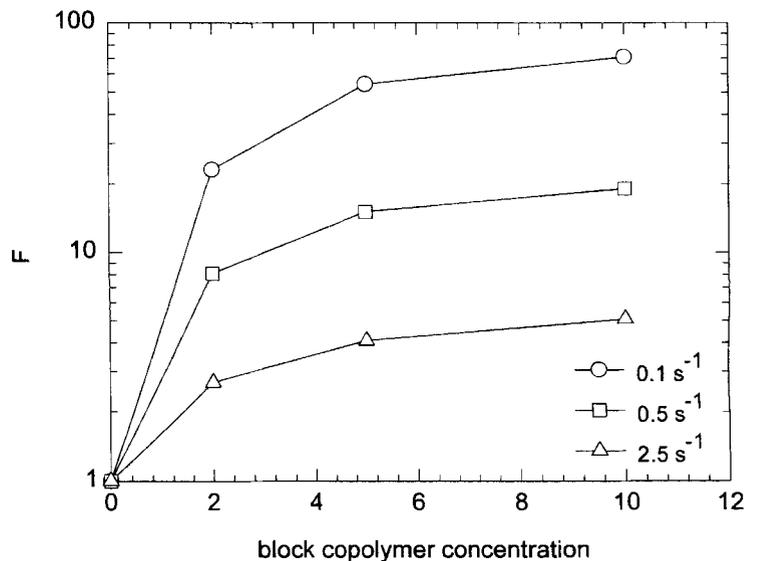
copolymer out of the gap between approaching droplets as resulting from an effective repulsive potential whose magnitude was estimated by assuming that the block copolymer perturbs the flow only slightly. The repulsion was then combined with the Stokes flow equations, and the trajectories of colliding droplets were analyzed by previously developed methods. It was demonstrated that the collision efficiency decreased strongly in the presence of block copolymer. The numerical results showed a steadily decreasing collision efficiency with increasing interaction force, vanishing completely at a finite value of the force. The interaction between the droplets was represented by a dimensionless force, proportional to the ratio of Marangoni stresses over hydrodynamic stresses. This interaction is proportional to block copolymer concentration

and inversely proportional to shear rate. Hence the contribution of the Marangoni stresses should be higher at lower shear rates. The results shown in Fig. 8 seem to confirm this conclusion.

4 CONCLUSIONS

In this paper, droplet deformation and coalescence are studied in blends in the presence of a compatibilizer. Droplets with pointed ends are observed at intermediate compatibilizer concentrations. They are believed to be due to the presence of gradients of compatibilizer concentration along the interface. These gradients cause Marangoni stresses, which stabilize the droplets. The observation that droplets with high concentrations of block copolymer do not deform significantly in shear flow is consistent with the presence

Fig. 8. Scaling factor F versus block copolymer concentration for various shear rates.



of gradients in compatibilizer concentration. Coalescence has been studied at various block copolymer concentrations and at various shear rates. Compatibilizers drastically change both the kinetic evolution of the droplet size and the final droplet size attained under steady shear conditions. Partially mobile and immobile interface coalescence theories do not describe the evolution of droplet sizes. An empirical modification of the partial mobile interface theory, based on an effective viscosity ratio, has been proposed. A good agreement was found between the calculated drop size evolution and the experimental data. Moreover, the changes of the effective viscosity with step-down ratio and block copolymer concentration seem to be in line with a recent coalescence theory for compatibilized blends by Milner and Xi.

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