Study of the Morphological Hysteresis in Immiscible Polymer Blends

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The effect of processing conditions (essentially the flow conditions) on the morphology of incompatible, immiscible polymer blends was investigated. In simple shear flow the steady-state morphology, that is, droplet size, of such blends is a single-valued function of the shear rate whenever a critical shear rate is exceeded. Below this critical value it becomes very difficult to reach a dynamic equilibrium between droplet breakup and coalescence, which gives rise to a hysteresis region for the size of the inclusions. Such regions were identified and studied for model-blend systems. The critical shear rate decreases with increasing concentration of the droplet phase. A large ratio of droplet over matrix viscosity seems to have the opposite effect. The hysteresis region is bounded by the critical curves for droplet breakup and coalescence. The accessibility of this region can therefore be used to evaluate models for the said phenomena in nondilute systems. Droplet breakup is nearly independent of droplet concentration, while elasticity of the dispersed phase seems to facilitate breakup. As expected, coalescence is enhanced by higher concentrations. Droplet elasticity induces a certain degree of "rigidity" to the interface, and therefore the mobile interface model for coalescence is not suitable for such systems.

Introduction

Polymer blending has gained considerable interest, since it constitutes an economical alternative to synthesizing new monomers in the development of new materials with improved properties. The mechanical characteristics of an immiscible polymer blend reflect in a rather complex way both the features of the constituents and the interfacial properties. The morphology that develops during processing is therefore of crucial importance for the quality of the final product. Predicting and optimizing the effect of the flow conditions on the resulting microstructure is still one of the major challenges of the polymer processing industry.

Whenever a dispersed phase can be clearly distinguished from a matrix phase, the steady-state morphology is generally considered to be the result of a dynamic equilibrium between the breakup of droplets and their coalescence (Takahashi et al., 1994). It has been suggested that this equilibrium is only reached when the shear rate is above a critical value (Elmendorp, 1986). This value is obtained as the crossover of the limiting curves for breakup and coalescence. Recently, Grizzuti and Bifulco (1997), by means of optical microscopy, and Minale et al. (1997), using rheological experiments, have confirmed that indeed a steady-state morphology can only be reached within a reasonable amount of time when a critical shear rate is exceeded.

An empirical expression for the limiting breakup curve in shear flow is available in the literature. This gives the critical droplet radius, as a function of the shear rate, $\dot{\gamma}$, and of the physical parameters of the blend, below which breakup cannot occur. From the dimensionless analysis it can be concluded that the result should be expressed in terms of a capillary number, Ca, expressing the ratio between the shear and the interfacial forces. When the former dominates, the droplets will break. The critical ratio depends on the shape and the internal flow of the droplets and, consequently, on the viscosity ratio p (i.e., the ratio of droplet viscosity over matrix viscosity). Based on experimental data obtained by Grace (1982), de Bruijn (1989) proposed the following fitting relation:

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$$\log\left(\frac{\eta_m \dot{\gamma} R}{\alpha}\right) = -0.506 - 0.0994\log(p) + 0.124\log^2(p) - \frac{0.115}{\log(p) - \log(p_{cr})}, \quad (1)$$

where $\log(x)$ is the decimal logarithm of x, α is the interfacial tension, η_m is the matrix viscosity, and $p_{cr} = 4.08$ is the viscosity ratio above which breakup is not possible anymore in shear flow. From Eq. 1 the critical capillary number, $Ca_{cr} = \eta_m \dot{\gamma} R/\alpha$, diverges either when the viscosity ratio tends to 0 or, as already said, when it tends to p_{cr}. Hence shear flow is unable to break either inviscid or very viscous drops. The breakup process is most effective in blends with viscosity ratio between 0.1 and 1, when Eq. 1 gives the minimum values of Ca_{cr}. Grace performed his experiments with isolated inelastic droplets immersed in an inelastic matrix.

In the present article only relatively small shear rates have been used. Therefore coalescence models based on the presence of flat films between colliding droplets have been considered to be suitable to describe the experimental results. Within this class, three models can be distinguished. They differ in the way in which the mobility of the interface is treated. This refers to the boundary conditions for the squeezing flow of the matrix fluid in the contact zone between colliding droplets. The models are the fully mobile interface (FMI; Chesters, 1975), the partially mobile interface (PMI; Chesters, 1988), and the immobile interface one (IMI; MacKay and Mason, 1963). Starting with these models and using some additional restrictive assumptions (Janssen, 1993; see also Minale et al., 1997, for a more extensive discussion), the critical mean radius of two colliding droplets above which coalescence cannot occur is estimated to be

$$\text{FMI:} \quad R\ln\left(\frac{R}{h_{cr}}\right) = \frac{2}{3}\frac{\alpha}{\eta_m \dot{\gamma}} \quad (2)$$

$$\text{PMI:} \quad R = \left(\frac{4}{\sqrt{3}}\frac{h_{cr}}{p}\right)^{2/5}\left(\frac{\alpha}{\eta_m \dot{\gamma}}\right)^{3/5} \quad (3)$$

$$\text{IMI:} \quad R = \left(\frac{32}{9}\right)^{1/4}\left(\frac{h_{cr}\alpha}{\eta_m \dot{\gamma}}\right)^{1/2}, \quad (4)$$

where $\ln(x)$ is the natural logarithm of x and h_{cr} is the critical thickness of the matrix fluid layer between approaching droplets below which spontaneous coalescence occurs. For nondilute blends, as those under investigation here, h_{cr} loses its physical meaning and becomes essentially a curve-fitting parameter essentially lumping all the concentration dependencies, as already discussed and motivated in Minale et al. (1997). All three models have been derived for isolated pairs of Newtonian droplets immersed in Newtonian matrices.

The breakup limiting curve, as well as the coalescence ones, have been derived for Newtonian droplets immersed in a Newtonian matrix; nevertheless both predictions will be used to describe our experimental results since, as discussed in the Experimental section, the constituents of the model blend we investigated are essentially Newtonian, or very slightly elastic, at the shear rates of interest.

At a given shear rate only droplets with a radius larger than a critical value (Eq. 1) can break. On the other hand, coalescence can only occur, at least on a reasonable time scale, when the average radius of the droplets is smaller than another critical value (Eqs. 2–4). The limiting curve for coalescence and that for breakup will eventually cross. Since the coalescence limiting curve is a weaker function of the shear rate than the corresponding curve for breakup, beyond the crossover point a dynamic equilibrium can be achieved between the two phenomena, resulting in a well-defined average droplet size for each shear rate. For shear rates below the critical value, a dynamic equilibrium cannot be obtained, at least not within a reasonable amount of time. In this region, the quasi-steady-state morphology depends on the shear history, and as a result hysteresis phenomena can be encountered. Whenever the radius of the droplets is larger than the coalescence limit but smaller than the breakup limit, neither breakup nor coalescence will occur. Actually the hysteresis region is bounded by the limiting curves for breakup and coalescence. If the limits of the hysteresis region could be determined, they could be used to evaluate and possibly extend the available theories for breakdown and coalescence.

Minale et al. (1997) demonstrated the existence of the hysteresis region and studied it on a particular model blend system at a fixed concentration. Their results seemed to indicate that the accuracy of the different coalescence models mentioned earlier changed with the viscosity ratio. Here the same model system has been used to study the effect of parameters such as the concentration of the dispersed phase, the viscosity ratio, and to a limited extent even elasticity, on the morphological hysteresis and on the mechanisms for flow-induced structural changes.

Experimental Studies

The components of the model blends studied here are polyisobutylene (PIB; Parapol 1300 from Exxon) and polydimethylsiloxane (PDMS; Rhodorsil 47V100000 from Rhône-Poulenc); their relevant physical characteristics are summarized in Table 1. These polymers are almost inelastic, so all the elastic properties of the blend can be attributed to the interfacial contributions. However, more elastic PDMS/PIB systems can be made to investigate the effect of this parameter as well. The Newtonian viscosities of the pure components nearly match at room temperature (23°C), but since their activation energies differ considerably, the viscosity ratio of the blend can easily be varied by changing the temperature. Both polymers are liquid at room temperature, thus avoiding degradation problems usually encountered with melts or problems with viscoelastic interfacial behavior induced by the presence of solvents when polymer solutions would be used.

Table 1. Characteristics of the Purepolymers (T = 23°C)

Materials	η_0 (Pa·s)	Ψ_1 (Pa·s^2)	ρ (Kg·m^{-3})	E_a (J·mol^{-1})
PDMS (47V100000)	100	1.66	973*	1.393×10^4
PIB (1300)	92.7	0.09	894**	7.2×10^4

*25°C.
**20°C.

For the interfacial tension the value that has been used is that reported by Sigillo et al. (1997) for a very similar blend. Their blend was a mixture of PIB (Parapol 1300 from Exxon) and PDMS (47V200000 from Rhône-Poulenc) that differs from the one investigated here by the use of a PDMS with a slightly higher molecular weight. The surface tension of a polymer is nearly independent of the molecular weight when it exceeds a critical value (Kobayashi and Owen, 1995). Assuming that the interfacial tension behaves in the same way, it seems acceptable to use the value of interfacial tension of 2.8×10^{-3} N/m as measured by Sigillo et al. (1997), since the molecular weight of the PDMS exceeds the critical value.

Different concentrations and viscosity ratios have been investigated. The composition is identified by means of the volume fraction of PIB. By changing the temperature, the viscosity ratio of the 90% PIB sample has been varied between 0.6 and 1.6. All the samples have been prepared according to the following procedure that has been proven to be adequate by Takahashi et al. (1994) and by Vinckier et al. (1996). A suitable amount of the two pure components is mixed by hand until the blend reaches a homogeneous milky appearance; the sample is then put in a vacuum oven overnight to remove the entrapped air bubbles. Before each experiment, the samples are preconditioned by shearing until a steady-state morphology is reached. The amount of strain units required to get to the stationary conditions had been estimated previously by means of stress transient experiments, since these have been proven to be very sensitive to the initial morphology (Takahashi et al., 1994; Vinckier et al., 1996). After shearing for 2,000–3,000 strain units at a given shear rate, the transient stress profiles do not depend anymore on the earlier preshear conditions, consequently this has been the minimal amount of straining used in all subsequent experiments.

Morphology Probing

Oscillatory experiments can be used to determine the droplet size in incompatible polymer blends. The frequency evolution of the dynamic moduli G' and G'' can be described by means of suitable models derived from emulsion theory. In this article, as elsewhere (Vinckier et al., 1996; Minale et al., 1997), use has been made of the Palierne model (1990), since it explicitly takes into account the viscoelasticity of the pure components and also, to a certain extent, the hydrodynamic interactions between the droplets. In the model the entire distribution function for the droplet radii can in principle be taken into account. The distribution can, however, be replaced by the volumetric mean radius of the droplets provided the polydispersity index of the blend does not exceed a value of about 2 (Graebling et al., 1993a,b). This approximation can be considered valid for the blends at hand (Grizzuti and Bifulco, 1997). If the interfacial tensor is also supposed to be isotropic, that is, independent of the local shear, the model predicts

$$G' = Re\left(G_m^* \frac{D + 3\Phi E}{D - 2\Phi E} \right), \tag{5}$$

with

$$D = (2G_d^* + 3G_m^*)(19G_d^* + 16G_m^*) + \frac{40\alpha}{\bar{R}_V}(G_d^* + G_m^*) \tag{6}$$

$$E = (G_d^* - G_m^*)(19G_d^* + 16G_m^*) + \frac{4\alpha}{\bar{R}_V}(5G_d^* + 2G_m^*), \tag{7}$$

where the subscripts m and d refer to the matrix and the dispersed phase, respectively; $Re(x)$ is the real part of x; G^* the complex modulus; α the interfacial tension; Φ the volumetric concentration of the dispersed phase; and $\bar{R}_V$ is the volumetric mean radius one wants to calculate here.

In Eqs. 5–7 the unknown parameter is the ratio of the interfacial tension over the volumetric mean radius of the droplets of the blend. As a consequence the interfacial tension of the blend can be estimated from dynamic experiments when the droplet mean radius is known from an independent experiment (Graebling et al., 1993a, 1994; Gramespacher and Meissner, 1992). Conversely, the volumetric mean radius can be estimated if the interfacial tension is already known (Vinckier et al., 1996; Minale et al., 1997). In principle different procedures can be used to extract $\bar{R}_V$ from the data. For the blends under investigation, a direct fitting of the Palierne model has been found to be reliable (Vinckier et al., 1996). Indeed, for a blend that differs from the one under investigation only by the grade of PDMS used (slightly higher than the one at hand), it resulted in a remarkable agreement with microscopy measurements (Vinckier et al., 1996). The same procedure is applied here.

A stress-controlled rheometer (Rheometrics DSR) was used to perform all the dynamic experiments. It was equipped with a cone and plate geometry (diameter: 0.025 m and cone angle 0.1 rad). This rather large angle minimizes the effect of misalignment of the tool, but narrows the range of accessible shear rates. The test temperature ranges from 17 ± 0.1°C to 28 ± 0.1°C and has been controlled by means of a Peltier element. Preliminary tests showed the behavior of the blends to be linear up to a strain amplitude of 10% at all frequencies used. In this amplitude range the oscillatory motion does not induce any real change in the morphology, but only perturbs it. It has also been checked that no bias from structural changes is present in the dynamic experiments after cessation of flow. Indeed, the droplets recover their spherical shape after stopping the flow on a very short time scale, actually before the first data point is recorded. On the other hand, coalescence after cessation of flow is here a process that takes longer than the duration of the entire experiment. It follows that dynamic experiments after cessation of flow probe the recoiled morphology of the blend as induced by the applied flow.

Concentration Effects

In Figure 1 the volumetric mean radii of three different blends with PIB dispersed in PDMS are shown as a function of shear rate. The experiments have been performed at 23°C, the viscosity ratio p therefore being equal to 0.93. In order to control the inital conditions, the experiments were performed in a specific sequence. First the dynamic moduli were recorded after shearing at systematically increasing shear rates. In this sequence the average diameter of the droplets before applying a given shear rate will never be smaller than the final steady-state value at that particular shear rate, for example, points 1 to 5 for 5% PIB. Subsequently the same experiments have been repeated in order of decreasing shear

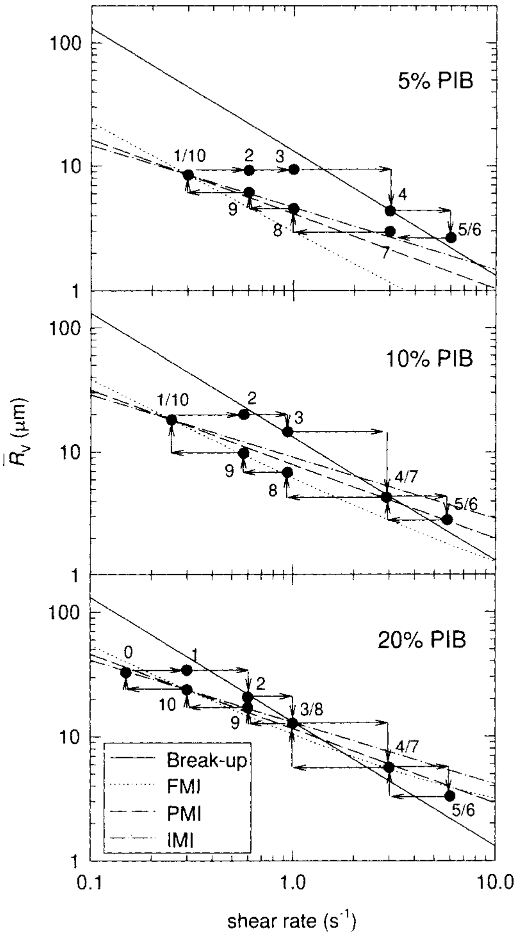

Figure 1. Hysteresis region for blends of PIB in PDMS (23°C, $p = 0.93$).

The lines represent the theoretical limiting curves for breakup and coalescence. The arrows indicate the order in which the experiments have been performed.

rates so as to have at each shear rate an initial morphology not coarser than the steady-state one, for example, points 6 to 10 for the 5% PIB blend.

The theoretical predictions of the limiting curve for breakup as well as for coalescence according to the three models are displayed in Figure 1. Determining the latter requires that a value for the parameter h_{cr} be specified for each coalescence model. These values have been obtained by imposing the limiting curves for coalescence to pass through the lowest shear-rate point in the hysteresis zone, that is, point 1/10 for the 5% and 10% PIB blends. In the case of the 20% PIB blend an additional experiment has been performed at still lower shear rates (point 0) to ensure that the points at the next shear rate (points 1 and 10) belonged indeed to the hysteresis region. To be consistent with the other experiments the fitting has again been done by imposing the coalescence curves to pass through point 10 rather than through point 0. In the hysteresis region the values for $\bar{R}_V$ at increasing shear rates should be bounded by the limiting curve for droplet breakup, whereas the values should be determined by the coalescence process at decreasing shear rates. When one starts from a point within the hysteresis region, no droplet refinement will occur upon increasing the shear rate until the limiting curve for breakup is crossed. At higher shear rates a real equilibrium steady-state morphology can be obtained at each shear rate, for example, points 4/7, 5/6 for 10% PIB in Figure 1.

From a comparison between the results for the three different concentrations in Figure 1 it can be concluded that the hysteresis region gets smaller when the concentration of the dispersed phase increases. This result has been confirmed by experiments performed on the 30% PIB blend, in which case no multiple steady states could be found at any shear rate down to the smallest value used, that is, 0.15 s^{-1}.

The same kind of experiments have been performed on blends with 80, 90 and 95% PIB. The PDMS now being the dispersed phase, the viscosity ratio becomes 1.08 at 23°C. The results for the droplet size are displayed in Figure 2. The parameter h_{cr} has again been fitted by imposing the coalescence curves to pass through the lowest coalescence points. For all the blends a hysteresis region can be identified, followed by a zone of dynamic equilibrium. The experiments are qualitatively well described by the theoretical predictions. Comparing the results of the three different blends, with PDMS as the dispersed phase, it is evident that the hysteresis

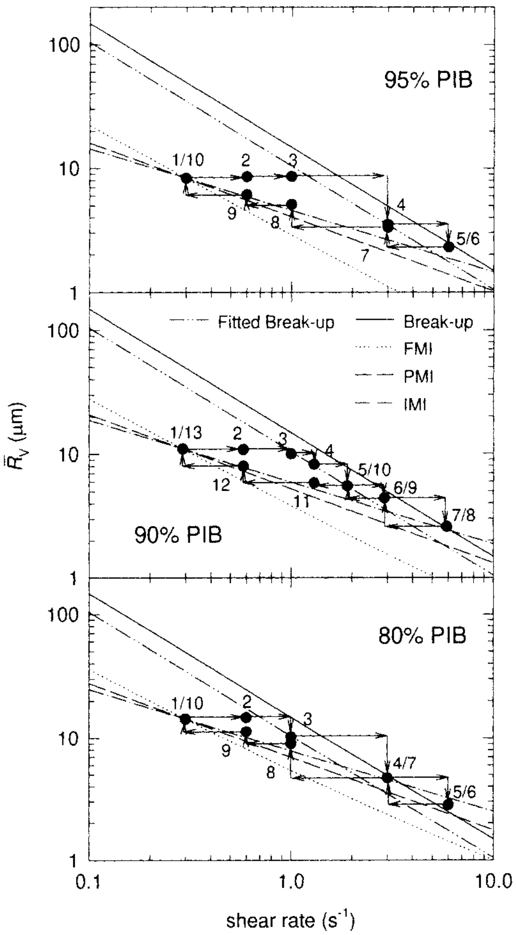

Figure 2. Hysteresis region for blends of PDMS in PIB (23°C, $p = 1.08$).

The dashed double dotted line is the breakup limiting curve as obtained by fitting the critical capillary number through the breakup points; other lines as in Figure 1.

region grows smaller with increasing concentration of the dispersed phase. To confirm this a 70% PIB blend was studied as well; as for the 30% PIB one, no hysteresis region could be found anymore.

The theoretical limiting curve for breakup does not describe accurately the measured breakup points, that is, point 4 for 90% and 95% PIB, and point 3 for 80% PIB. Considering, for instance, the 90% PIB blend, the theoretical limiting curve for breakup predicts a significantly coarser morphology than that measured. Since, for example, point 4 of such a blend is obtained by refining the morphology in the region where coalescence is not supposed to occur, it should lie on the breakup limiting curve. A critical capillary number can therefore be estimated from the position of this line, giving a value of 0.345 ± 0.005 for all three blends (95% PIB, 90% PIB, and 80% PIB). The fact that a single value of Ca_{cr} can describe the data for different concentrations (see Figure 2) seems to indicate that this is a physically meaningful parameter for the system under consideration. The discrepancy between the theoretical and the experimental values cannot be attributed to the use of the matrix shear stress instead of the whole-blend shear stress in the evaluation of Ca. Indeed if Ca is defined as $\eta_b \dot{\gamma} R/\alpha$, the experimental Ca_{cr} for the 90% would be 0.39, which is still in poor agreement with the theoretical prediction (η_b was obtained experimentally at $\dot{\gamma} = 1$ s^{-1}). The results for PIB as dispersed phase, Figure 1, were, however, described quite well by Eq. 1. This equation was derived for a Newtonian droplet immersed in a Newtonian matrix. As mentioned before, the PIB is essentially Newtonian at the shear rates under investigation, while the PDMS displays some degree of viscoelasticity, even at relatively low shear rates (Minale et al., 1997).

The present results could suggest that the breakup process is much more sensitive to the nature of the droplet phase than to that of the matrix. More specifically it could be concluded that breakup is enhanced by the elasticity of the droplet. A similar trend has been observed by Milliken and Leal (1991), although only for viscosity ratios smaller than unity. De Bruijn (1989) observed the opposite trend, however, but the subject is still unresolved for complex flows, as in mixers and extruders (Sundararaj and Macosko, 1995) as well as for more controlled flows (Utracki and Shi, 1992). Our findings are nevertheless in agreement with the theoretical study of the breakup of a viscoelastic thread immersed in a viscoelastic matrix undergoing a cylindrical Poiseuille flow (Chin and Han, 1980). This stability analysis for a Jeffreys fluid indicates that an increase of the ratio of the elasticity of the droplet phase over that of the matrix phase enhances the breakup. This is also in agreement with the results obtained studying the stability of a liquid film flowing down an inclined plane. The instability of this film is driven by surface forces, just as the droplet breakup is driven by interfacial forces. Also in this case the instability is enhanced by the elasticity of the fluid for both an Oldroyd-B fluid (Lai, 1967; Gupta and Rai, 1967) and a Coleman and Noll second-order fluid (Gupta, 1967; Gupta and Rai, 1968; Minale and Astarita, 1996).

From Figures 1 and 2 it is clear that, while all coalescence models describe the data with PIB as dispersed phase well, the FMI theory is not suitable for the systems with PDMS as dispersed phase. PDMS is significantly more elastic than PIB, and consequently this result could mean that the elasticity of the droplet contributes to the rigidity of the interface.

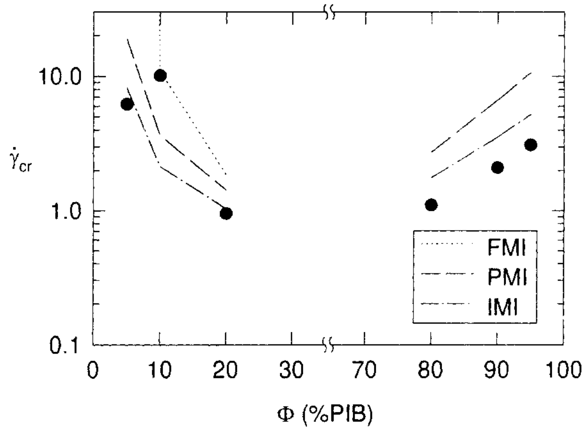

Figure 3. Comparison between experimental (symbols) and theoretical values for the critical shear rate.

To validate the observation of a hysteresis region that shrinks with increasing concentration of the dispersed phase, the observed values for the critical shear rate, $\dot{\gamma}_{cr}$, are plotted in Figure 3 as a function of concentration. They were calculated as the intersection between the breakup limit and the power law obtained as the best fit of the coalescence data. The experimental values of $\dot{\gamma}_{cr}$ are compared with the values corresponding to the intersection between the breakup curve and the various limiting coalescence curves. For the blends with PDMS as dispersed phase, the limiting breakup curve was based on the critical capillary number deduced from the experimental data, as discussed earlier. For these blends the coalescence model based on a fully mobile interface was not considered since, as already mentioned, this theory is not accurate in this case.

The coalescence models seem to have the tendency to overpredict the values for the critical shear rate, even if at least the predictions of the IMI theory lie within the uncertainties of the experiments. This can be explained by considering that the coalescence theories are based on the hypothesis that the interface of the colliding droplets deforms to become flat. This is definitely true at low shear rates, but it can become rather questionable at higher shear rates as those where the transition takes place.

As mentioned earlier, h_{cr} loses its physical meaning for nondilute blends and becomes essentially an adjustable parameter. The values obtained by fitting the experimental data points are always larger than the theoretical predictions. In Figure 4 the values of h_{cr}, as evaluated from the data reported in Figures 1 and 2, are shown for the three coalescence models. It can be seen that the values of h_{cr} become larger, and therefore coalescence becomes more effective, with increasing concentration of the dispersed phase. Furthermore, the range of theoretical values of h_{cr}, that is, 10^{-2}–10^{-3} μm (Chesters, 1991), is approached as the concentration of the dispersed phase tends to zero. It should be recalled that the coalescence phenomenon is ruled by two parameters: the probability of collision of two droplets and the duration of the collision. The higher the collision probability and the longer the collision time, the more effective the

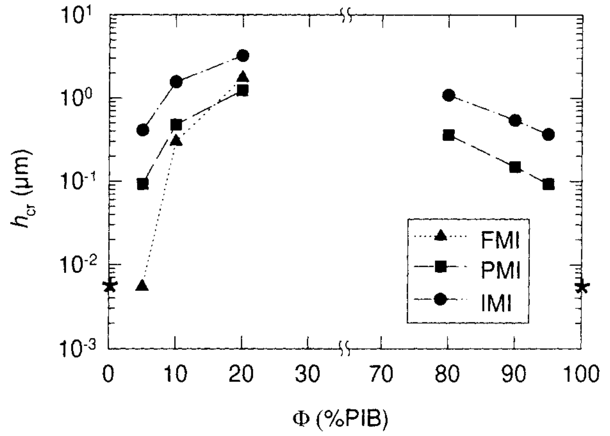

Figure 4. Effect of concentration on h_{cr} calculated according to the different models.

The $*$ indicates a value in the range of the theoretical predictions (10^{-2}–10^{-3} μm).

collision will be. In the coalescence models, Eqs. 2–4, the collision probability has been set to 1, therefore an increase of h_{cr} translates into an increase of the duration of the collision. This is in agreement with the visual picture that, in more concentrated blends, it becomes more difficult for a droplet to escape from touching another droplet.

In Figure 5 the steady-state, or possibly pseudo-steady-state values, for the radii as obtained after shearing at 0.3 s^{-1} and 6 s^{-1} are reported as a function of concentration. The morphologies corresponding to $\dot{\gamma} = 0.3$ s^{-1} have been chosen to represent those determined solely by coalescence, whereas the ones at $\dot{\gamma} = 6$ s^{-1} reflect the dynamic equilibrium between coalescence and breakup. The radii resulting only from coalescence increase significantly with the concentration of the dispersed phase, whereas the morphologies determined by a dynamic equilibrium change only slightly. The latter result can be explained by a combination of coalescence that is enhanced by droplet concentration and breakup that is independent of it. The steady-state morphologies are constrained to belong not only to the coalescence region but also to the breakup one. Therefore they cannot vary as much with an increase in the concentration of the dispersed phase as at lower shear rates, although a slight increase can still be detected, in agreement with published results on similar systems (Vinckier et al., 1996).

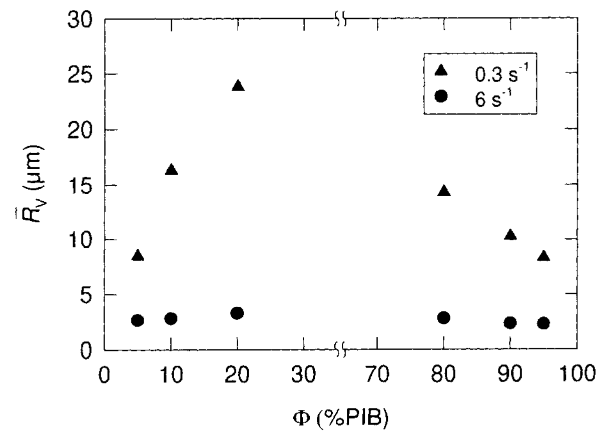

Figure 5. Volumetric mean radii at $\dot{\gamma} = 0.3$ s^{-1} (coalescence points) and $\dot{\gamma} = 6$ s^{-1} (equilibrium points) for the different mixtures of PIB and PDMS ($T = 23°C$).

Effect of the Viscosity Ratio

In order to vary the viscosity ratio of the blends it suffices to alter the temperature, because the activation energy for the viscosity of PIB is larger than that of PDMS (see Table 1). Consequently the hysteresis phenomenon has been studied for the 90% PIB blend at lower and higher temperatures, that is, at 17°C and 28°C, achieving viscosity ratios of 0.66 and 1.6, respectively. The results are displayed in Figure 6.

As in earlier experiments, Eq. 1 systematically overpredicts the droplet dimensions caused by breakup. If a critical capillary number is estimated from the data, one finds $Ca_{cr} = 0.322$ for $p = 0.66$ and $Ca_{cr} = 0.345$ for $p = 1.6$, which have to be compared to the values predicted from Eq. 1, that is, $Ca_{cr} = 0.46$ and $Ca_{cr} = 0.578$, respectively. The fact that the relative error is not directly related to the temperature is not in disagreement with the argument that the elasticity of the droplet phase enhances the breakup. Indeed for this blend the dispersed phase is PDMS, the activation energy of which is rather small; therefore its elasticity is almost independent of the temperature.

By changing the temperature the effect of the viscosity ratio on the accuracy of the different coalescence models can be evaluated. Over the whole range of viscosity ratios the fully mobile interface model provides a rather unsatisfactory description of the various experimental data. As already mentioned, this seems to be associated with an increase in the rigidity of the interface caused by the elasticity of the

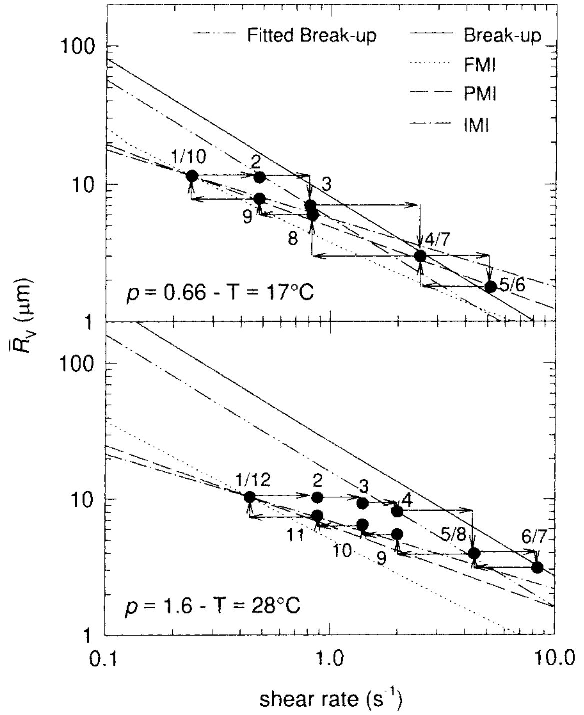

Figure 6. Change of hysteresis region with temperature for a 90% PIB blend.

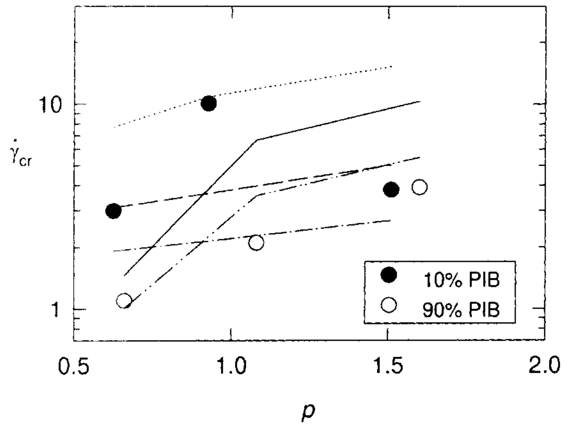

Figure 7. Experimental (symbols) and theoretical (lines) values of the critical shear rate for the 90% PIB and the 10% PIB blends (from data of Minale et al., 1997); effect of viscosity ratio.

Theoretical predictions for the 90% PIB blend: (——) PMI; (—·-·—) IMI; and for 10% PIB one: (····) FMI; (– – –) PMI; (—·-—·-) IMI.

droplet material. For a 10% PIB blend a decrease in temperature was found to result in improved predictions of the immobile interface model and worse predictions of the fully mobile interface model (Minale et al., 1997). The activation energy for the viscosity of PIB is rather large, therefore a decrease of temperature gives rise to a significant increase of its elasticity. For the 90% PIB blend it is found here that the accuracy of the PMI and IMI coalescence models seems to be independent of the viscosity ratio, that is, of the temperature. Both results can be reconciled by considering that the elasticity of the PDMS, although higher than that of the PIB, is almost independent of temperature.

The effect of the viscosity ratio on coalescence can be expressed through the value of h_{cr}. The fact that the temperature, and consequently viscosity ratio, hardly changes this value indicates that the effectiveness of the coalescence is not affected by the viscosity ratio. In agreement with the results for the 10% PIB blend (Minale et al., 1997), the hysteresis region of the 90% PIB blend also expands with increasing viscosity ratio. This can be seen in Figure 7 where the experimental and theoretical values for $\dot{\gamma}_{cr}$ are plotted as a function of the viscosity ratio for both the 10% (calculated from Minale et al., 1997), and the 90% blend.

Conclusions

In this article the effect of concentration and viscosity ratio on the morphological hysteresis region of a model blend have been studied. The boundaries of the hysteresis region are used to investigate separately droplet coalescence and breakup. The hysteresis region is found to shift to smaller shear rates as the concentration of the dispersed phase increases. At the same time the volumetric mean radius of the droplet phase grows larger with this concentration. The effect is very pronounced when the pseudo-steady-state morphology is controlled solely by coalescence. From the coalescence data a critical thickness of the matrix film between colliding droplets has been determined. For concentrated blends this becomes an adjustable parameter that increases with the concentration of the dispersed phase. Hence the coalescence phenomenon is enhanced by the droplet concentration. Since the collision probability has been set to one in the coalescence models, this means that the collision time increases with the concentration of the droplet phase. The theoretical value of the critical thickness of the matrix film between colliding droplets is recovered when the concentration becomes very low.

Breakup and coalescence predictions, deduced for isolated droplets, have been used here to discuss experimental results on rather concentrated blends. Even if this is debatable from a theoretical point of view, it provides a means of expressing the effect of concentration on these phenomena; in fact, the comparison with the theories for infinitely diluted blends, the only available ones, turned out to be suitable. Similarly, the effectiveness of coalescence is quantified with a fitting parameter. Although it ignores the real physics behind the phenomenon, it turns out to be an effective and useful engineering procedure; once a more complete theory is available, the latter can be evaluated with the present results.

The viscosity ratio has been varied by altering the temperature of the PIB/PDMS blends, the activation energies of the two components being widely different. In this manner the viscosity ratio has been changed from 0.6 to 1.6. Within this range the hysteresis region grows when the viscosity ratio increases, while the critical film thickness remains almost constant. Irrespective of droplet concentration or temperature, a difference can be noticed between blends with PDMS as the dispersed phase and those with PIB droplets. The former polymer is more elastic, which seems to cause a more rigid interface. Indeed, the droplet phase of PDMS results in poor accuracy for the model based on a fully mobile interface, whereas the accuracy of the model with immobile interface improves.

The theoretical predictions for the breakup curve underestimate the measured droplet size at the breakup limit when PDMS constitutes the dispersed phase. Again elasticity of the droplets might be the cause of this discrepancy; although a more elastic matrix material does not lead to deviations from the theory.

The study of the hysteresis region on a model blend has its practical impact on "real" blends, not only because such phenomena can also occur in engineering blends, but because it gives one an opportunity to properly and systematically investigate the role of viscoelasticity in polymer blends.

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Notation

D = parameter defined in Eq. 6, $m^{-2} \cdot kg^2 \cdot s^{-4}$
E = parameter defined in Eq. 7, $m^{-2} \cdot kg^2 \cdot s^{-4}$
G' = elastic modulus, $m^{-1} \cdot kg \cdot s^{-2}$
G'' = loss modulus, $m^{-1} \cdot kg \cdot s^{-2}$
R = radius, m
Φ = volumetric fraction of PIB

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