Modeling of Coalescence in Polymer Blends

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Coalescence in polymer blends was modeled by combining population dynamics with three coalescence theories: Smoluchowski, trajectory, and film drainage. Modeling results are compared with our previous coalescence experiments on polystyrene/high density polyethylene blends. Comparison of the Smoluchowski theory (no hydrodynamic interactions) with our experiments reveals that ideal collisions are the main mechanism of coalescence. Coalescence efficiency, however, decreases with increasing shear rate and particle-size difference. Most interestingly, increasing the ratio of particle to matrix viscosity causes coalescence efficiency first to increase and then to decrease. The effects of particle-size difference on coalescence efficiency can be modeled by considering changes in trajectory due to hydrodynamic interactions between particles. By considering particle deformation, film drainage theory predicts that coalescence efficiency decreases with increasing shear rate. Comparison with the experiments was only qualitatively correct. However, the prediction that coalescence efficiency decreases with increasing the viscosity ratio by both the trajectory theory and film drainage theory is not consistent with the experimental results. The reasons for the disagreements are discussed in terms of large deformation of colliding particles.

Introduction

Physical properties of immiscible polymer blends strongly depend upon their multiphase morphology which is controlled to a great degree by particle-particle coalescence during flow. Theoretical studies of the flow driven coalescence can be tracked back to Smoluchowski (1917). Smoluchowski treated coalescence as an ideal collision process with particle interaction being neglected. Lin et al. (1970) and Batchelor and Green (1972) calculated the hydrodynamic interactions between particles and their effect on particle trajectories under flow. By considering these hydrodynamic interactions, Zeichner and Schowalter (1977) and Wang et al. (1994) added a coalescence efficiency to Smoluchowski theory. Chesters made a different correction to Smoluchowski's theory by considering particle deformation and squeezing flow of matrix, known as film drainage. There have been good reviews of this theory by Chesters (1991) and Janssen and Meijer (1995). Recently, Rother (1999) and Rother and Davis (2001) have combined the trajectory theory with small drop deformation. Further correction to the coalescence efficiency was obtained.

Experimental coalescence studies are beginning to appear. Vinckier et al. (1998) reported a flow driven coalescence using a polyisobutadiene (PB)/polydimethylsiloxane (PDMS) system. Kim et al. (1998) studied coalescence in polystyrene-acrylonitrile (SAN)/polycyclohexyl methacrylate (PCHMA) blends compatibilized with polystyrene-polymethylmethacrylate (PS-PMMA). Lyu et al. (1999, 2000) reported studies of a polystyrene (PS)/high density polyethylene (HDPE) system. Rusu and Peuvrel-Disdier (1999) and Borschig et al. (2000) have also reported their investigations of particle coalescence. All these researchers used a similar method: coalescence was monitored after a step down in shear rate. These blend samples were pre-sheared at higher rates to form smaller and relative uniform particle morphologies. This ensured that the flow driven coalescence was separated from breakup.

The polymer materials in these studies were quite diverse in rheology, glass transition temperature, and interfacial tension. However, all of these investigations reached two common conclusions: (1) coalescence rate increased with increasing particle concentration and (2) coalescence efficiency de-

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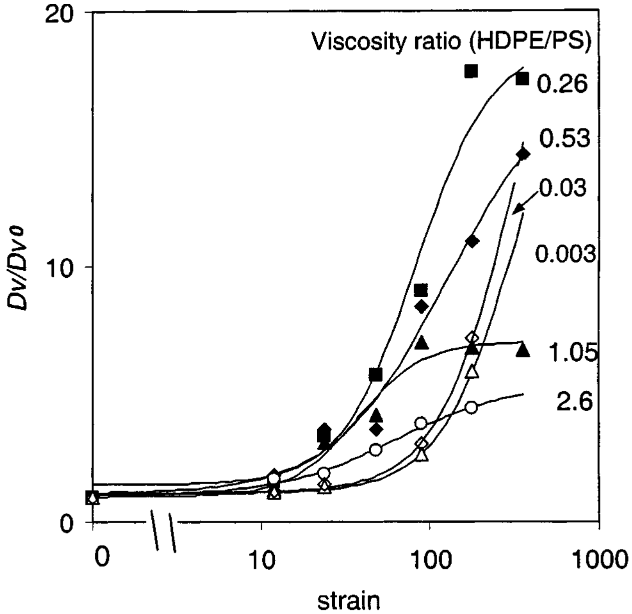

Figure 1. Reduced volume average particle diameters vs. strain for coalescence at 0.1 s^{-1} after breakup to steady state at 10 s^{-1} in PS/HDPE (87.3/12.7 vol) blends with viscosity ratio of 0.003, 0.03, 0.26, 0.53, 1.05, and 2.6 at 200°C.

The viscosity ratio was changed by using different HDPEs while keeping the viscosity of the matrix PS at 610 Pa·s (over the frequency range 0.1 to 10 s^{-1}) (Lyu, 2000).

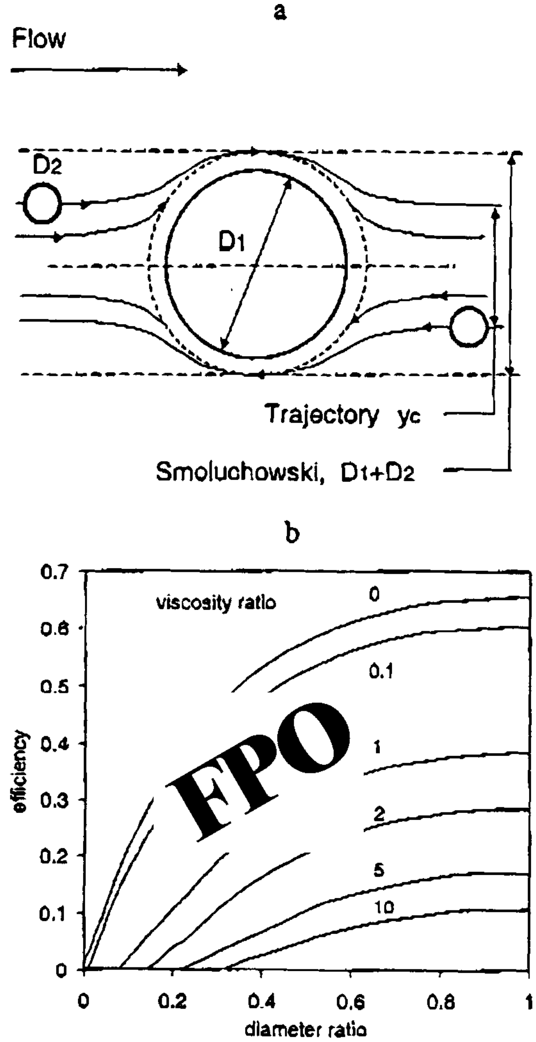

Figure 2. (a) Trajectories and capture diameters of particles moving towards each other; (b) calculated coalescence efficiency, $\sim (y_c/(D_1+D_2)/2)^2$, vs. particle-size ratio and viscosity ratio under simple shear (re-plotted from Wang et al., 1994).

For (a) $(D_1+D_2)/2$ is the capture diameter for the simple ballistic model of Smoluchowski. This decreases to y_c when hydrodynamic interactions are considered.

creased with increasing shear rates. This can be qualitatively explained in the first case by increased number of collision (Smoluchowski, 1917) and in the second case in terms of particle deformation that causes greater resistant force to coalescence (Chesters, 1991). In addition to these two common conclusions, Lyu et al. (2000) found coalescence efficiency decreases when particle sizes differ. This result directly confirms the importance of hydrodynamic interactions between particles due to trajectories as proposed by Zeichner and Schowalter (1977) and Wang (1994). Second, Lyu (2000) found that coalescence rate does not monotonically decrease with increasing viscosity ratio (defined as particle phase viscosity divided by matrix phase viscosity) as predicted by all the current theories. Instead, with increasing viscosity ratio, the coalescence rate increased first and then decreased. There was a maximum in the coalescence rate within a viscosity ratio range between 0.1 to 1, as shown in Figure 1 where the coalescence was conducted at 0.1 s^{-1} for blends containing 12.7 vol. % HDPE.

In this article the coalescence models of the Smoluchowski (1917), Chesters (1991), and Wang et al. (1994) with populations dynamics, are combined and the results are compared to our previous experiments. This comparison will help to determine the major mechanisms that control flow driven coalescence in polymer blends.

Review of Coalescence Theories

In the simplest coalescence theory only collision is considered. All particle-particle interactions are neglected. Smoluchowski calculated the coalescence rate of this ballistic process in 1917. In simple shear flow coalescence rate is

$$J_{ij}^0 = n_i \cdot n_j \cdot R_{ij} = \frac{1}{6} n_i n_j \left(D_i + D_j \right)^3 \dot{\gamma} \tag{1}$$

where n_i is the number concentration of particles with diameter of D_i, R_{ij} is the coalescence rate coefficient between the particle D_i and particle D_j, and $\dot{\gamma}$ is the shear rate.

Smoluchowski's theory, in an analogy with ideal molecular collision theory, reflects the main mechanism of coalescence. However, it neglects all particle-particle interactions that exist in real coalescence processes. Zeichner and Schowalter (1977) improved Smoluchowski's theory by considering hydrodynamic interaction that is related to the trajectories of particles. For simplicity, we refer to this as trajectory theory here.

As shown in Figure 2a, in a simple shear field without hydrodynamic interaction (Smoluchowski case) particle trajectories are straight lines. In such a case a collision occurs for all the small particles that move towards the large one within the cylinder defined by $D_1 + D_2$. However, in reality, hydrodynamic interactions cause the trajectories of particles to deviate from straight lines. Only those particles in a reduced cylindrical region of diameter y_c will collide with the large one. Particles outside the region of y_c will follow the streamlines around the large particle and pass by without colliding with it (Zhang and Davis, 1991). The coalescence efficiency E_{ij}, defined as the ratio of the corrected coalescence rate to Smoluchowski rate, is proportional to $y_c^2 / (D_1 + D_2)^2$

$$E_{ij} = \frac{J_{ij}}{J_{ij}^0} \propto \frac{y_c^2}{(D_1 + D_2)^2} \tag{2}$$

Wang et al. (1994) calculated this coalescence efficiency in simple shear flow. The number values of E_{ij} are re-plotted in Figure 2b as a function of viscosity ratio and particle-size ratio (details regarding the calculation can be found in Wang et al. (1994). As Figure 2b illustrated, trajectory theory predicts that E_{ij} decreases with increasing viscosity ratio and decreasing particle-size ratio, approaching zero when the particle sizes are too different.

It should be pointed out that the trajectory theory assumes the particles are nondeformable. Yiantsios and Davis (1990, 1991) showed that particle interfaces will deform when a modified capillary number $(D\eta_m\dot{\gamma}/\Gamma)\cdot(D/h)$ is larger than the order of magnitude of 1 (where h is the separation between two particle surfaces at the nearest location, or the thickness of the matrix film between the particles). Here, D is the average particle size. Such deformation will result in a greater hydrodynamic interaction, causing the coalescence rate to decrease. Film drainage theory (Chesters, 1991; Janssen and Meijer, 1995) considers this particle deformation effect.

Film drainage is a squeezing flow of the matrix film between two approaching particles (Figure 3). It results in a resistance that slows the particles approach. The coalescence efficiency due to this resistance depends on interfacial mobility of the particles. Assuming that the particles approach the long line of the centers, the relationship between the force and approaching velocity of the particles was calculated using a lubrication approximation (Chesters, 1991). It was assumed that coalescence occurs when the gap between two particles reaches a critical value h_c at which the matrix film between particles automatically ruptures. It was theoretically shown that $h_c = (A\overline{D}/16\pi\Gamma)^{1/3}$ where A is Hamaker constant (Vrij, 1966; Vrij and Overbeek, 1968; Chesters, 1991). $\overline{D}$ is an average particle diameter defined as $\overline{D} = 2(1/D_i + 1/D_j)^{-1}$. The typical value of h_c for micron-sized polymer particles is about 5 nm (Janssen and Meijer, 1995). Coalescence efficiency was then calculated for three ranges of viscosity ratio (called "mobile," "partially mobile," and "rigid interfaces" in the original article). For example, in the case where the viscosity ratio is near unity the coalescence efficiency is (Janssen and Meijer, 1995)

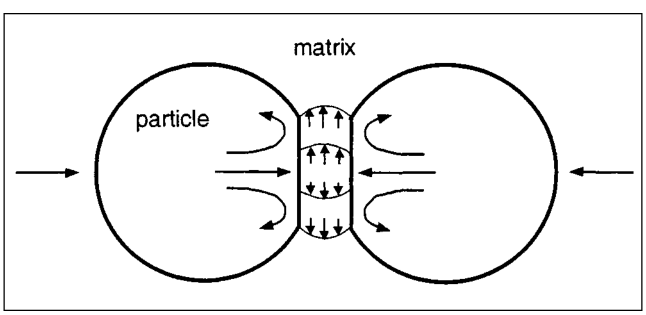

Figure 3. Two drops deformable colliding, illustrating film drainage theory.

$$E_{ij} = \exp\left(-0.077 \left(\frac{\eta_m \overline{D}\dot{\gamma}}{\Gamma} \right)^{1.5} \left(\frac{\overline{D}}{h_c} \right) \left(\frac{\eta_d}{\eta_m} \right) \right) \tag{3}$$

where η and Γ are viscosity, interfacial tension, and shear rate respectively. Subscripts m and d indicate the continuous (matrix) and dispersed phase, respectively. Since $\overline{D}$ is an average diameter, film drainage theory does not consider the particle-size distribution effect on the coalescence efficiency. Equation 3 predicts that the coalescence efficiency decreases with viscosity ratio, capillary number, and the ratio of the average particle size to the minimum film thickness. However, unlike the trajectory theory, film drainage theory does not consider hydrodynamic interaction due to the trajectories of the particles. In the following sections these theories will be incorporated into a population dynamics model and then tested against the experimental results with PS/HDPE blends reported previously (Lyu et al., 2000; Lyu, 2000).

Numerical Scheme

Particle size in most blends is not uniform, thus, particle-particle coalescence has to be described with a population dynamics equation that includes both gain and loss terms. In this article we start with a population dynamics Eq. 4 that includes both coalescence and breakup to make numerical studies more accurate. Following Milner and Xi (1996), we calculate the evolution of particle sizes as follows

$$\frac{dn_i}{dt} = \left(\frac{1}{2} \cdot \sum_{V_l + V_k = V_i} J_{lk} - \sum_{V_{j=0}}^{\infty} J_{ij} \right) + \left(2B_{2V_i} - B_{V_i} \right) \tag{4}$$

The terms in the first bracket of the righthand side of Eq. 4 describe the gain and loss due to coalescence and the terms in the second bracket describe particle breakup (B_{Vi}). The coalescence rate was calculated using the following equation

$$J_{lk} = k \cdot E_{lk} \cdot J_{lk}^0 \tag{5}$$

where J_{lk}^0 is the Smoluchowski's ideal coalescence rate (Eq. 1). k is an adjustable coalescence rate parameter for fitting experimental data. The coalescence efficiency E_{lk} was chosen in the following way: for Smoluchowski theory $E_{lk} = 1$; for trajectory theory, we used the coalescence efficiency calculated by Wang et al. (1994) (Figure 1b); and for the film drainage theory, coalescence efficiency was estimated based on Eq. 3.

Breakup rate B_{Vi} was calculated using the equation proposed by Milner and Xi (1996)

$$B_{Vi} = \begin{cases} b \cdot n_i & \text{if} \quad D > D_c \\ 0 & \text{otherwise} \end{cases} \tag{6}$$

When the size of a particle is larger than a critical value (D_c), it will break up into two equal particles at a rate constant b. Below D_c, the particle does not breakup. Putting coalescence and breakup together and reducing the population dynamic equation by the shear rate, we get

$$\frac{dn_i}{d\gamma} = k\left(\frac{1}{2} \cdot \sum_{V_l + V_k = V_i} \frac{1}{6} E_{lk} n_l n_k (D_l + D_k)^3 - \sum_{V_j = 0}^{\infty} \frac{1}{6} E_{ij} n_i n_j (D_i + D_j)^3\right) + (2n_{2V_i} - n_{V_i}) \cdot b_c \tag{7}$$

where $\gamma = t \cdot \dot{\gamma}$ is strain or dimensionless time, $b_c = b/\dot{\gamma}$ is the dimensionless breakup rate, and n_{2Vi} is the number concentration of particles with volume twice that of particle i. Equation 7 with Eq. 6 contain three adjustable parameters: the coalescence parameter k, the breakup rate parameter b_c, and the critical size D_c.

Equation 7 was integrated by use of a fourth-order Runge-Kutta numerical method. A population of particles with sizes ranging from 0.01 to 1,000 microns was discretized into 500 slices in log scale. An initial log-normal particle-size distribution was produced with the constraints that the number and volume average particle sizes were equal to the experimental values and the total volume fraction of particles was equal to the experimental volume fraction of minor phase (HDPE). The main error in this numerical study is from fluctuation of the volume fraction of the particle phase resulting from discretization of particle-size distribution. We used an adjustable particle categorization method to keep the volume fluctuation within 1%. Specifically, when the diameter of a product particle (D_x) is between two neighbor particle categories D_m and D_{m+1}, it will be set into slice $m+1$ if $D_x > (D_m + D_{m+1})/2 + \delta$, otherwise into slice m. The parameter δ was a small number with its value automatically adjusted during integrating based on how much the current total particle volume was bigger or smaller than the initial value so that the fluctuation of particle volume is kept within 1%. Adjusting δ is like a feedback control on the calculation. The typical value of (δ/D_m) is about 0.1 under the present conditions.

Numerical Results and Discussion

Smoluchowski's theory

We first calculated the Smoluchowski coalescence by setting the parameters $k = 1.0$ and $E_{ij} = 1.0$. D_c was chosen to best fit the maximum particle size in the late stage of coalescence. When b_c was varied over a range of 1–2.5, it did not significantly change the calculated particle-size evolution.

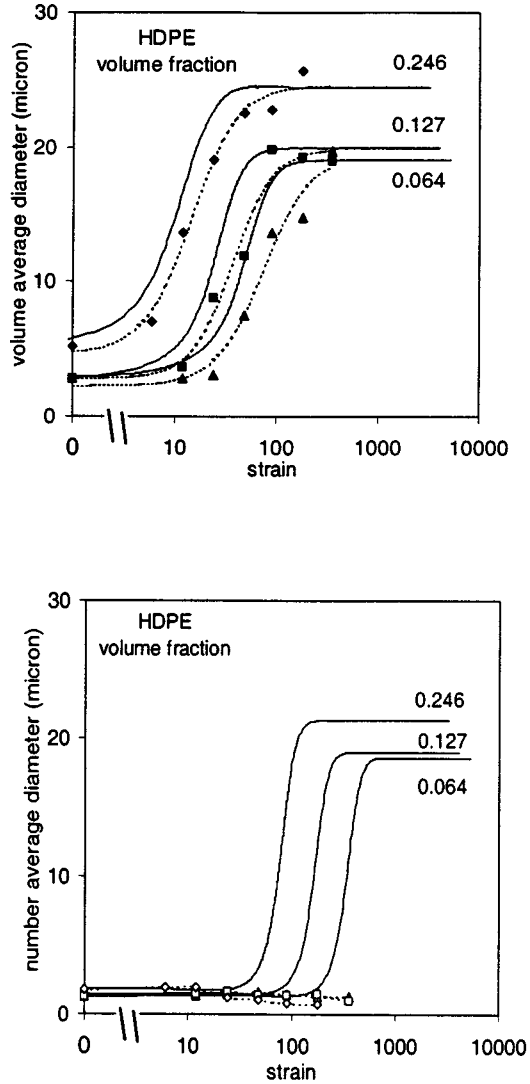

Figure 4. Smoluchowski coalescence (solid lines) and experimental results for D_V and D_n vs. strain in blends with various volume fractions of HDPE particle phase in PS matrix (viscosity ratio of HDPE to PS = 1.05) at shear rate of 0.1 s^{-1}.

The dashed lines are to guide the eye through the experimental data.

Thus, for simplicity, b_c was chosen to be 1.25 in all subsequent calculations.

Coalescence at 0.1 s^{-1} in blends containing 6.4, 12.7, 24.6% HDPE is shown in Figure 4. Viscosity ratio (viscosity of the HDPE particle phase divided by the viscosity of the PS matrix) $\eta_{PE/PS} = 1.05$ in these blends (and also in subsequent blends, if not specified). D_V is predicted to increase faster for higher volume fraction. The predicted shape of D_V vs. coalescence strain (that is, the product of strain rate and time) is similar to that determined from experiment. If we normalize D_V by its initial value D_{V0} and plot it vs. the product of coalescence strain and volume fraction ($\gamma.\phi$) (Figure 5), three curves for different volume fractions approximately overlap with each other. This is similar to the experimental results

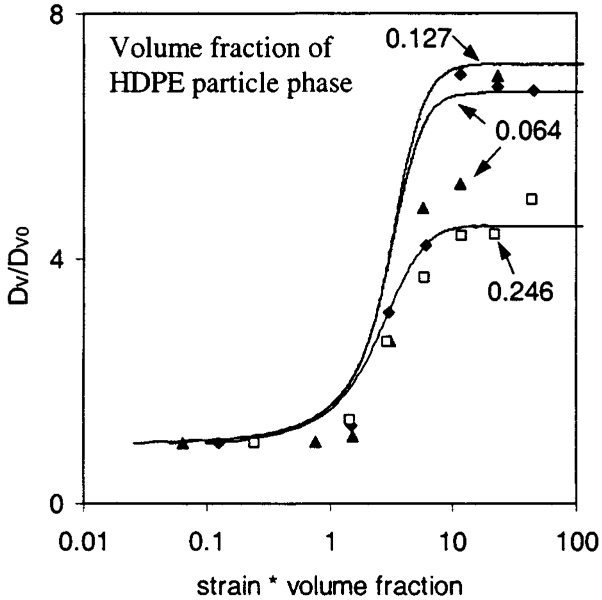

Figure 5. Reduced volume average diameter vs. product of strain and volume fraction of HDPE particle phase.

Lines are Smoluchowski theory and symbols are experimental results (from Figure 4). Both collapse to single onset curves for different volume fractions.

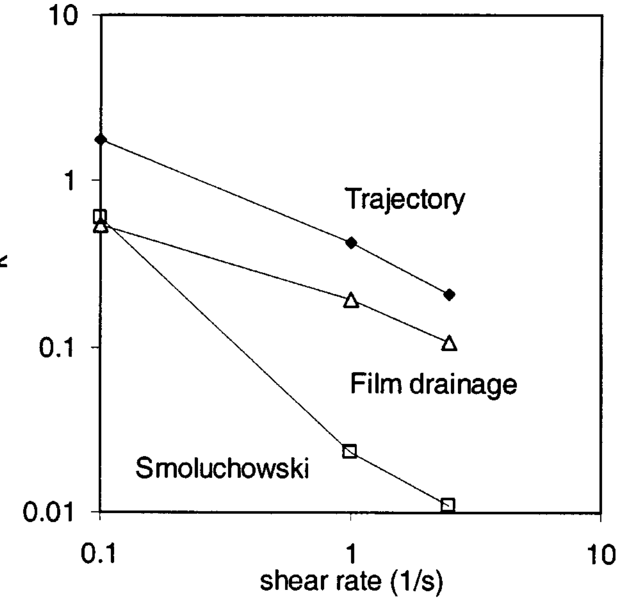

Figure 6. Coalescence parameter *k* vs. shear rate needed to force Smoluchowski, film drainage, and trajectory theories to fit experimental data of Lyu et al. (2000).

where D_V/D_{V0} vs. $\gamma.\phi$ also overlap (Lyu et al., 2000; Vinckier et al., 1998). Such similarity suggests that the dominant mechanism of flow driven particle coalescence in these experiments in binary particle collision. That is, the Smoluchowski theory reflects the major part of coalescence process.

The calculated increase in D_V/D_{V0} based on theory was faster than the experimental results for all these three volume fractions. In order to fit the experimental D_V/D_{V0} the coalescence parameter k has to be reduced to 0.6 for all these three volume fractions. Similar difference was also seen in the effects of shear rates and viscosity ratios on coalescence. Figure 6 shows the fitted k vs. shear rate; k is not only smaller than 1, but also decreases with shear rate, suggesting a continuous decrease in coalescence efficiency with increasing shear rate. Increasing shear causes two results: (1) capillary number increases, leading to stronger particle-particle repulsive interaction due to squeezing flow of the matrix between them; (2) particle interaction time (reciprocal to shear rate) is reduced. Both of these effects reduce coalescence probability. However, the data in Figure 6 cannot distinguish which effect is more important.

k vs. viscosity ratio is plotted in Figure 7. As expected, there is a maximum in k when the viscosity ratio is roughly between 0.1 and 1. What is not expected is the decrease at higher viscosity ratios. Coalescence efficiency is reduced for all these viscosity values, but the reduction was minimum when the viscosity ratio was roughly between 0.1 and 1. Apparently, particle-particle repulsive interaction changes with viscosity ratio. It is interesting to note that coalescence efficiency is highest over the same viscosity ratio range that produces the minimum critical capillary number for drop breakup (Grace, 1982). Although it is not clear whether there is a common mechanism behind these two phenomena, similar viscosities of the particle and matrix phases does reduce the heterogeneity of the stresses.

Smoluchowski theory predicts a sharp increase in D_n, the number average diameter (see Figure 4b). This is different from what has been observed in experiments where D_n

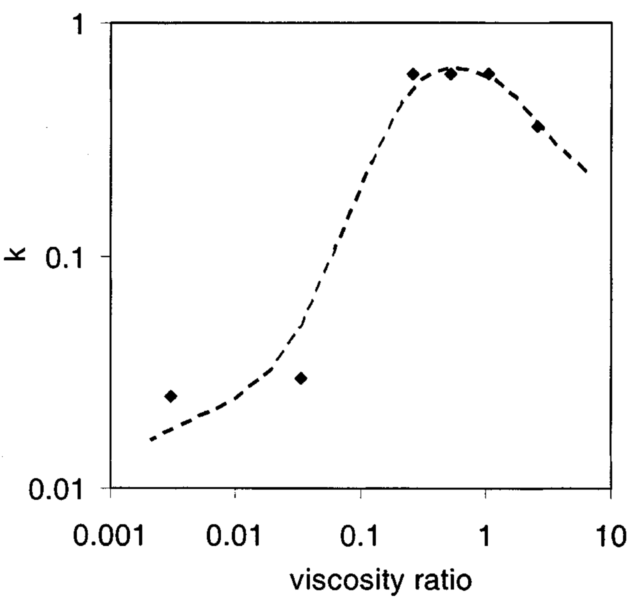

Figure 7. Coalescence parameter *k* vs. viscosity ratio needed to force Smoluchowski theory to fit the data of Figure 1.

The line is to guide the eye.

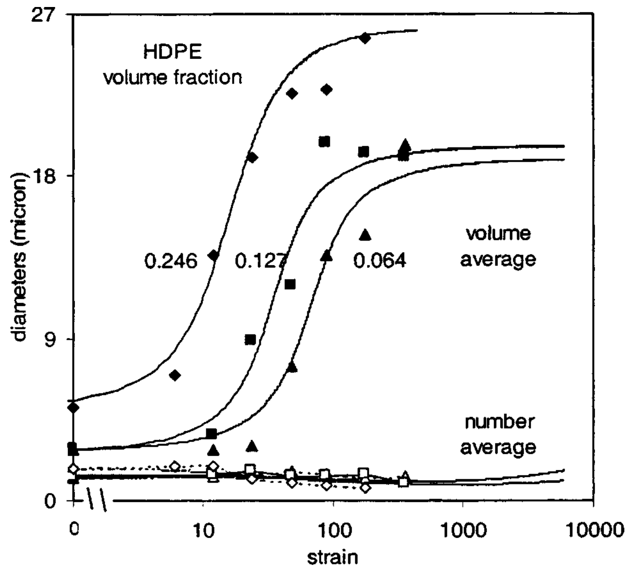

Figure 8. Trajectory theory (solid lines) and experimental D_V and D_n vs. strain results in the blends having various volume fraction of HDPE particle phase at shear rate = 0.1 s^{-1} and viscosity ratio = 1.05.

Note the agreement between the theoretical and experimental D_n.

changes very slightly at low shear rate for shear strain < 360 regardless of volume fractions and viscosity ratios (Lyu et al., 2000; Lyu, 2000). This suggests that another particle interaction causes smaller particles to coalesce more slowly. In the following section we will examine these interactions with the trajectory and film drainage theories.

Trajectory theory

For the trajectory theory, E_{ij} was taken from Figure 2b. The coalescence parameter k was determined by best fitting the experimental sharp increase in D_V, similar to that for Smoluchowski theory.

Figure 8 shows the predicted D_V and D_n vs. strain in comparison with the experimental results at a shear rate of 0.1 s^{-1} for various volume fractions of HDPE. Parameter k was fitted to be 1.8 for all three volume fractions. Clearly, the predicted D_V and D_n based on the trajectory theory overlap well with the experimental results. One significant improvement of the trajectory theory is that the sharp increase in D_n that occurred in Smoluchowski's theory has been eliminated.

The difference between the trajectory and Smoluchowski's theories lies in that hydrodynamic interactions due to the trajectories of particles are considered in the trajectory theory. As a result, the coalescence efficiency between small and large particles is significantly reduced. This reduced coalescence efficiency, together with the cubic dependence of the coalescence rate on their diameter as indicated in Eq. 1, leads to a result that the larger particles coalescence with themselves rapidly, leaving the smaller particles to slowly coalesce with either themselves or larger ones. Notice that D_V reflects the behavior of larger particles, while D_n reflects the smaller ones.

While the trajectory theory correctly predicts the reduction of coalescence efficiency of small particles, this theory neglects the effects of shear rate on particle deformation, and, furthermore, on the coalescence rate. As a result, the predicted results do not agree with the experiments, as shown in Figure 6 where the fitted coalescence parameter k for the trajectory theory decreases significantly with increasing shear rate. Additionally, Figure 2b shows that the trajectory theory, which predicts the coalescence efficiency, decreases monotonically with increasing viscosity ratio. This again does not agree with experimental results shown in Figure 1.

Film drainage theory

As mentioned above, film drainage theory accounts for particle deformation by considering the squeezing flow of the matrix film between two approaching particles. The fitting procedure for the film drainage theory was similar to that for the trajectory theory. Equation 3 was used to calculate E_{ij}. The viscosities of HDPE and PS were taken from our measurements (Lyu, 2000), and the interfacial tension Γ was chosen to be equal to 5 mN/m (Elemans et al., 1990). We take the critical film thickness h_c to be equal to 5 nm as suggested by Janssen and Meijer (1995) and calculate the coalescence in the blends containing 12.7% HDPE and at 0.1 s^{-1}. The calculation, however, yields a slow increase in D_V: the slope of the D_V curve is much smaller than that of the experiments (Figure 9). Increasing the coalescence parameter k only makes the increase in D_V start earlier, but the slope of the curve is still small. If we treat both the k and h_c as fitting parameters, good agreement between calculation and experiments is obtained (Figure 9). In such a case the parameter k decreases, but h_c increases with increasing shear rate (Figure 6 and 10, respectively) and h_c is more than an order of magnitude larger than expected. As discussed by Vrij (1966) and Vrij and Overbeek (1968), h_c is related to the thin film instability. It is a physical property of the materials and should be independent of shear rate. Thus, the dependence of k and h_c on shear rate suggests that the film drainage theory cannot give a quantitative prediction of coalescence vs. shear rate, although it does consider drop deformation. Besides the disagreement in k and h_c, the film drainage theory also predicts a sharp increase in number average diameter D_n, which, similar to Smoluchowski's theory, disagrees with the experiments.

It is seen that the Smoluchowski theory predicts the qualitative mechanism of coalescence. The trajectory theory yields a significant improvement in predicting the reduction in coalescence efficiency between particles of different sizes. The film drainage theory leads to some qualitative improvement in dealing with the drop deformation as shown in Figure 6, where k fitted with the film drainage theory decreases slower than that fitted with the trajectory theory. However, none of these theories predict the dependency of coalescence efficiency on viscosity ratio.

Manga and Stone (1993, 1995), Zhang et al. (1993), Rother et al. (1997), and Rother and Davis (2000) have combined trajectory and particle deformation. Rother and Davis (2001) predicted coalescence efficiency decreases with increasing shear rate, as well as with decreasing particle-size ratio. These results are encouraging, however, coalescence efficiency is still predicted to increase monotonically with viscosity ratio.

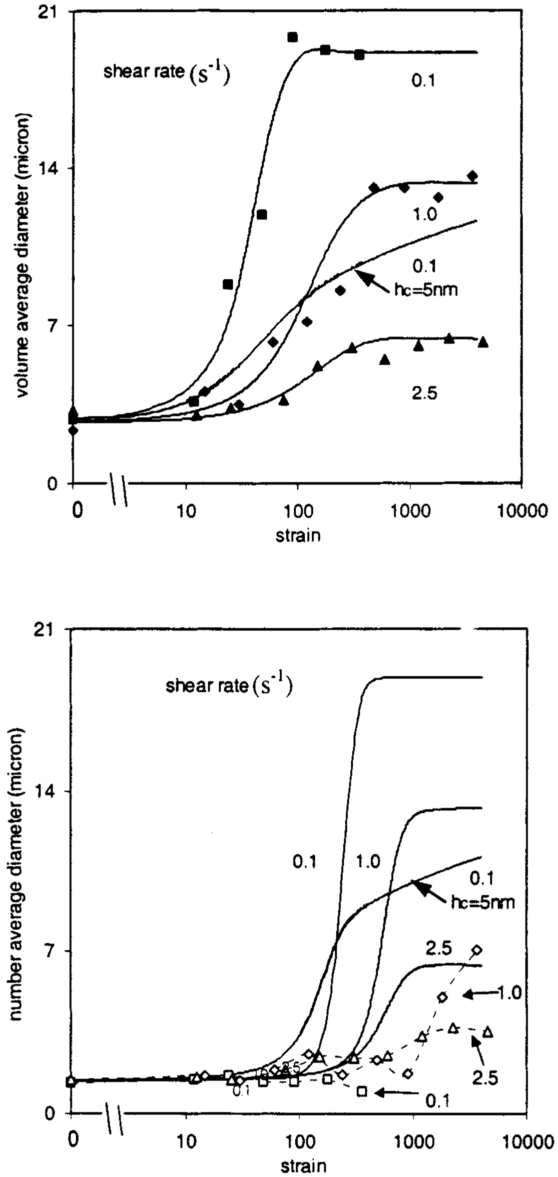

Figure 9. Film drainage calculations and experimental values of D_V and D_n vs. strain in blends containing 12.7% HDPE in PS matrix at various shear rates.

$h_c = 5$ nm if indicated and otherwise h_c is varied to better fit the data (see Figure 10). Dotted lines are to guide the eye through the D_n data.

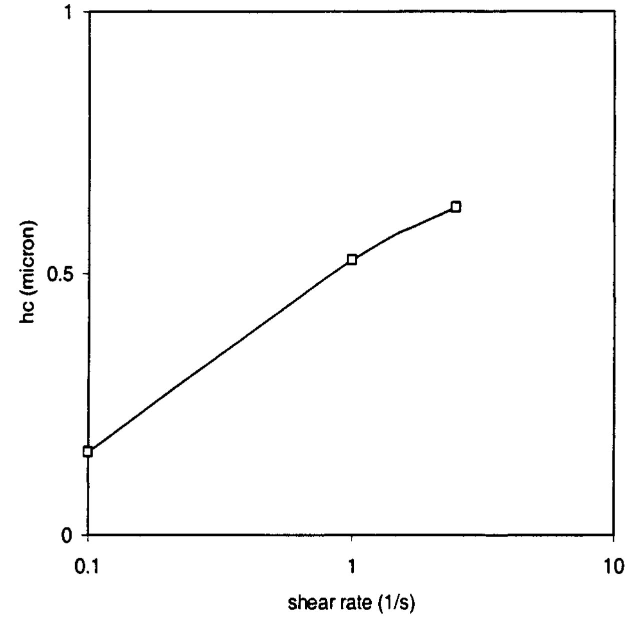

Figure 10. Critical film thickness value h_c need to force the film drainage theory to fit experimental coalescence vs. shear rate date.

Based on van der Waals interaction, h_c should be about 5 nm.

Therefore, improvement made by this theory is limited.

It is worthwhile to discuss why Rother et al.'s theory that combines trajectory and particle deformation cannot give qualitatively correct predictions with viscosity ratio. Our speculation is as follows: when two particles move together the external force not only squeezes the matrix out of the particle gaps, but also causes the particles to deform. If the viscosity ratio is high (>1), the fountain flow inside particle is weak. As a result the particle surfaces do not move and help to drag the matrix out of the particle gap. Thus, coalescence efficiency decreases. However, in the case of low viscosity ratio ($\ll 1$), the magnitude of fountain flow inside particles increases, which results in an increase in particle deformation, and, subsequently, an increase in the contact area between them. As a result, the approach velocity of two deformed particles greatly decreases and the coalescence efficiency is also reduced as in the high viscosity ratio case but for a different reason.

From the speculation above, the force that is related to the particle deformation should be a function of viscosity ratio. In the film drainage theory this force depends only on the shear drag force, which is independent of viscosity ratio. This might be the reason why the theory disagrees with the experiments in the low viscosity ratio regime. Rother et al. combined the trajectory analysis and particle deformation. However, the allowed deformation magnitude in their work was small. This may be responsible for the disagreement between this theory and the experiments in the low viscosity ratio range where particle deformation is expected to be large. In addition, Rother et al. (2000) suggest that the consideration of the van der Waals interaction that determines the critical thickness of the particle gap was not sufficient in their theory. This may cause quantitative difference between theory and experiments in all the cases. Modeling of large-scale particle deformation is needed to confirm the speculation above.

Conclusions

We modeled flow driven coalescence based on Smoluchowski, trajectory, and film drainage theories using a population dynamics equation. Our model predicts the entire particle-size distribution and shows that the volume average diameter increases much more rapidly than the number average during coalescence. The numerical results were compared with experimental results on polystyrene/polyethylene (PS/HDPE) blends for several volume fractions of dispersed phase at various shear rates and viscosity ratios. The effect of volume fraction scaled linearly with volume fraction up to 25% indicating binary collisions dominate the coalescence process. The effect of shear rate and viscosity ratios reveal that there are at least two types of hydrodynamic interactions that play important roles during coalescence. One is due to the changes in the trajectory of particles predicted by the trajectory theory. It causes the coalescence efficiency to decrease with the particle-size ratio, resulting in slower coalescence rates for smaller particles, and leading to a slower increase in number average particle size, especially at low shear rate. Another hydrodynamic interaction is related to the squeezing flow of matrix between particles. The coalescence efficiency decreases with increasing shear rate. As a result, the volume average particle size grows more slowly with coalescence strain at higher shear rate.

Although some researchers have used the trajectory and film drainage theories to explain coalescence experiments, we caution the use of these theories. Both give the wrong qualitative prediction of the dependence of coalescence efficiency on viscosity ratio. The fact that the critical film thickness of the film drainage theory has to be changed drastically in order to fit the theory with experiments exposes a fundamental limitation of this theory.

Acknowledgments

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