A Theoretical Model for Quiescent Coarsening in Immiscible Polymer Blends

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The coalescence rate in immiscible polymer blends predicted by all existing models is two or three orders of magnitude lower than that observed experimentally. The model developed in this study considers for the first time that coarsening is driven by van der Waals forces and there is slippage at the interfacial boundaries between the moving particles and the matrix. The growth rate of the average radius of the particles, $\mathbf{R}$*, can be approximately expressed as*

$$\frac{d\mathbf{R}}{dt} = \frac{A \exp(-\sigma^2)}{9\pi\eta\beta\mathbf{R}^2}$$

where β *is a function of the interfacial slippage length b,* $\mathbf{R}$*, and the average surface distance between the particles* $\mathbf{h}$*. The parameter b depends on the incompatibility and the degree of entanglement at the interface between the two polymers of the blend. The fact that the coarsening rate is decreased by the presence of a copolymer can be explained by a decrease in the value of b.*

Introduction

Polymer blends are an important family of polymer materials. However, most polymer pairs are immiscible and polymer blends are often phase-separated and thermodynamically unstable. For example, under quiescent conditions, that is, without flow, the domain size of the dispersed phase tends to increase with time. The thermodynamic reason responsible for this coarsening is a reduction of the interfacial area or interfacial energy. Mechanisms most frequently considered for coarsening in molten quiescent polymer blends are coalescence and Ostwald ripening (Crist and Nesarikar, 1995). A coalescence mechanism considers that particles grow by moving through the matrix and colliding with one another to form fewer and larger particles. The simplest view of Smoluchowski (Levich, 1962) is that particles move by random Brownian motion in the matrix phase and only binary collisions are possible. By contrast, Ostwald ripening (Voorhees, 1985; Voorhees, 1992) considers that small droplets are dissolved in the matrix as single polymer chains. The latter then diffuse to large droplets. As a result, small droplets become smaller until they disappear and large ones become larger. During dissolution, the centers of mass of the small droplets are stationary. Interestingly, both mechanisms yield the same general time dependence of the particle size

$$\mathbf{R}^3 = \mathbf{R}_0^3 + Kt \tag{1}$$

Equation 1 indicates that whatever the mechanism of coarsening (Brownian motion or Ostwald ripening), the cube of the number-average particle radius $\mathbf{R}^3$ increases linearly with time t with a coarsening constant K, starting from the initial value $\mathbf{R}_0^3$ at a reference time $t = 0$. The coarsening constant K depends on the mechanism and is given as follows:

Coalescence by Brownian motion

$$K_C = \frac{2kT\Phi}{\pi\eta\mathbf{R}^3/\mathbf{R}^3} \tag{2}$$

Ostwald ripening

$$K_{OR} = \frac{8DV\Phi_{dm}\Gamma/9kT}{(1+0.74\Phi^{1/2})^3} \tag{3}$$

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Equation 2 indicates that the rate constant of Brownian-motion-driven coalescence, K_C, depends only on temperature, T, the dispersed phase volume fraction, Φ, and the matrix viscosity, η. From Eq. 3, coarsening by Ostwald ripening characterized by the Ostwald ripening rate constant, K_{OR}, is expressed by the molecular diffusion coefficient, D, and the dispersed-phase molar volume, V, the equilibrium molar fraction of the dispersed phase solubilized in the matrix phase, Φ_{dm}, and interfacial tension between the two phases, Γ. It is believed that during coarsening, both Brownian-particle-motion-driven coalescence and molecular-diffusion-driven Ostwald ripening can operate at the same time and their relative importance depends on hydrodynamic and thermodynamic conditions. For example, Brownian-motion-driven coalescence is favored in blends with a low matrix viscosity, η, or a high volume fraction of the dispersed phase, Φ. Ostwald ripening, on the other hand, is dominant when diffusivity, D, and solubility of the dispersed phase in the matrix Φ_{dm}, and the interfacial tension between the matrix and dispersed phases, Γ, are large.

While the two models expressed by Eqs. 2 and 3 apparently have grasped most of the physics influencing coarsening, they are often unable to describe quantitatively the coarsening rate in immiscible polymer blends under quiescent conditions (Guo et al., 1998). In fact, predictions are often two or three orders of magnitude too low with respect to experimentally observed coarsening rates. To fit experimental data, the value of viscosity in Eq. 2 has to be unreasonably low (by two or three orders of magnitude) or the value of the diffusion coefficient in Eq. 3 has to be unreasonably high (by two or three orders of magnitude). Moreover, the dependence of coarsening on the volume fraction of the dispersed phase expressed by Eq. 2 is too weak. Thus, Eq. 2 is likely invalid for concentrated polymer-blend systems. Fortelny and Kovar (Fortelny and Kovar, 1988) modified the Smoluchowski theory by taking the high-viscosity characteristics of polymers into consideration and arrived at the following equation

$$\boldsymbol{R}^3 = \boldsymbol{R}_0^3 + \frac{4\sqrt{3}\,\Phi}{\pi}\sqrt{\frac{kT\boldsymbol{R}_0^3 t}{\eta}} + \frac{12\Phi^2 kTt}{\pi^2\eta} \tag{4}$$

Although the coalescence rate predicted by Eq. 4 is slightly higher than that given by the original Smoluchowski theory, it is still too low compared with experiments.

Moreover, the classic theories as shown in Eqs. 2, 3, and 4 cannot explain fully the fact that the presence of an appropriate copolymer greatly stabilizes the morphology of an immiscible polymer blend (Sundararaj and Macosko, 1995). According to Eq. 2, the coalescence rate constant has nothing to do with the interfacial tension. Thus, a decrease in interfacial tension by the presence of a copolymer should not bring about a decrease in coarsening if Brownian motion expressed by Eqs. 2 or 4 is the mechanism of coarsening and if the matrix viscosity is not altered by the presence of the copolymer. Equation 3 shows that a decrease in interfacial tension does slow down the Ostwald ripening rate constant. However, the magnitude of a decrease in interfacial tension is often much less than that in the experimentally observed coarsening rate constant.

Macosko et al. (1996) proposed an interesting mechanism to explain a decrease in coalescence rate by the presence of a copolymer. Compared to two bare droplets whose surfaces are not covered by a layer of a copolymer, the collision of two droplets whose surfaces are covered by a layer of the copolymer will less likely lead to coalescence because of the steric hindrance effect. Limited experimental data available in the literature seem to be supportive of this mechanism. However, the latter in its present form is qualitative or semiquantitative. On the other hand, since two droplets can feel the steric hindrance effect only when they are within colliding distance, this mechanism only describes the role of a copolymer for colliding droplets. Before two droplets collide, they first should move through the matrix in order to approach each other. The rate of their movement can be altered by the presence of the copolymer at the interfaces between the droplets and the matrix. This effect is not taken into account in the mechanism.

In view of all the facts just mentioned concerning quiescent coalescence in immiscible polymer blends, this article proposes a model based on van der Waals forces. More importantly, the concept of slippage at polymer–polymer interfaces is introduced for the first time.

Theoretical Derivation

Quiescent coarsening in immiscible polymer blends is described in the following manner. Consider a three-dimensional space in which spherical particles of the dispersed phase are distributed in a certain way, for example, randomly. The distances between the surfaces of the particles, h, are not the same and satisfy a certain distribution. A particle feels more or less the existence of other particles by van der Waals forces. The latter allow particles to approach their nearest neighbors by draining the matrix between them until the surface distance between them, h, reaches a critical value, h_c, below which film rupture occurs (Chesters, 1991).

When particles move in the matrix, there are at least three types of forces acting on them: van der Waals force, hydrodynamic resistance force, and random force. The latter is responsible for Brownian motion. The motion of a particle of radius R_1 approaching another particle of radius R_2 can be described by the following Newtonian equation

$$ma = F_w + F_f + \tilde{f} \tag{5}$$

or

$$F_w - ma + \tilde{f} = -F_f \tag{5'}$$

where m is the mass of the smaller particle of the two, a is the relative acceleration, F_w is the van der Waals force, F_f is the hydrodynamic resistance force, and $\tilde{f}$ is the random force originated from random collisions of the matrix molecules on the particle. Equations 5 or 5′ are stochastic differential equations because of $\tilde{f}$ and likely have no analytical solutions. As will be shown later, both the inertial force, ma, and the random forces, $\tilde{f}$, are very small compared with van der Waals forces, F_w. Equation 5′ can then be reduced to

$$F_w = -F_f \tag{6}$$

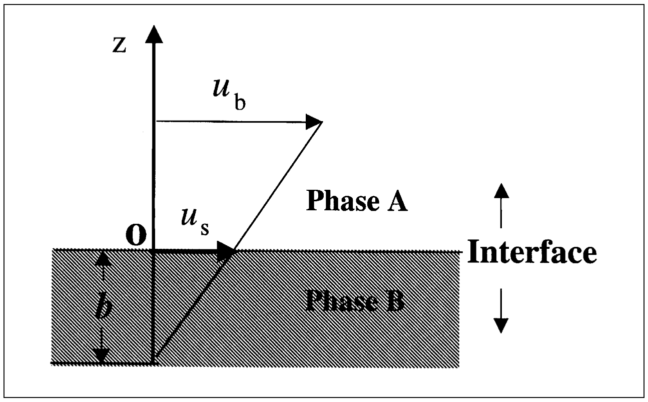

Figure 1. Interfacial slippage: $u_s = b(\partial u_b/\partial z)$, where u_s and u_b are the velocity of slippage and the relative velocity between phases *A* and *B*, respectively.

The van der Waals force between two spheres of radii R_1 and R_2 is given by (Israelachvili, 1992)

$$F_w(h) = \frac{A}{6h^2}\frac{R_1R_2}{(R_1+R_2)} \tag{7}$$

where A is the Hamaker constant and is about 10^{-20} J for most polymer pairs (Chesters, 1991; Israelachvilli, 1992). For monodisperse systems, particles have the same radius and Eq. 7 reduces to

$$F_w(h) = \frac{AR}{12h^2} \tag{8}$$

When a particle moves in the matrix, slippage may exist at the interfacial boundary between the particle surface and the matrix. The extent of interfacial slippage is characterized by a so-called slippage length, b, which is defined as the ratio of slippage velocity and shear rate (Figure 1) (Vinogradova, 1995)

$$u_s = b\dot{\gamma} = b\left(\frac{\partial u_b}{\partial z}\right) \tag{9}$$

where u_s is the slippage velocity and $\dot{\gamma}$ is the local shear rate. The value of b is zero when there is no slippage. Slippage between polymer melts and solid surfaces, as well as between incompatible polymer interfaces, have been investigated theoretically and experimentally (Newby et al., 1995; Migler et al., 1993, 1994; Brochard-Wyart et al., 1990, 1994; Brochard and De Gennes, 1992). Equation 10 gives the hydrodynamic force resisting two spheres of radii R_1 and R_2, respectively, from approaching each other under the hypothesis of interfacial slippage (Vinogradova, 1995)

$$F_f = -\frac{2\pi R_e^2\eta}{b}\left[\left(1+\frac{h}{6b}\right)\ln\left(1+\frac{6b}{h}\right)-1\right]\frac{\partial h}{\partial t} \tag{10}$$

where η is the viscosity of the matrix, h is the surface distance between two spheres, and R_e is the effective radius and is given by

$$R_e = \frac{R_1R_2}{R_1+R_2} \tag{11}$$

If $R_1 \gg R_2$, then $R_e = R_2$ and the hydrodynamic resistance force becomes unrelated to the larger particle. Equation 10 shows that the hydrodynamic resistance force is a monotonic decreasing function of slippage length.

Substituting Eqs. 7 and 10 into Eq. 6 leads to

$$\frac{12\pi\eta h^2}{b}\left[\left(1+\frac{h}{6b}\right)\ln\left(1+\frac{6b}{h}\right)-1\right]\frac{\partial h}{\partial t} = \frac{A}{R_e} \tag{12}$$

Equation 12 has an analytical solution given by

$$t(h,R_e) = \frac{6\pi R_e\eta}{A}\alpha(h,h_c,b) \tag{13}$$

where $t(h,R_e)$ is the drainage time during which the surface distance between two particles is decreased from h to a critical distance h_c, and $\alpha(h,h_c,b)$ is a function of surface distance between the two particles, the critical distance, and slippage length. The function $\alpha(h,h_c,b)$ can be written as

$$\begin{aligned}\alpha(h,h_c,b) = \Bigg(& \frac{2h^3\ln(h+6b)}{3b} + 36b^2\ln(h+6b) \\ & -\frac{h^3}{2b} + \frac{1}{2}h^2 - 6bh - \frac{2h^3\ln(h)}{3b} + \frac{h^4\ln(h+6b)}{12b^2} \\ & -\frac{h^4\ln(h)}{12b^2} - \frac{2h_c^3\ln(h_c+6b)}{3b} - 36b^2\ln(h_c+6b) \\ & +\frac{h_c^3}{2b} - \frac{1}{2}h_c^2 + 6bh_c + \frac{2h_c^3\ln(h_c)}{3b} \\ & -\frac{h_c^4\ln(h_c+6b)}{12b^2} + \frac{h_c^4\ln(h_c)}{12b^2}\Bigg)\end{aligned} \tag{14}$$

Equation 13 shows that the drainage time is proportional to R_e and η and inversely proportional to the Hamaker constant. Moreover, the relationship between drainage time and surface distance or slippage length is nonlinear.

The particle number density, n, defined as the particle number per unit volume decreases as coalescence proceeds, and can be described by (Fortelny and Zivny, 1995)

$$\frac{dn}{dt} = -\frac{n}{\mathbf{t}_c} \tag{15}$$

where $\mathbf{t}_c$ is the average time necessary for two particles to get close to each other to within a critical surface distance, h_c, where coalescence occurs. The value of h_c is typically of the order of 5 nm for immiscible polymer systems (Chesters, 1991).

Experimental results show that for the majority of binary polymer blends, the particle-size distribution of the dispersed phase fits a log-normal distribution. In other words, the logarithm of the radius fits a normal distribution (Liu et al., 1997). The log-normal distribution of particle radius reads (Liu et al., 1997)

$$f_{\ln R}(\ln R) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{\ln^2 (R/\boldsymbol{R})}{2\sigma^2} \right) \qquad -\infty < \ln R < \infty \tag{16}$$

or

$$f_R(R) = \frac{1}{\sqrt{2\pi}\,\sigma R} \exp\left(-\frac{\left(\ln (R/\boldsymbol{R}) + \sigma^2/2\right)^2}{2\sigma^2} \right) \tag{17}$$

where $\boldsymbol{R}$ is the number-average radius and σ is the standard deviation of the logarithm of radius. For a log-normal particle-size distribution, n is related to the number-average radius of particles by

$$n = \frac{3\Phi}{4\pi \boldsymbol{R}^3} \exp(-3\sigma^2) \tag{18}$$

Substituting Eq. 18 into Eq. 15 leads to

$$\frac{d\boldsymbol{R}}{dt} = \frac{\boldsymbol{R}}{3\boldsymbol{t}_c}. \tag{19}$$

For a swarm of particles distributed over a three-dimensional space, driven by van der Waals force, which is inversely proportional to the square of the surface distance of two particles, the two nearest ones will most likely approach each other provided that the particle-size distribution is not very large. To calculate the coarsening time of such a system as expressed by Eq. 13, the nearest-surface distribution function of the particles, $p(z, R)$, has to be determined. According to Lu and Torquato (Torquato et al., 1990; Lu and Torquato, 1992, 1993), the nearest-surface distribution function of particles whose sizes follow a log-normal distribution is

$$\begin{aligned} p(x) = \frac{\Phi}{(1-\Phi)} \Bigg\{ & 3\exp(-2\sigma^2) + \left[6\exp(-3\sigma^2) + \frac{9\Phi \exp(-4\sigma^2)}{(1-\Phi)} \right](1+x) + \Bigg[3\exp(-3\sigma^2) \\ & + \frac{9\Phi\exp(-5\sigma^2)}{2(1-\Phi)} + \frac{9\Phi^2 \exp(-6\sigma^2)}{(1-\Phi)^2} \Bigg] (1+x)^2 \Bigg\} \exp(-M) \end{aligned} \tag{20}$$

where Φ is the volume fraction of the minor phase, $x = h/\boldsymbol{R}$, and M is given by

$$\begin{aligned} M = \frac{\Phi}{1-\Phi} \Bigg\{ & 3\exp(-2\sigma^2)x + \left[3\exp(-3\sigma^2) + \frac{9\Phi\exp(-4\sigma^2)}{2(1-\Phi)} \right](x^2+2x) \\ & + \left[\exp(-3\sigma^2) + \frac{3\Phi\exp(-5\sigma^2)}{2(1-\Phi)} + \frac{3\Phi^2\exp(-6\sigma^2)}{(1-\Phi)^2} \right] (x^3+3x^2+3x) \Bigg\} \end{aligned} \tag{21}$$

Since $h_c/\boldsymbol{R} \ll 1$, the average nearest-surface distance, $\boldsymbol{h}$, is the first-order moment of h

$$\boldsymbol{h} = \boldsymbol{R}\int_{h_c/\boldsymbol{R}}^{\infty} \{xp(x)\}\, dx \cong \boldsymbol{R}\int_0^{\infty} \{xp(x)\}\, dx \qquad (h_c \sim 5nm,\ h_c/R \approx 0)$$

or

$$\int_0^{\infty} \{xp(x)\}\, dx \cong \frac{\boldsymbol{h}}{\boldsymbol{R}} \tag{22}$$

For a log-normal particle-size distribution, the number average of R_e is expressed as

$$\boldsymbol{R}_e = \frac{1}{2}\boldsymbol{R}\exp(-\sigma^2) \tag{23}$$

Substituting Eqs. 22 and 23 into Eq. 13 leads to

$$\boldsymbol{t}_c = \frac{3\pi \boldsymbol{R}^3 \eta}{A} \beta \exp(-\sigma^2) \tag{24}$$

with

$$\begin{aligned} \beta &= \int_0^{\infty} \alpha(x\boldsymbol{R}, h_c, b) p(x)/\boldsymbol{R}^2 dx \\ &\approx \Bigg(\frac{2\delta^3 \ln(\delta + 6\lambda)}{3\lambda} + 36\lambda^2 \ln \boldsymbol{R} + 36\lambda^2 \ln(\gamma + 6\lambda) \\ &\qquad - \frac{\delta^3}{2\lambda} + \frac{1}{2}\delta^2 - 6\delta\lambda - \frac{2\delta^3 \ln(\delta)}{3\lambda} \\ &\qquad + \frac{\delta^4 \ln(\delta + 6\lambda)}{12\lambda^2} - \frac{\delta^4 \ln(\delta)}{12\lambda^2} \Bigg) \\ &\quad - \frac{1}{\boldsymbol{R}^2} \Bigg(\frac{2h_c^3 \ln(h_c + 6b)}{3b} - \frac{h_c^3}{2b} + \frac{1}{2}h_c^2 \\ &\qquad + 36b^2 \ln(h_c + 6b) - 6bh_c - \frac{2h_c^3 \ln(h_c)}{3b} \\ &\qquad + \frac{h_c^4 \ln(h_c + 6b)}{12b^2} - \frac{h_c^4 \ln(h_c)}{12b^2} \Bigg) \\ \delta &= \int_0^{\infty} \{xp(x)\} dx \cong \frac{\boldsymbol{h}}{\boldsymbol{R}} \\ \lambda &= b/\boldsymbol{R} \end{aligned}$$

From Eqs. 19 and 24, the following equation is obtained

$$\frac{d\boldsymbol{R}}{dt} = \frac{A \exp(-\sigma^2)}{9\pi\eta\beta\boldsymbol{R}^2} \tag{25}$$

or

$$\frac{d\boldsymbol{R}^3}{dt} = \frac{A \exp(-\sigma^2)}{3\pi\eta\beta} \tag{25a}$$

Equation 25 or 25a has no explicit analytical solution because β is a very complicated function of $\boldsymbol{R}$. However, it can be shown numerically that β is a weak increasing function of $\boldsymbol{R}$. Moreover, when the slippage length is smaller than the particle radius ($b/\boldsymbol{R} < 1$), the value of β is then not affected much by $\boldsymbol{R}$. Under these conditions, β in Eq. 25a can be approximated as a constant and

$$\boldsymbol{R}^3 = \boldsymbol{R}_0^3 + \left\{\frac{A \exp(-\sigma^2)}{3\pi\eta\beta}\right\} t \tag{26}$$

where σ, the standard deviation of the log-normal particle-size distribution, is assumed to be constant during the whole coarsening process. Note that Eq. 26 has a form similar to that of Eqs. 2 and 4. It is also worth noting that, as will be shown later, b is on the order of 10 to 25 μm for most immiscible polymer pairs. Therefore, $b/\boldsymbol{R} > 1$ and Eq. 25 or 25a should be used, instead of Eq. 26.

Results and Discussion

Influence of the interfacial slippage on the motion of particles

The relative velocity (u) between two approaching particles under van der Waals force is defined as

$$u = \frac{dh}{dt} \tag{27}$$

According to Eqs. 13 and 14, Eq. 27 can be written as

$$u = \frac{dh}{dt} = \frac{A}{6\pi R_e \eta} \frac{1}{\dfrac{d\alpha}{dh}} \tag{28}$$

with

$$\frac{d\alpha}{dh} = \left\{ \begin{array}{l} \dfrac{2h^2 \ln(h+6b)}{b} + \dfrac{2h^3}{3b(h+6b)} + \dfrac{36b^2}{(h+6b)} - \dfrac{13h^2}{6b} + h - 6b \\ -\dfrac{2h^2 \ln h}{b} + \dfrac{h^4}{12b^2(h+6b)} + \dfrac{h^3 \ln(h+6b)}{3b^2} - \dfrac{h^3 \ln h}{3b^2} - \dfrac{h^3}{12b^2} \end{array} \right\} \tag{29}$$

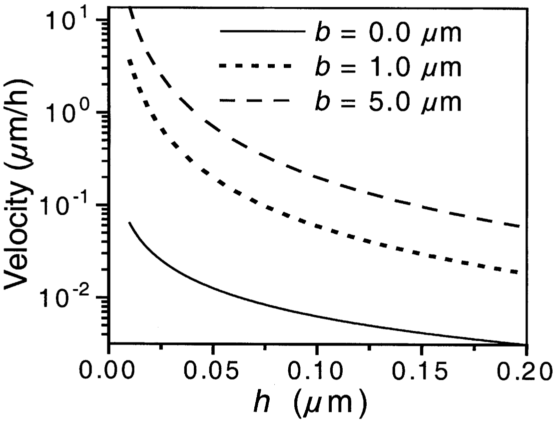

Figure 2. Effect of interfacial slippage on the velocity with which two particles approach each other under van der Waals force.

Solid curve: $b = 0$ μm; dotted curve: $b = 1$ μm; dashed curve: $b = 5$ μm. $\eta = 1{,}000$ Pa·s, $A = 1 \times 10^{-20}$ J, $R = 1.0$ μm.

Equation 28 shows that the relative velocity is proportional to the Hamaker constant and inversely proportional to the viscosity of the matrix. Moreover, it is influenced by the extent of interfacial slippage characterized by the interfacial slippage length, b, through $d\alpha/dh$. The latter is given in Eq. 29. It can be shown numerically from Eq. 28 that increasing the interfacial slippage leads to an increased approach velocity, through a reduction of hydrodynamic resistance force due to faster removal of the matrix liquid separating the two droplets.

Figure 2 shows the effect of the interfacial slippage on the motion of particles. The relative approaching velocity of two particles is greatly enhanced by the interfacial slippage. The relative velocity with an interfacial slippage length of 5 μm is more than 100 times as high as that without interfacial slippage. This shows that the interfacial slippage has to be taken into account when modeling coarsening processes in a quantitative manner. The fact that all existing models underestimate the coarsening rate is because they ignore interfacial slippage.

Influence of the inertial force

The inertial force (ma) has been neglected in the preceding derivation of the rate of coarsening driven by van der Waals forces. In what follows, it will be shown that this simplification is rational. The acceleration of two approaching particles, a, is the differential of the velocity, namely

$$a = \frac{du}{dt} = u\frac{du}{dh} = -\frac{3A^2}{(2\pi\eta R_e)^2}\xi(h,b) \tag{30}$$

with

$$\xi(h,b)=\frac{[h\ln(h+6b)-h\ln(h)-6b-4b\ln(h)+4b\ln(h+6b)]b^4}{[h\ln(h+6b)-h\ln(h)-6b-6b\ln(h)+6b\ln(h+6b)]^3h^5}$$

According to Eqs. 6 and 30, the ratio between the inertial and van der Waals forces, ma/F_w, is

$$\frac{ma}{F_w}=-\frac{18mAh^2\xi(h,b)}{R_e(2\pi R_e\eta)^2}\approx-\frac{48\rho Ah^2\xi(h,b)}{\pi\eta^2} \tag{31}$$

where ρ is the mass density of the particles. Figure 3 shows that $ma/F_w \ll 1$ over a wide range of h ($\eta = 1{,}000$ Pa·s, $A = 1\times10^{-20}$ J, $\rho = 1{,}000$ kg/m^3), confirming that the effect of the inertial force on coarsening is indeed negligible.

Brownian-motion-driven coalescence

In the preceding derivation of the rate of coarsening, the random force responsible for Brownian motion is also neglected. In order to justify this simplification, the rate of coalescence caused by the Brownian motion will be compared with that driven by the van der Waals force. Coalescence-driven Brownian motion without interfacial slippage is described by Eq. 2 or 4. When the interfacial slippage is taken into account, then the hydrodynamic force resisting the motion of a particle of radius R in a fluid of viscosity η is given by Eq. 10 or by the following simpler and more classic equation (Vinogradova, 1995)

$$F_z=-\frac{6\pi\eta Ru}{1+b/R} \tag{32}$$

This equation is slightly less accurate than Eq. 10, but greatly facilitates our discussion on the influence of interfacial slippage on the Brownian motion. Equation 32 shows that the presence of interfacial slippage decreases the hydrodynamic resistance force by a factor of $1/(1+b/R)$. This amounts to decreasing the viscosity by this factor. In other words, the effective viscosity at the interfacial boundaries between the particle and the matrix is $\eta/(1+b/R)$. Thus, interfacial slippage is expected to accelerate the Brownian-motion-driven coalescence as well. Substituting the effective viscosity into Eqs. 2 and 4 yields the increase in particle radius as a result of the Brownian-motion-driven coalescence with interfacial slippage

$$\boldsymbol{R}^3=\boldsymbol{R}_0^3+\frac{2kT(1+b/\boldsymbol{R}_0)\Phi}{\pi\eta\overline{\boldsymbol{R}}_0^3/\boldsymbol{R}_0^3}t \text{ (Smoluchowski)} \tag{33}$$

$$\boldsymbol{R}^3=\boldsymbol{R}_0^3+\frac{4\sqrt{3}\,\Phi}{\pi}\sqrt{\frac{kT(1+b/\boldsymbol{R}_0)\boldsymbol{R}_0^3t}{\eta}}+\frac{12(1+b/\boldsymbol{R}_0)\Phi^2kTt}{\pi^2\eta} \text{ (Fortelny and Kovar)} \tag{34}$$

Figure 4 shows the ratio between the rate of coarsening caused by van der Waals force (Eq. 25a) and that by Brownian motion (Eq. 34), $(\boldsymbol{R}_{\text{van}}-R_0)/(\boldsymbol{R}_{\text{Brownian}}-R_0)$, for the following conditions: $R_0 = 1$ μm, $T = 200$°C, $\eta = 1{,}000$ Pa·s, $\Phi = 20\%$, and $b = 10$ μm. The coarsening rate caused by Brownian motion is much slower than that caused by van der Waals force. Therefore, the random Brownian-motion term in Eq. 5 can be disregarded.

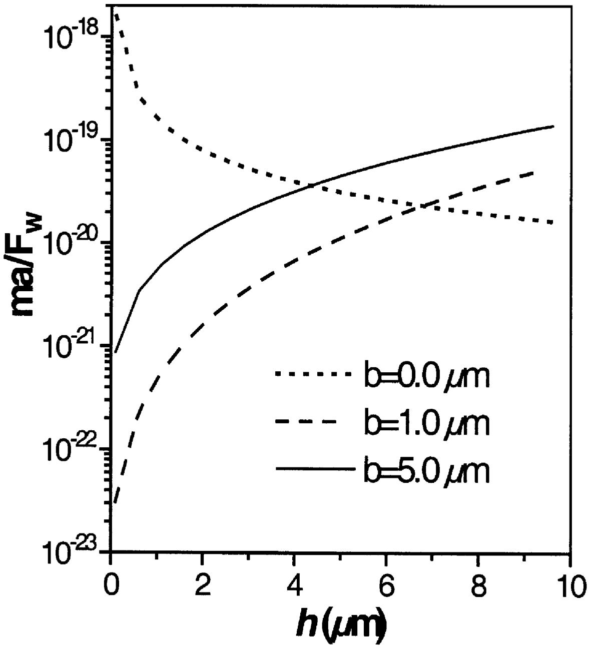

Figure 3. Ratio between the inertial and van der Waals forces, ma/F_w· $\eta = 1{,}000$ Pa·s, $A = 1\times10^{-20}$ J, and $R = 1.0$ μm.

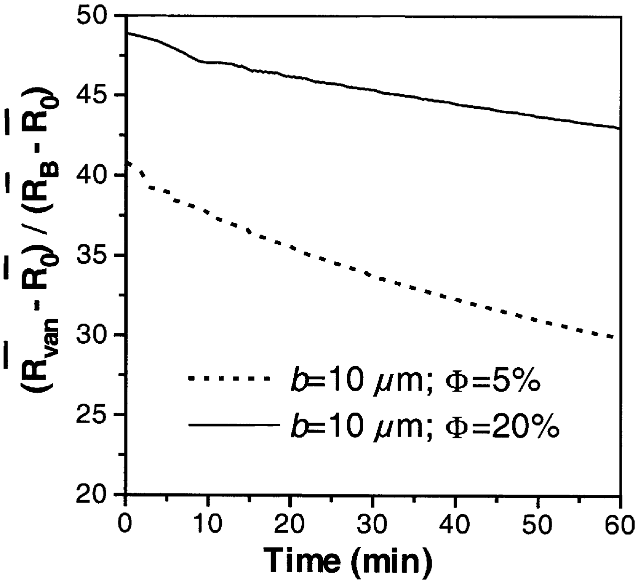

Figure 4. $(R_{\text{van}}\text{-}R_0)/(R_{\text{Brownian}}\text{-}R_0)$ for $b = 10.0$ μm.

$R_0 = 1$ μm; $\eta = 1{,}000$ Pa·s; $A = 1\times10^{-20}$ J; $T = 200$°C; $\Phi = 5$, and 20%. Equation 34 was used to calculate Brownian motion-induced coalescence.

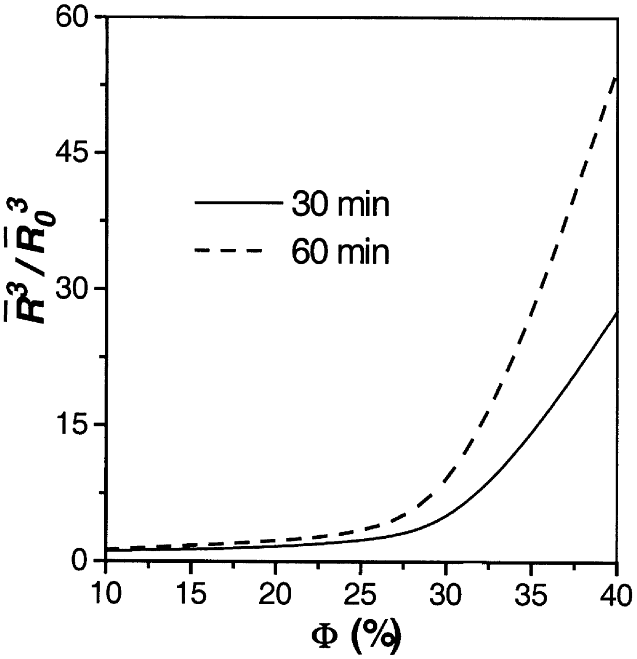

Figure 5. Influence of the volume fraction of the dispersed phase, Φ, on coarsening as predicted by Eq. 25.

$\eta = 1{,}000$ Pa·s; $R_0 = 1.0$ μm; $b = 10$ μm; $A = 1\times10^{-20}$ J.

Influence of the volume fraction of the dispersed phase

Figure 5 shows the evolution of $\bar{R}^3/\bar{R}_0^3$ as a function of Φ predicted by the model developed in this study (Eq. 25). The dependence of coarsening on the volume fraction of the dispersed phase predicted by the model developed in this study is stronger than that predicted by Brownian-motion-induced coalescence (Eqs. 33 or 34) or Ostwald ripening (Eq. 1). Experimentally observed dependence of coarsening on the volume fraction of the dispersed phase is also stronger than that predicted by models based on Brownian-motion-driven coalescence or Ostwald ripening (Fortelny and Kovar, 1988; Favis, 1990).

Influence of the interfacial slippage length on coalescence

It has been well-established that the presence of an interfacial agent or compatibilizer can stabilize the morphology of blends and hinder coarsening (Sundararaj and Macosko, 1995; Baker et al., 2001). It is believed that there are two reasons for the stabilizing effect of compatibilizers. First of all, it reduces the interfacial tension (Lepers et al., 1997). Second, the location of the copolymer at the interfaces acts as a steric protecting layer (Sundararaj and Macosko, 1995) to hinder coarsening. According to the model developed in this study, this steric hindrance effect is related to reduced interfacial slippage at the polymer–polymer interfaces. It should be noted that the concept of interfacial slippage at polymer–polymer interfaces is relatively new and is, thus, poorly understood (Newby et al., 1995; Migler et al., 1993, 1994; Brochard-Wyart et al., 1990, 1994; Brochard and De Gennes, 1992). Brochard-Wyart et al. (1990) theoretically investigated slippage at a polymer–polymer interface and arrived at the following expression for the slippage length

$$b = \frac{aN^3}{N_e^2}\sqrt{\chi} \tag{35}$$

where a is the molecular unit size, N the degree of polymerization, and N_e the threshold of entanglements ($N_e \approx 100$), and χ the Flory–Huggins interaction parameter. Equation 35 shows that b is proportional to the square root of χ. The latter is a measure of the incompatibility or interfacial tension between two polymers, because (Helfand and Tagami, 1971)

$$\Gamma = kTa\rho_0(\chi/6)^{1/2} \tag{36}$$

where ρ_0 is the uniform number density of monomers.

Inspection of Eqs. 35 and 36 yields

$$b \sim \frac{N^3}{N_e^2}\frac{\Gamma}{kT\rho_0} \tag{37}$$

From Eq. 37, the slippage length b is affected not only by interfacial tension but also the degree of entanglement at the interface between two polymers. The fact that the coarsening rate is largely reduced by the presence of a copolymer shows that the copolymer not only reduces the interfacial tension but also and more importantly promotes entanglements at the interfaces between two polymers. The second effect of the copolymer is probably more important than the first one. In other words, while coarsening is driven by interfacial tension, the coarsening rate depends on both interfacial tension and interfacial slippage at the interface.

The value of b is typically of the order of 10 μm for $a = 0.5$ nm, $\chi = 0.05$, $N = 1{,}000$, and $N_e = 100$. Figure 6 shows the numerical results for the coalescence at different slippage lengths for $\Phi = 25\%$ and $\eta = 1{,}000$ Pa·s. The higher the value of slippage length, the more rapid is coarsening. Figure 7 compares the coarsening data reported in the literature concerning a PP/PC (77/23 by volume) blend and the predictions of different models, including the one developed in this study. The FK model (Eq. 34) largely underestimates the coarsening rate if the parameters involved are not adjusted, that is, $\eta =$ 920 Pa·s. In order for it to fit the experimental data, η has to be adjusted to 0.3 Pa·s, which is unreasonably low. The model developed in this study fits well with the experimental results when the value of b is taken as 25 μm. This value seems to be reasonable because PP and PC are highly incompatible.

It may be somewhat confusing that the interfacial slippage length, b, is on the order of 10 to 25 μm, whereas the average droplet size is only on the order of 1 μm. The much larger dimension of the interfacial slippage than that of the droplet size does not suggest that there is no resistance to the flow of liquid around the droplets. In fact, there is no relation between these two geometrical parameters. According to Eq. 9, b is a proportionality constant between interfacial slippage velocity, u_s, and the local shear rate, $\dot{\gamma}$. For a given

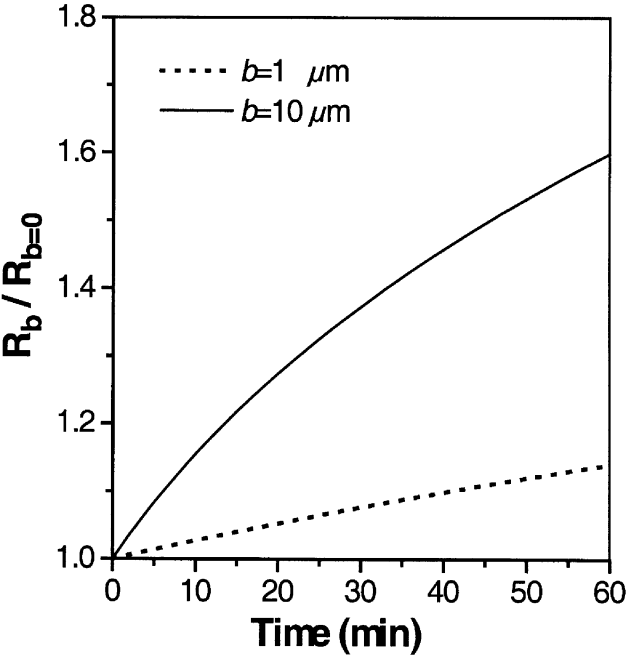

Figure 6. Influence of the interfacial slippage length on coarsening.

$\eta = 1{,}000$ Pa·s; $\Phi = 25\%$; $b = 1.0$ (dot) and 10.0 μm (solid).

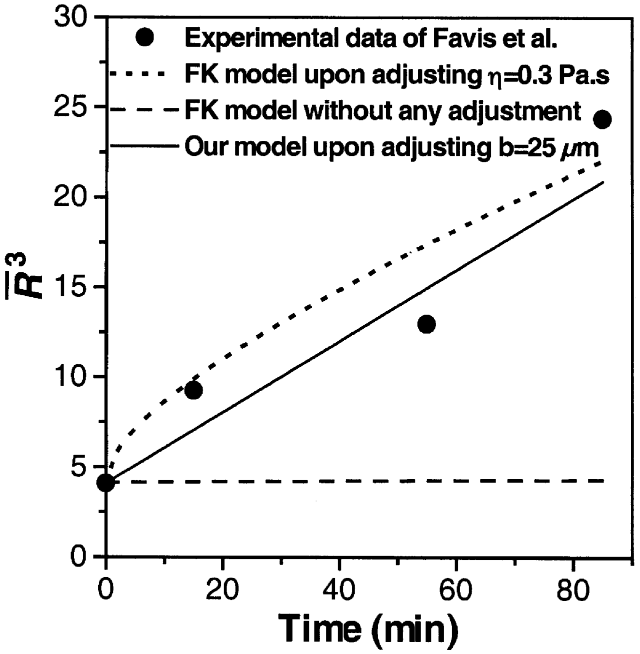

Figure 7. Comparison between prediction and experimental results (Favis, 1990) for a PC/PP (77/23 by volume) blend whose viscosity η Pa·s.

Solid curve: fit of the model developed in this study with $b = 25$ μm and $A = 2\times10^{-20}$ J; dashed curve: prediction by Fortelny and Kovar coalescence model (Eq. 34); dotted curve: fit of Eq. 34 with $\eta = 0.3$ Pa·s, which is more than three orders of magnitude lower than the real viscosity of the blend.

value of $\dot{\gamma}$, the higher the value of b, the higher the value of u_s. Based on Figure 2, $\dot{\gamma}$ is on the order of 1×10^{-3} to 1×10^{-2} s^{-1}. Thus, when b is on the order of 20 μm, u_s is on the order of 2×10^{-2} to 2×10^{-1} μm/s. This means that a droplet of 1 μm in diameter would need 5 to 50 s to move over a distance equivalent to its diameter.

It may be a bit early to ascertain that interfacial slippage is responsible for the high quiescent coalescence rate generally observed in immiscible polymer blends before reliable data are available for their slippage lengths. Nevertheless, the model developed in this study, which is based on the interfacial slippage and van der Waals force, describes reasonably well the quiescent coarsening phenomenon in polymer blends.

However, it should be pointed out that the model developed in this study only takes into consideration the effect of the copolymer on the resistance to movement of droplets through the matrix and disregards its steric hindrance effect on coalescence of colliding droplets. This latter is taken into account, at least qualitatively, by Macosko et al. (1996). A more comprehensive model can be developed based on these two studies.

Conclusion

In this study, a theoretical model is developed to describe the rate of coalescence of immiscible polymer blends in a quiescent state. The fundamental basis of the model is that coalescence is driven by van der Waals forces and that slippage exists at the interfacial boundaries between the moving particles and the matrix. Calculations show that the rate of coalescence driven by van der Waals forces is much more rapid than that driven by Brownian motion. Moreover, the rate of coalescence very much depends on the extent of interfacial slippage, which is characterized by the slippage length, b. The latter is proportional to the square root of the Flory–Huggins interaction parameter between the two polymers of the blend, χ, and is of the order of 10 μm. The value of b obtained by fitting the model to some coalescence data reported in the literature is of the same order of magnitude, confirming the pertinence of the model. The fact that the addition of a copolymer decreases the rate of coalescence can be explained by a decrease in the value of b. Compared to classic coalescence models based on Brownian motion or Ostwald ripening, the model predicted in this study also better predicts the strong dependence of the rate of coalescence on the volume fraction of the dispersed phase, especially at high volume fractions. There is still room for improvement of the model reported in this article.

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