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Film drainage between droplets during their coalescence in quiescent polymer blends

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The approach of dispersed droplets in molten quiescent polymer blends from an initial distance comparable with their radii was analysed. It was shown that a substantial flattening of the droplets appears only at distances comparable with the critical distance for rupture of the matrix film between droplets. The time of coalescence is controlled by the film drainage between practically undeformed spherical droplets. The effect of viscoelasticity on the rate of coalescence was studied for the Maxwell model of the matrix. It was shown that the rate of coalescence increases with increasing relaxation time of the matrix. The theory of coalescence caused by Brownian motion or molecular forces predicts rates of coalescence which are comparable with those determined experimentally. Neglecting synergism between the Brownian motion and molecular forces, approximations used in the description of droplet distribution and neglecting the simultaneous approach of three or more droplets still limit the applicability of the theory for a quantitative prediction of coalescence rate. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: molten polymer blends; droplet coalescence; film drainage)

INTRODUCTION

In addition to their composition and mixing conditions, the phase structure of polymer blends is also controlled by their thermal history. Substantial coarsening of the phase structure was observed for a number of polymer blends kept for a certain time in the molten state at rest[1–8]. The coarsening is usually explained as a consequence either of coalescence of the dispersed droplets[2–8] or Ostwald ripening[5–7]. It was shown that the Smoluchowski theory of coalescence[9] and its modification for systems with high viscosity of the matrix[2] predict a very small effect for blends with original droplet radii higher than 0.5 μm and a typical value of matrix viscosity[2]. This is in strong disagreement with experimental results for many systems[2–4]. Recently, coarsening of the phase structure in hydrogenated polybutadiene/linear polyethylene blends was described by the theory of Ostwald ripening[6,7]. However, pronounced growth of the droplets in blends with medium and high interfacial tension and original droplet radius higher than 0.5 μm cannot be explained even by the Ostwald ripening theory.

Very recently, a theory of coalescence in blends with a higher content of the dispersed phase was proposed[10]. The theory is based on the assumption that the film drainage between droplets, and not the approach of distant droplets, controls the rate of coalescence. Coalescence rates were calculated for commonly used models with mobile, partially mobile and immobile interfaces[11]. It was shown, however, that these models do not describe coalescence in molten quiescent polymer blends in an adequate manner because they predict larger rates of coalescence for weaker driving force[10]. Therefore, film drainage between the droplets in systems where coalescence is caused by weak forces, such as Brownian motion and molecular forces, in molten quiescent polymer blends, is analysed in this paper. Besides the relationships for Newtonian droplets in a Newtonian matrix, the effect of matrix elasticity on the course of coalescence was also studied. It should be mentioned that film drainage between liquid droplets is a very complex process[11–14]. Even analysis of its individual parts frequently leads to equations which are self-consistent or can be solved only approximately or by numerical methods. Because the main aim of this paper is understanding the overall coalescence process in quiescent polymer blends, we must use several quite rough approximations in this study.

THEORY

Interaction of droplets in a Newtonian matrix

In the literature, the course of coalescence is described in the following manner[10,12]. After approaching at a certain distance, the tops of the droplets are quickly deformed and a flat film is formed between them. During this process, the width of the film is constant, but mass centres of the droplets approach as a consequence of their deformation. The process is followed by film thinning from the initial thickness h_0 to the critical thickness h_c, where film rupture occurs. During film thinning, the radii of flattened parts of the droplets are almost constant. This description of the process is based on the assumption that the driving force for the coalescence is independent of the distance between the droplets. For the velocity of film thinning, approximate relationships for systems with mobile, partially mobile and immobile interface were derived[11]. These relationships are mutually inconsistent and there are no transitions among them if parameters of the system are changed.

It was shown in our preceding paper[10] that most droplets have their nearest neighbour at a distance comparable to (or shorter than) their radii. At these distances, molecular and Brownian forces are comparable[10]. The following equation

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is valid for van der Waals' force F_w ([10])

$$F_W = \frac{32AR^6}{3h^2(2R+h)^3(4R+h)^2} \approx \frac{AR}{12h^2} \qquad (1)$$

where A is the Hamaker constant, R is the droplet radius and h is the distance between droplets. It is difficult to describe correctly film drainage between droplets the approach of which is caused by Brownian motion. However, we believe that the magnitude of the effect can be roughly estimated if the force, F_B, is defined as the ratio of the energy of Brownian motion and the distance h between the droplets. F_B can be estimated as[10]

$$F_B = \frac{kT}{2h} \qquad (2)$$

where k is the Boltzmann constant and T is the absolute temperature.

The rate of coalescence is controlled by the time necessary for film thinning from h_0 to h_c. First, we try to estimate the radius, r_f, of the plane-parallel film formed between droplets after their deformation. Usually, r_f is determined from the balance between pressure caused by external force and Laplace pressure inside the droplet[11,15]

$$\frac{F}{\pi r_f^2} = \frac{2\sigma}{R} \qquad (3)$$

where σ is the interfacial tension. It follows from equation (3) that r_f can be expressed as

$$r_f = \left(\frac{RF}{2\pi\sigma}\right)^{1/2} \qquad (4)$$

Substitution for F from equation (1) into equation (4) and choosing the values $R = 1\ \mu$m, $\sigma = 0.005$ N m^{-1} and $A = 10^{-20}$ J leads to $r_f = 0.33$ nm for $h = h_0 = 0.5\ \mu$m and $r_f = 33$ nm for $h = h_c = 5$ nm. Substitution for F from equation (2) and choosing $T = 473$ K, the same R and σ lead to $r_f = 0.46$ nm at $h_0 = 0.5\ \mu$m and $r_f = 4.6$ nm at $h_c = 5$ nm. It can be seen that $r_f \ll R$ during the whole process of coalescence. Only for h not much larger than h_c (5 nm seems to be a lower estimation of h_c) and van der Waals' forces, is the condition $r_f > h$, which is commonly used for derivation of equations describing the rate of film drainage between droplets[11,12], fulfilled. For this reason, it seems that the decisive contribution to the coalescence time is given by the approach of practically undeformed spheres. For this part of the droplets' approach, film drainage between undeformable spheres is a more adequate model than film drainage between flattened surfaces.

Coalescence of viscous undeformable droplets was studied by Zhang and Davis[14]. A general analytical relationship between the velocity of the droplets' approach and the driving force for coalescence is not available. For a long distance between the droplets, i.e. large h, the following equation is valid

$$F = -\pi\eta_m R \frac{3\eta_d/\eta_m + 2}{\eta_d/\eta_m + 1}\frac{dh}{dt} \qquad (5)$$

where η_m and η_d are viscosities of the matrix and the dispersed phase, respectively, and $-dh/dt$ is the velocity of the droplets' approach. For droplets which are very close to each other, lubrication theory can be used for analysis of the dependence of the velocity of their approach on the driving force[14,16]. Use of lubrication theory leads to the equation[14,16]

$$-\frac{1}{h}\frac{dh}{dt}g(m) = \frac{2F}{3\pi\eta_m R^2} \qquad (6)$$

The function $g(m)$ can be approximated by the following Padé-type expression[14]

$$g(m) = \frac{1 + 0.402m}{1 + 1.711m + 0.461m^2} \qquad (7)$$

where m is defined as

$$m = \frac{\eta_m}{\eta_d}\left(\frac{R}{2h}\right)^{1/2} \qquad (8)$$

It should be mentioned that slightly different numerical coefficients in expression for $g(m)$ are used in refs. 14 and 16.

For $m \to 0$ (fully immobile interface), $g(m) = 1$, and equation (6) transforms into the well-known equation for rigid spheres[11]

$$-\frac{1}{h}\frac{dh}{dt} = \frac{2F}{3\pi\eta_m R^2} \qquad (9)$$

For $m \gg 1$ (fully mobile interface), equation (6) transforms into the equation

$$-\frac{0.402\sqrt{2}}{0.461}\frac{1}{h^{1/2}}\frac{dh}{dt} = \frac{2F}{3\pi\eta_d R^{3/2}} \qquad (10)$$

As will be shown below, the starting distance between a droplet and its nearest neighbour, h_0, in typical polymer blends ($\varphi \geq 0.2$) is substantially shorter than $R/2$. Therefore, we believe that for most polymer blends the decisive contribution to the coalescence time is given by the approach of droplets from those distances for which equation (6) is applicable. For blends with a lower content of the dispersed phase, the trajectory of the droplets should be divided into parts for which the relevant equations for long, medium and short distances between droplets are applied[14]. It should be mentioned that for rigid spheres (with immobile interface), velocities calculated from equations (5) and (9) are equal for $h = R/2$. The value $R/2$ is used in the literature[3,17] for the distance at which film drainage starts. Generally, the limits of applicability of equation (6) are dependent on the ratios $2h/R$ and η_d/η_m. This is discussed in more detail in ref. 16. Substitution from equations (1), (7) and (8) into equation (6) and its integration from h_0 to h_c leads to the following equation for the coalescence time (time of film drainage), t_c, in the case of coalescence caused by van der Waals' forces

$$t_c = \frac{18\pi\eta_m R}{A}G_V \qquad (11)$$

where

$$\begin{aligned} G_V = {} & 0.5(h_0^2 - h_c^2) - A_1 pR^{1/2}(h_0^{3/2} - h_c^{3/2}) + A_2 p^2 R(h_0 - h_c) \\ & - A_3 p^3 R^3 (h_0^{1/2} - h_c^{1/2}) + A_4 p^4 R^2 \\ & \times \ln \frac{2h_0 + 1.711\sqrt{2}pR^{1/2}h_0^{1/2} + 0.461p^2R}{2h_c + 1.711\sqrt{2}pR^{1/2}h_c^{1/2} + 0.461p^2R} \\ & - A_5 p^4 R^2 \ln \frac{(4h_0^{1/2} + 0.948pR^{1/2})(4h_c^{1/2} + 3.892pR^{1/2})}{(4h_0^{1/2} + 3.892pR^{1/2})(4h_c^{1/2} + 0.948pR^{1/2})} \end{aligned} \qquad (12)$$

where A_1 to A_5 are numerical constants and

$$p \equiv \eta_m/\eta_d \qquad (13)$$

It should be pointed out that for large p, the value of G_V is extremely sensitive to the respective values of A_i and their round-off errors, which can lead to quite false values of G_V. In this case numerical integration of equation (6) leads to better results.

When the approach of droplets is caused by Brownian motion [equation (2) is used for F], substitution from equations (2), (7) and (8) into equation (6) and its integration leads to the following equation for t_c

$$t_c = \frac{3\pi\eta_m R^2}{kT} G_B \qquad (14)$$

where

$$\begin{aligned} G_B = {} & h_0 - h_c - B_1 p R^{1/2}(h_0^{1/2} - h_c^{1/2}) + B_2 p^2 R \\ & \times \ln \frac{2h_0 + 1.711\sqrt{2}pR^{1/2}h_0^{1/2} + 0.461p^2R}{2h_c + 1.711\sqrt{2}pR^{1/2}h_c^{1/2} + 0.461p^2R} \\ & - B_3 p^2 R \left(\ln \frac{4h_0^{1/2} + 0.948pR^{1/2}}{4h_0^{1/2} + 3.892pR^{1/2}} \right. \\ & \left. - \ln \frac{4h_c^{1/2} + 0.948pR^{1/2}}{4h_c^{1/2} + 3.892pR^{1/2}} \right) \end{aligned} \qquad (15)$$

where B_1, B_2 and B_3 are constants. As in the case of G_V, the function G_B is for large p extremely sensitive to values of the constants B_i. For $h_0 \gg h_c$ and $p^2R \gg h_c$, t_c values given by equations (11) and (14) are independent of h_c but are strongly dependent on the value of h_0. On the contrary, coalescence times of deformable droplets with immobile and partially mobile interfaces are dependent on h_c and not on h_0[10,11]. t_c for systems with a fully mobile interface is dependent on the ratio h_0/h_c.

Determination of h_0 is a necessary step for the description of coalescence in a system of undeformable spheres. For a system of monodisperse spheres which uniformly increase their volume during the coalescence (the model used in the preceding paper[10]), h_0 is the distance of a sphere from its nearest neighbour. The distribution function and average value of the distance between a reference sphere and its nearest neighbour for a system of impenetrable monodisperse spheres were derived by Torquato *et al.*[18]. If we define

$$h_0 = l - 2R \qquad (16)$$

where l is the distance between the centres of the nearest-neighbour spheres, it follows from equation (6.11) in [18]

$$\begin{aligned} \bar{h}_0 = 2R \int_1^{\infty} \exp\left\{ - \frac{8\varphi(1+\varphi)}{(1-\varphi)^3}(x^3 - 1) \right. \\ \left. + \frac{6\varphi^2(3+\varphi)}{(1-\varphi)^3}(x^2 - 1) - \frac{12\varphi^3}{(1-\varphi)^3}(x - 1) \right\} \mathrm{d}x \end{aligned} \qquad (17)$$

where $\bar{h}_0$ is the average value of h_0. The integral in equation (17) must be calculated numerically. For large φ, however, the following analytical asymptotic expression was found[18]

$$\bar{h}_0 = R\frac{(1-\varphi)^3}{6\varphi(2-\varphi)} \qquad (18)$$

This expression is relatively accurate for $\varphi \geq 0.2$. Since our theory is oriented on the description of coalescence in systems with higher contents of the dispersed phase, $\bar{h}_0$ given by equation (12) will be substituted for h_0 during further calculations.

In the preceding paper[10] an equation for change in the droplet radius per unit time was derived. For a blend where all droplets take part in coalescence,

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{R}{3t_c} \qquad (19)$$

Substitution from equations (11) and (18) into equation (19) leads to the following equation for a system with van der Waals' forces:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{A}{54\pi\eta_m H_V}\frac{1}{R^2} \qquad (20)$$

where H_V can be expressed as

$$H_V = \frac{1}{R^2}\int_0^{Rf} \frac{2h^2 + 0.402\sqrt{2}pR^{1/2}h^{3/2}}{2h + 1.711\sqrt{2}pR^{1/2}h^{1/2} + 0.461p^2R}\,\mathrm{d}h \qquad (21a)$$

or

$$\begin{aligned} H_V = {} & 0.5f^2 - A_1pf^{3/2} + A_2p^2f - A_3p^3f^{1/2} \\ & + A_4p^4 \ln\frac{2f + 1.711\sqrt{2}pf^{1/2} + 0.461p^2}{0.461p^2} \\ & - A_5p^4 \ln\frac{15.568f^{1/2} + 3.69p}{3.792f^{1/2} + 3.69p} \end{aligned} \qquad (21b)$$

The function f is defined as

$$f = \frac{(1-\varphi)^3}{6\varphi(2-\varphi)} \qquad (22)$$

It should be pointed out that for large p, calculation of H_V from equation (21a) by numerical methods seems to be more advantageous than using equation (21b).

Solution of equation (20) leads to the equation:

$$R^3 = R_0^3 + \frac{A}{18\pi\eta_m H_V}t \qquad (23)$$

where R_0 is the droplet radius at $t = 0$.

For coalescence induced by the Brownian motion and neglecting h_c, the equation for the time derivative of R can be derived by substitution from equations (14) and (18) into equation (19):

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{kT}{9\pi\eta_m H_B}\frac{1}{R^2} \qquad (24)$$

where

$$H_B = \frac{1}{R}\int_0^{Rf} \frac{2h + 0.402\sqrt{2}pR^{1/2}h^{1/2}}{2h + 1.711\sqrt{2}pR^{1/2}h^{1/2} + 0.461p^2R}\,\mathrm{d}h \qquad (25a)$$

or

$$\begin{aligned} H_B = {} & f - B_1pf^{1/2} + B_2p^2 \ln\frac{2f + 1.711\sqrt{2}pf^{1/2} + 0.461p^2}{0.461p^2} \\ & - B_3p^2\left\{ \ln\left(1 + \frac{4}{0.948}\frac{f^{1/2}}{p}\right) - \ln\left(1 + \frac{4}{3.892}\frac{f^{1/2}}{p}\right) \right\} \end{aligned} \qquad (25b)$$

Similarly to the previous case, using equation (25b) is not suitable for large values of p.

Equation (24) has the solution:

$$R^3 = R_0^3 + \frac{kT}{3\pi\eta_m H_B}t \tag{26}$$

Generally, H_V and H_B are functions of the ratio η_m/η_d and of volume fraction of the dispersed phase. For $p \rightarrow 0$ (immobile interface), the equations $H_V = 0.5f^2$ and $H_B = f$ are valid. Therefore, rate of coalescence is independent of the viscosity of the dispersed phase. In the case of the fully mobile interface ($p \rightarrow \infty$), equations (21) and (25) pass to the equations

$$H_V = 0.49\frac{f^{5/2}}{p}$$

$$H_B = 0.83\frac{f^{3/2}}{p}$$

It can be seen that for systems with a mobile interface, the rate of coalescence is a function of η_d but it is independent of η_m.

The effect of elastic properties of the matrix

For the drag force, $\vec{F}_D$, acting on the particle, which moves with velocity $\vec{u}$ in a quiescent medium with viscoelastic properties described by using the Maxwell model, the following equation was derived[19,20]:

$$\vec{F}_D = \zeta\vec{u} - \tau_m \frac{d\vec{F}_D}{dt} \tag{27}$$

where ζ is the frictional resistance of the particle and τ_m is the relaxation time of the Maxwell model of viscoelastic matrix. In the description of the Brownian motion, Stasiak and Cohen[20] assumed that inertial forces are negligible (this assumption is usually fulfilled for motion of small particles in a highly viscous medium) and, therefore, the following equations are valid:

$$\vec{F}_B + \vec{F}_D = 0 \tag{28}$$

$$\frac{d\vec{F}_B}{dt} + \frac{d\vec{F}_D}{dt} = 0 \tag{29}$$

Further calculations are based on the assumption that equations (28) and (29) are valid for any driving force of the particle motion and that equation (27) is also valid if ζ is determined not only by the frictional resistance of the medium but also by hydrodynamic interactions of the particles. Hydrodynamic interaction is calculated in the same manner as for a Newtonian liquid. This approximation should not lead to a qualitative change of the results because, in the limit of very weak hydrodynamic interaction, a correct expression for $\vec{F}_D$ should transform to equation (27). In this case, equation (6) for the velocity of approach of undeformable spheres can be substituted by the equation:

$$-\frac{1}{h}\frac{dh}{dt}g(m) = \frac{2}{3\pi\eta_m R^2}\left(F + \tau_m \frac{dF}{dt}\right) \tag{30}$$

It follows from equation (30) that the velocity of the droplets' approach is quicker in a viscoelastic matrix than in a Newtonian one with the same viscosity if the driving force of coalescence increases with decreasing distance between the droplets. For F decreasing with decreasing h, the velocity of the droplets' approach is lower in a viscoelastic matrix than in a related Newtonian one. This result is in agreement with the intuitive idea that transient viscosity, defined as the ratio of the shear stress to the shear rate, controls the droplet motion. It is well known that after a step increase in the shear rate (caused by an external force), the shear stress in a viscoelastic liquid increases only gradually to the steady value. Therefore, the transient viscosity is lower than the steady one. Substitution for F from equation (1) into equation (30) leads to the following equation for coalescence induced by van der Waals' forces:

$$-\left(g(m) - \frac{A\tau_m}{9\pi\eta_m R h^2}\right)\frac{dh}{dt} = \frac{A}{18\pi\eta_m R h} \tag{31}$$

On solving equation (31), the expression for t_c was obtained:

$$t_c = \frac{18\pi\eta_m R}{A}G_V - 2\tau_m \ln\frac{h_0}{h_c} \tag{32}$$

For t_c of coalescence induced by the Brownian motion, the following equation was derived by substitution from equation (2) into equation (30) and its solution:

$$t_c = \frac{3\pi\eta_m R^2}{kT}G_B - \tau_m \ln\frac{h_0}{h_c} \tag{33}$$

For systems with a lower content of the dispersed phase, i.e. larger distances between droplets at the origin of the coalescence, equation (30) should be substituted by an equation in which hydrodynamic interaction between droplets is described in a relevant manner.

It can be seen from comparison of equations (32) and (33) with related equations (11) and (14) that coalescence is quicker in a viscoelastic matrix than in a Newtonian one with the same zero shear viscosity. The decrease of t_c due to matrix elasticity is independent of the frictional resistance, but is dependent on the driving force of coalescence. The correction of the coalescence time is higher for steeper growth of the driving force with decreasing distance between the droplets. For a driving force of coalescence independent of the droplet distance, t_c is independent of the elastic properties of the matrix.

The equation describing the time dependence of the droplet radius in a system where coalescence is induced by van der Waals' forces can be derived by substitution from equation (32) into equation (9):

$$R^3 - \frac{A\tau_m}{6\pi\eta_m H_V}\ln^2\frac{fR}{h_c} = R_0^3 - \frac{A\tau_m}{6\pi\eta_m H_V}\ln^2\frac{fR_0}{h_c} + \frac{A}{18\pi\eta_m H_V}t \tag{34}$$

By using equations (19) and (33), the equation for R in a system with the Brownian-motion-induced coalescence can be derived in an analogous manner:

$$R^3 - \frac{kT\tau_m}{2\pi\eta_m H_B}\ln^2\frac{fR}{h_c} = R_0^3 - \frac{kT\tau_m}{2\pi\eta_m H_B}\ln^2\frac{fR_0}{h_c} + \frac{kT}{3\pi\eta_m H_B}t \tag{35}$$

DISCUSSION

If the assumption is made that the coalescence is controlled by the approach of undeformed droplets in a Newtonian matrix, the time dependence of the droplets' radius can be expressed as

$$R^3 = R_0^3 + Kt \tag{36}$$

where K is independent of R, R_0 and t. Equation (36) is valid for any driving force of coalescence [cf. equations (23) and

(26)]. Also, the Smoluchowski theory of coalescence[9], the theory of Ostwald ripening[6,7] and the theory of film drainage between flattened droplets in systems with a partially mobile interface and gravity driving force, and with an immobile interface and van der Waals' driving force[10], lead to an equation similar to equation (36). Moreover, a modification of the Smoluchowski theory for systems with high viscosity of the matrix[2] gives the equation:

$$R^{3/2} = R_0^{3/2} + Kt^{1/2} \tag{37}$$

It can be seen that dependences (36) and (37) can be hardly distinguished experimentally, especially for lower R_0, because experimental data show considerable scatter[2–8]. It is clear that no conclusions about the coarsening mechanism in polymer blends can be made from the shape of the dependence of R on t only.

If the approach of undeformed spheres is the decisive step in coalescence, the rate of coalescence increases with growing volume fraction of the dispersed phase and decreases with increasing viscosities of the matrix and dispersed phase. An increase in the rate of coalescence with decreasing η_d in systems with a given η_m is pronounced for systems with η_d comparable to or lower than η_m (cf. *Figure 1*). It is independent explicitly of interfacial tension. These conclusions are valid for coalescence induced by both van der Waals' forces and Brownian motion. However, interfacial tension is related to the effective Hamaker constant A in the blend, which affects the rate of coalescence induced by van der Waals' forces. In this case, the rate of coalescence increases with increasing interfacial tension. It follows from equations (34) and (35) [or equations (32) and (33)] that the rate of coalescence in a viscoelastic matrix increases with the relaxation time of the Maxwell model of the matrix. The growth of the coalescence rate with increasing volume fraction of the dispersed phase and decreasing viscosity of the matrix is in qualitative agreement with previous experimental results[5–8]. For blends with partially crosslinked inclusions, a decrease in the coalescence rate with increasing degree of crosslinking (i.e. viscosity of the dispersed phase) was found[3]. Conclusive results from experimental studies on the effect of interfacial tension or elastic

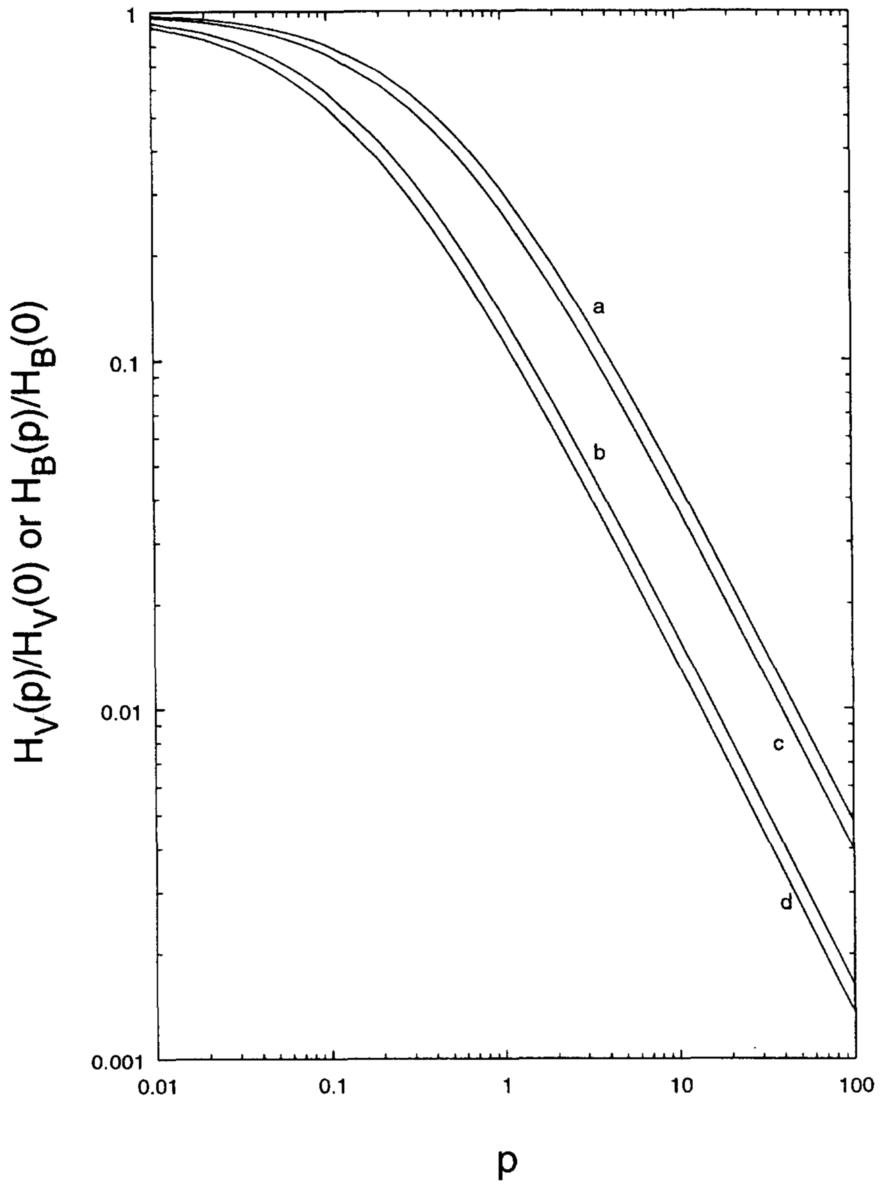

Figure 1 The functions $H_V(p)/H_V(0)$ and $H_B(p)/H_B(0)$ of the ratio of viscosities $p = \eta_m/\eta_d$. Curves: (a) and (b) $H_V(p)/H_V(0)$; (c) and (d) $H_B(p)/H_B(0)$; (a) and (c) $\varphi = 0.2$; (b) and (d) $\varphi = 0.5$

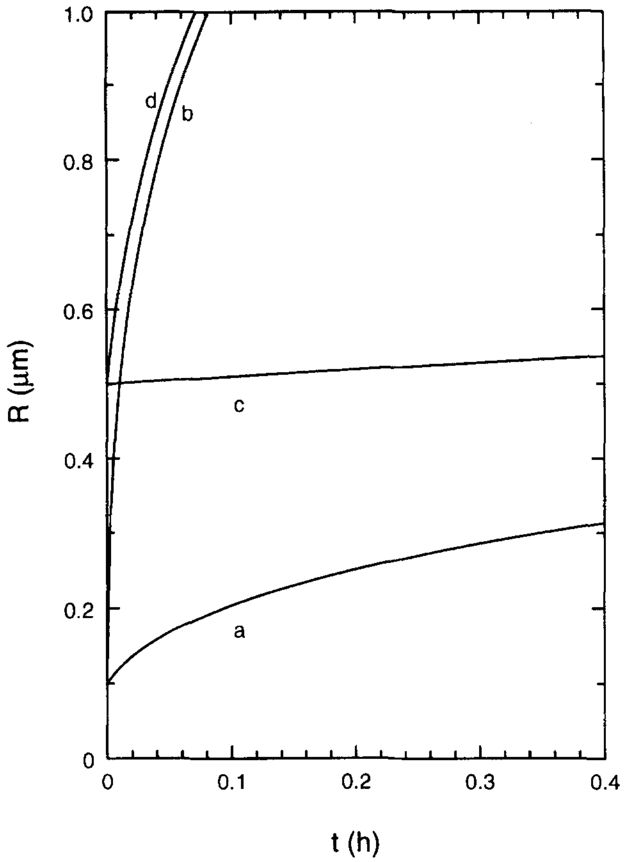

Figure 2 The time dependence of the droplet radius $R(t)$ for the van der Waals' driving force of coalescence ($\tau_m = 0$ s, $p = 1$). Curves: (a) and (b) $R_0 = 0.1$ μm; (c) and (d) $R_0 = 0.5$ μm; (a) and (c) $\varphi = 0.2$; (b) and (d) $\varphi = 0.5$

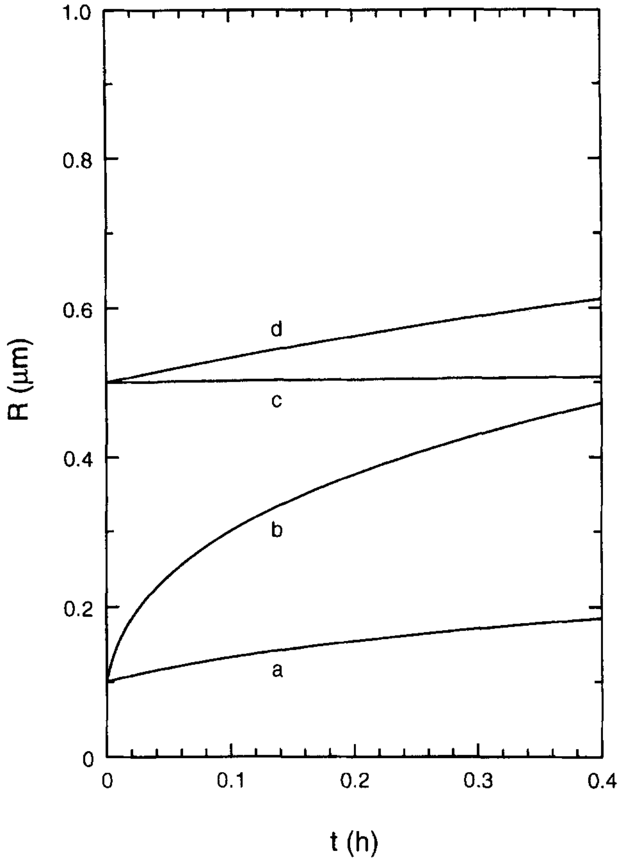

Figure 3 The time dependence of the droplet radius $R(t)$ for the Brownian driving force of coalescence ($\tau_m = 0$ s, $p = 1$). Curves: (a) and (b) $R_0 = 0.1$ μm; (c) and (d) $R_0 = 0.5$ μm; (a) and (c) $\varphi = 0.2$; (b) and (d) $\varphi = 0.5$

properties of the matrix on coalescence are not available in literature.

If values $\eta_m = 10^3$ Pa s, $\eta_m/\eta_d = 1$, $A = 10^{-20}$ J and $T = 473$ K are used for calculation of the time dependence of R according to equations (23) and (26), a strong increase in R during several minutes is predicted for systems with a higher φ (cf. *Figures 2 and 3*). The increase in rate of coalescence with φ is much stronger in systems where van der Waals' force is the driving force of coalescence. For systems with a moderate content of the dispersed phase ($\varphi = 0.2$), the increase in R during several tens of minutes is substantial for systems with low R_0 ($R_0 = 0.1$ μm) and quite small for systems with a larger R_0 ($R_0 = 0.5$ μm). It can be seen from *Figure 4* that for τ_m equal to several tens of seconds (a usual value for polymers with $\eta_m = 10^3$ Pa s), the preceding conclusions are also valid if equations (32) and (33) for systems with a viscoelastic matrix are used. For large τ_m and small R_0, equations (32) and (33) have non-monotonic solutions. This is probably caused by approximations used for the description of the problem.

In derivation of the relationships for the dependence of droplet radius on time [equations (23), (26), (34) and (35)], a number of approximations are used. Equations (23) and (34) are based on the assumption that the driving force for coalescence is a van der Waals' interaction only. On the other hand, in derivation of equations (26) and (35), it is assumed that the coalescence is caused by the Brownian motion only. Moreover, description of the Brownian motion by using the force F_B is a very rough approximation. As in polymer blends, forces F_W and F_B are comparable if the distance between droplets lies between h_0 and h_c, and a correct theory of coalescence should consider the Brownian motion and molecular forces simultaneously. It should be pointed out that the theories of Danov *et al.*[12] and Zhang and Davis[14] considering the Brownian motion and molecular forces cannot be applied straightforwardly to polymer blends. These theories are based on the assumption that a steady diffusion flux is established in the system. The assumption is not fulfilled for polymer blends[2]. A certain underestimation of the coalescence rate can be caused by the approximation used in the derivation of h_0. In our calculation, we substituted the real distribution of h_0 by its average value. If we assume that average t_c should be used in equation (19), $\overline{h_0^2}$ instead of $(\bar{h}_0)^2$ should be used for coalescence induced by van der Waals' force. If $\overline{t_c^{-1}}$ is substituted in equation (19), $\overline{h_0^{-2}}$ and $\overline{h_0^{-1}}$ instead of $(\bar{h}_0)^{-2}$ and $(\bar{h}_0)^{-1}$ should be used. The difference between a certain moment of the distribution and the related power of $\bar{h}_0$ can be pronounced. It is not quite clear which approach is more consistent with the basic approximate assumption of a uniform increase in the sphere volume[10] during coalescence. Therefore, relationships between various moments of the nearest-neighbour distribution should be the object of further research. We believe that the important reason for the possible discrepancy between theory and experimental results can be neglecting the simultaneous approach of three or more droplets. Since coalescence was studied experimentally for blends with high contents of the dispersed phase, the contribution of simultaneous interactions of three or more droplets is probably fundamental.

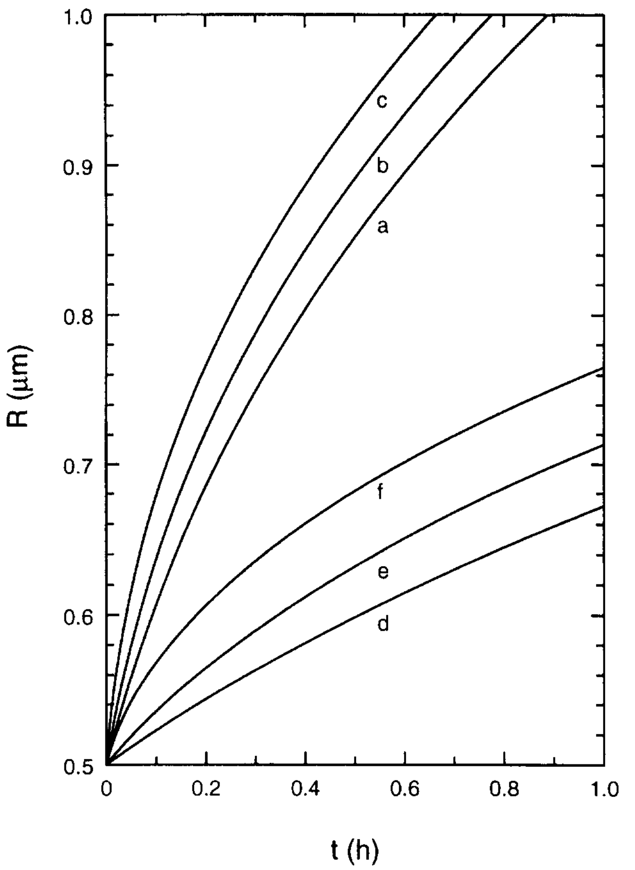

Figure 4 The influence of the relaxation time τ_m on the time dependence of the droplet radius $R(t)$. $R_0 = 0.5\ \mu m$, $\varphi = 0.35$, $p = 1$. Curves: (a), (b) and (c) van der Waals' driving force; (d), (e) and (f) Brownian driving force; (a) and (d) $\tau_m = 0$ s; (b) $\tau_m = 40$ s; (c) $\tau_m = 80$ s; (e) $\tau_m = 500$ s; (f) $\tau_m = 1000$ s

CONCLUSIONS

In quiescent molten polymer blends, non-negligible flattening of coalescing droplets appears only at the distances which are comparable to the critical distance, h_c, of film rupture. Therefore, the coalescence time is controlled by the time of the approach of undeformed droplets from the initial distance, h_0 (shorter than the droplet radius), to the distance h_c. The contributions of Brownian motion and molecular forces to the droplets' approach are comparable. The approach of the droplets is affected by their hydrodynamic interactions.

Coalescence is quicker in blends with a viscoelastic matrix than in blends with a Newtonian matrix of the same viscosity. The coalescence time decreases with increasing relaxation time of the Maxwell model of the matrix.

The equations, derived for the time dependence of droplet radius with the assumption that coalescence is caused by molecular forces or Brownian motion, predict a reasonable order of the rate of coalescence and its dependence on the parameters of the system. The approximations used in the description of the droplets' distribution, the neglecting of the synergism between Brownian motion and molecular forces and neglecting the simultaneous coalescence of three and more droplets should be the subjects of further investigation.

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