BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 21, pp. 4113–4118, 1995

0032-3861/95/$10.00+0.00

Coalescence in molten quiescent polymer blends

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(Received 30 August 1994; revised 13 December 1994)

A theory for the coalescence of droplets dispersed in molten quiescent polymer blends has been derived. The theory is based on the idea that, in blends with a higher content of the dispersed phase, a great part of the dispersed droplets are located in the close vicinity of other droplets. Drainage of the liquid film of the matrix between the colliding droplets is the decisive step in coalescence. The time dependences of droplet radius for systems with different interface mobilities and driving forces for coalescence have been compared. It has been shown that different combinations of interface mobility and driving force can lead to the same shape of the time dependence of droplet radius. The theory predicts a somewhat higher rate of coalescence than that which has been determined experimentally. It follows from the discussion of commonly used expressions for the coalescence time with partially mobile and immobile interfaces that these expressions fail in the case of a weak driving force for coalescence. The derivation of more adequate expressions for systems with a weak driving force for coalescence is necessary for a further improvement of the theory.

(Keywords: molten polymer blends; droplet coalescence; interface mobility)

INTRODUCTION

Properties of immiscible polymer blends are to a great extent determined by their morphology[1]. The morphology of polymer blends is affected by their change of structure during processing, by mechanical loading or by being at rest. For this reason, elucidation of the changes of the phase structure in molten quiescent polymer blends is one of the prime conditions for the control of their performance. Growth in the size of droplets dispersed in a matrix was observed in molten binary polymer blends kept at a constant temperature at rest[2–5]. The increase in the droplet size is apparently caused by their coalescence. However, so far there has been no satisfactory theory of coalescence describing the increase in droplet size with time.

The course of coalescence of dispersed droplets can be divided into four steps[6,7]:

1. *approach* of the droplets;
2. *deformation* of the droplets due to the axial force and removal of the continuous phase trapped between the droplets;
3. *rupture* of the remainder of the continuous phase, usually by the formation of a 'hole' on the thinnest spot;
4. *evolution* of the 'neck' to form a coalesced droplet.

Before the formulation of a theory of coalescence, the individual steps should be analysed. At rest, the approach of the droplets may be caused by Brownian motion or gravity. In molten polymer blends, owing to the high viscosity of the matrix and the small difference in densities of the components, gravity leads to a very slow motion[6]. Moreover, coalescence induced by a strong gravitational force should lead to a gradient of concentration of the dispersed phase in the direction of gravity. Brownian motion is generally considered as the reason for coalescence in colloid systems[8]. The theory of coalescence induced by Brownian motion was already elaborated by Smoluchowski[9]. This theory describes the time dependence of the size of dispersed droplets in emulsions rather successfully[8]. The Smoluchowski theory is focused mostly on the first step of coalescence, i.e. on the approach of droplets. Further steps of coalescence are taken into account by calculation of the probability that the collision of droplets is followed by their fusion.

The attempt to apply straightforwardly the Smoluchowski theory to the description of coalescence in polymer blends was not successful, because the theory predicted a much slower (practically immeasurable) increase in droplet size with time than that obtained experimentally[2]. In the preceding work[3], we tried to modify the Smoluchowski theory by removing the approximation for droplet flux, which is justified only for systems with low viscosity of the matrix. For blends with highly viscous matrix the modified theory predicts substantially quicker coalescence than the original theory. However, the modified theory still predicts substantially slower coalescence than the one determined experimentally[3]. We believe that the main reason for the contradiction between the modified theory and experiment is the fact that this theory was derived for dilute systems where only collisions of pairs of droplets, which

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are far from each other at the start of coalescence, are taken into account. On the other hand, coalescence has been studied experimentally only for systems containing a high percentage (more than 10%) of the dispersed phase. We believe that a second possible reason for the discrepancy, i.e. neglect of the elastic properties of the components of polymer blends, has lower importance.

Van Gisbergen and Meijer[4] tried to calculate the rate of coalescence using the assumption that the second step of coalescence fully determines its rate. They compared three expressions for the coalescence time: for mobile, partially mobile and immobile interfaces. For the mobile interface, a quicker coalescence than that experimentally observed is predicted. Coalescence times for systems with partially mobile and/or immobile interfaces are explicitly dependent on the driving force for coalescence[4,10,11]. Too short coalescence times were obtained for systems with partially mobile and immobile interfaces if gravity was used as the driving force for coalescence. A reasonable description of coalescence in a polystyrene/polyethylene blend was obtained when a much stronger force than gravity (with the same dependence on particle size) was substituted into the expression for the coalescence time of systems with partially mobile interface. Moreover, their treatment leads to the independence of the coalescence rate on the concentration of dispersed droplets. This is in strict disagreement with other experimental results[3].

In this work, we try to formulate a theory that adequately describes coalescence in polymer blends with a higher content of the dispersed phase. This study will be focused on the effect of the content of the dispersed phase and on the effect on coalescence of various driving forces that can be operative in quiescent polymer blends. We use the idea that in these blends many droplets are at such short distances from each other that the second step of coalescence between them can start immediately after the end of mixing. The coalescence rate will be determined by the number of pairs of close droplets, which is dependent on the volume fraction of the dispersed phase, and by the course of the second step of coalescence. The contribution of the third step of coalescence will be substantially smaller than that of the second one[6,12]. The inclusion of the fourth step into the coalescence time depends on the decision whether coalescence is finished by the merging of the droplets or after the formation of a new droplet with spherical shape. In the present theory, the fourth step will not be taken into account. In the theory, the contribution of originally distant droplets, which approach by Brownian motion, is neglected. In blends with high viscosity of the matrix and higher content of the dispersed phase, this contribution will not be important. In blends with a volume fraction of the dispersed phase, ϕ, higher than 0.1, many droplets practically touch, because a system of spheres has its percolation threshold at $\phi = 0.156$[13]. However, in a blend with very low content of the dispersed phase, the rate of coalescence is determined by the first step, which is adequately described by our preceding theory[3].

THEORY

A system of monodisperse spheres, randomly distributed in space at time $t = 0$, will be studied. The assumption is made that a sphere takes part in coalescence if the distance of its surface from the surface of any other sphere is less than the critical distance τ. The time of coalescence, t_c, will be determined by the duration of the second step. For this model, the change in the number of spheres per unit time, dn/dt, due to coalescence, is described by the equation:

$$dn/dt = -fpn \tag{1}$$

where n is the number of spheres in unit volume, p is the probability that the surface of a certain sphere is less than the critical distance from the surface of any other sphere, and the frequency of coalescence, f, is given by:

$$f = 1/t_c \tag{2}$$

where t_c is the time of coalescence determined by the second step of coalescence[4,12].

For the distribution function, $P(z)$, of distances between surfaces of randomly distributed spheres of radius R, Lu and Torquato[14] derived the equation:

$$P(z) = [\pi n R^2/(1-\phi)] \exp[-\pi n R^2 z/(1-\phi)] \tag{3}$$

where ϕ is the volume fraction of spheres and z is the distance between the surfaces of the spheres. For the probability, p_1, that in a certain direction the distance between the surface of a chosen sphere and that of its nearest neighbour is shorter than τ, the following equation is valid:

$$p_1 = \int_0^\tau P(z)\, dz \tag{4}$$

After substitution from equation (3) into equation (4), it follows that:

$$p_1 = 1 - \exp[-\pi n R^2 \tau/(1-\phi)] \tag{5}$$

In the description of coalescence, we will suppose that during coalescence systems of spheres remain monodisperse. Only the radii of spheres are time-dependent. In the preceding paper[3], we showed that, for the Smoluchowski theory of coalescence, this assumption leads to the same result as the usually applied approximation for the coefficient of the mutual diffusion. Also Van Gisbergen and Meijer[4] assumed that the system of spheres remains monodisperse. Under this assumption equation (1) is valid during the whole coalescence, not only at its start. The quantities n and R are related, at an arbitrary time t, by the equation:

$$n(t) = 3\phi/\{4\pi[R(t)]^3\} \tag{6}$$

Equation (6) makes it possible to exclude one of these variables from the preceding equations. Because R is determined from experiments, we will study the time dependence of R. After substitution from equation (6), equation (5) can be rewritten as:

$$p_1 = 1 - \exp\{-3\phi\tau/[4(1-\phi)R]\} \tag{7}$$

Searching for the probability, p, that in the neighbourhood of a certain sphere there exists a sphere with a distance from the surface of the chosen sphere shorter than τ, we assume that in six perpendicular directions (axes of the Cartesian coordinate system), the distributions of distances between spheres are mutually independent. The probability p_1 in an individual direction is given by equation (7). Under these assumptions, for the probability p the following equation holds:

$$p = 1 - \exp\{-9\phi\tau/[2(1-\phi)R]\} \qquad (8)$$

The time of coalescence, t_c, is dependent on the mobility of the interface and on the driving force of the particles[4,10,12]. There are three theories that model the process of drainage of the film between particles. They differ in the mobility of the interfaces: fully mobile, partially mobile or immobile interfaces are taken into account. The theory for the fully mobile interface is based on the assumption that during film drainage the interface is effectively shear-stress-free and flows with the velocity of the matrix film between droplets. This assumption is adequate for systems with low viscosity of the droplets. For systems with partially mobile interface, the assumption is made that the flow generated in the droplet by the draining film controls removal of the matrix material trapped between the droplets. For systems with immobile interface, no motion of the interface in the direction perpendicular to the film thinning direction is assumed. This assumption is reasonable for systems with very high viscosity of the dispersed phase or containing surfactants. All three theories of film drainage are approximate. Their derivation is described in Chesters' paper[10].

The rate of film drainage, dh/dt, for the fully mobile interface is given by[6,10,11]:

$$-dh/dt = 2\sigma h/(3\eta_m R) \qquad (9)$$

where σ is the interfacial tension, h is the distance between the surfaces of the colliding droplets and η_m is the viscosity of the matrix.

In the case of partially mobile interface, the rate of film drainage is described by the equation[10,11]:

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

where η_d is the viscosity of the dispersed phase and F is the driving force for coalescence.

For a system with immobile interface, the following expression for dh/dt was derived[6,10,11]:

$$-dh/dt = 8\pi\sigma^2 h^3/(3\eta_m R^2 F) \qquad (11)$$

Equations (10) and (11), describing systems with partially mobile and immobile interfaces, contain explicitly the force, F, that induces the mutual approach of the droplets. While for flow-induced coalescence the driving force is evident[6,10], the situation is not quite clear for quiescent polymer blends. We believe that, generally, the driving force can be gravity (taken into account by Van Gisbergen and Meijer[4]), Brownian motion (of spheres as a whole and/or fluctuation of droplet shape) or molecular forces (e.g. van der Waals) between droplets. We try to estimate the magnitude of these forces in typical blends of immiscible polymers.

The gravitational force, F_g, affecting a droplet can be expressed as:

$$F_g = (4/3)\pi g \Delta\rho R^3 \qquad (12)$$

where g is the acceleration due to gravity and $\Delta\rho$ is the density difference between the dispersed phase and the matrix. For $R = 10^{-6}$ m and $\Delta\rho = 100\,\mathrm{kg\,m^{-3}}$, $F_g = 4.2 \times 10^{-15}$ N. However, it should be pointed out that the gravitational force given by equation (12) leads to simultaneous motion of monodisperse droplets to the bottom or top of the system. It does not induce the mutual approach of the droplets, if hydrodynamic interaction between them and their polydispersity are neglected.

It is difficult to formulate a relation for the force F_B causing Brownian motion of droplets. However, we believe that F_B can be estimated as the ratio of the energy of Brownian motion ($kT/2$ per degree of freedom) and the distance h between droplets. Thus F_B can be expressed as:

$$F_B = kT/(2h) \qquad (13)$$

For $T = 473$ K and $h = 5 \times 10^{-7}$ m ($h = R/2$), from equation (13) it follows that $F_B = 6.5 \times 10^{-15}$ N.

The van der Waals force between two equally sized droplets with radius R at distance h is described by the equation[6]:

$$F_W = 32AR^6/[3h^2(2R+h)^3(4R+h)^2] \qquad (14)$$

where A is the Hamaker constant. For $A = 10^{-20}$ J, $R = 10^{-6}$ m and $h = 5 \times 10^{-7}$ m, equation (14) gives $F_W = 1.35 \times 10^{-15}$ N.

It can be seen that individual forces depend in a different manner on the size of droplets, distance between them and properties of the blend components. It should be pointed out that Brownian and van der Waals forces increase with decreasing distance between particles, i.e. during the thinning of the continuous phase trapped between the droplets. For parameters typical of polymer blends at the start of coalescence, forces F_g, F_B and F_W are of the same order of magnitude.

Because the ratio of magnitudes of the forces mentioned above is different in different polymer blends, the effect of all these forces on coalescence will be studied for the systems with partially mobile and immobile interfaces.

Mobile interface

The coalescence time, t_c, is defined as the time during which the distance between droplets, h, decreases from the distance at the origin of coalescence, τ, to the critical distance, h_c, at which a hole is created. It follows from equation (9) that:

$$t_c = [3\eta_m R/(2\sigma)]\ln(\tau/h_c) \qquad (15)$$

Combination of equations (1), (2) and (6) leads to the equation:

$$dR/dt = pR/(3t_c) \qquad (16)$$

After substitution from equations (8) and (15) into equation (16), it follows that:

$$\frac{dR}{dt} = \frac{2\sigma\{1 - \exp[-9\phi\tau/(2(1-\phi)R)]\}}{9\eta_m \ln(\tau/h_c)} \qquad (17)$$

Frequently, the assumption[4]:

$$\tau = R/2 \qquad (18)$$

is made. Using assumption (18) and the condition:

$$R(0) = R_0 \qquad (19)$$

equation (17) has the following solution:

$$R\{\ln[R/(2h_c)] - 1\} = R_0\{\ln[R_0/(2h_c)] - 1\} + [2\sigma/(9\eta_m)] \times \{1 - \exp[-9\phi/(4(1-\phi))]\}t \tag{20}$$

If τ is not proportional to the first power of R, equation (17) must be solved by a numerical method.

Partially mobile interface

For a force independent of h, it follows from equation (10) for t_c that:

$$t_c = [0.5\pi\eta_d F^{1/2} R^{3/2}/(2\pi\sigma)^{3/2}](1/h_c - 1/\tau) \tag{21}$$

In the systems studied:

$$h_c \ll \tau \tag{22}$$

For this reason, in further calculations $1/\tau$ will be neglected compared with $1/h_c$. For the gravity-induced coalescence, the equation for t_c can be obtained by substitution from equation (12) into equation (21). It follows that:

$$t_c = (g\Delta\rho)^{1/2}\eta_d R^3/[\sqrt{3}(2\sigma)^{3/2}h_c] \tag{23}$$

Substitution from equations (23) and (8) into equation (16) leads to the following equation for $\mathrm{d}R/\mathrm{d}t$:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{(2\sigma)^{3/2}h_c}{(3g\Delta\rho)^{1/2}\eta_d R^2}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{24}$$

Using assumption (18) and condition (19), the solution of equation (24) can be expressed as:

$$R^3 = R_0^3 + \frac{2\sqrt{6}\sigma^{3/2}h_c}{\eta_d(g\Delta\rho)^{1/2}}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \tag{25}$$

For Brownian motion-induced coalescence, t_c can be determined by solution of equation (10) after substitution for F from equation (13). For t_c, the following expression holds:

$$t_c = \eta_d(kT)^{1/2}R^{3/2}/(12\pi^{1/2}\sigma^{3/2}h_c^{3/2}) \tag{26}$$

After substitution from equations (26) and (8) into equation (16) it follows that:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{4\pi^{1/2}\sigma^{3/2}h_c^{3/2}}{\eta_d(kT)^{1/2}R^{1/2}}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{27}$$

Using equations (18) and (19), solution of equation (27) leads to the expression:

$$R^{3/2} = R_0^{3/2} + \frac{6\pi^{1/2}\sigma^{3/2}h_c^{3/2}}{\eta_d(kT)^{1/2}}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \tag{28}$$

For coalescence induced by van der Waals forces, substitution from equation (14) into equation (10) and solution of the latter equation leads to the following expression for t_c:

$$t_c = A^{1/2}\eta_d R^2/[16(6\pi)^{1/2}\sigma^{3/2}h_c^2] \tag{29}$$

After substitution from equations (29) and (8), equation (16) can be rewritten as:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{16(6\pi)^{1/2}\sigma^{3/2}h_c^2}{3A^{1/2}\eta_d R}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{30}$$

For $\tau = R/2$, the solution of equation (30) can be expressed as:

$$R^2 = R_0^2 + \frac{32(6\pi)^{1/2}\sigma^{3/2}h_c^2}{3A^{1/2}\eta_d}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \tag{31}$$

Immobile interface

For F independent of h, the following equation for t_c can be derived from equation (11):

$$t_c = 3\eta_m R^2 F/(16\pi\sigma^2 h_c^2) \tag{32}$$

Substitution for F from equation (12) into equation (32) leads to the following equation for the time of coalescence induced by a gravitational force:

$$t_c = \eta_m g\Delta\rho R^5/(4\sigma^2 h_c^2) \tag{33}$$

After substitution from equations (8) and (33), it follows from equation (16) that:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{4\sigma^2 h_c^2}{3\eta_m g\Delta\rho R^4}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{34}$$

With assumption (18) and condition (19), equation (34) has the solution:

$$R^5 = R_0^5 + \frac{20\sigma^2 h_c^2}{3\eta_m g\Delta\rho}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \tag{35}$$

If coalescence is induced by Brownian motion, expression (13) must be substituted into equation (11). In this case, the following equation for t_c is obtained by solution of equation (11):

$$t_c = \eta_m R^2 kT/(16\pi\sigma^2 h_c^3) \tag{36}$$

Substitution from equations (8) and (36) into equation (16) leads to the equation:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{16\pi\sigma^2 h_c^3}{3\eta_m kTR}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{37}$$

For $\tau = R/2$, the following time dependence of R is obtained by solution of equation (37):

$$R^2 = R_0^2 + \frac{32\pi\sigma^2 h_c^3}{3\eta_m kT}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \tag{38}$$

For coalescence induced by van der Waals forces, the following equation for t_c can be derived by solution of equation (11), where F is substituted from equation (14):

$$t_c = 3\eta_m AR^3/(128\pi\sigma^2 h_c^4) \tag{39}$$

After substitution from equations (8) and (39) into equation (16), the following equation is derived for a system with immobile interface where a van der Waals force is the driving force for coalescence:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{128\pi\sigma^2 h_c^4}{9\eta_m AR^2}\left[1 - \exp\left(\frac{-9\phi\tau}{2(1-\phi)R}\right)\right] \tag{40}$$

If equations (18) and (19) are taken into account, equation (40) has the solution:

$$R^3 = R_0^3 + \frac{128\pi\sigma^2 h_c^4}{3\eta_m A}\left[1 - \exp\left(\frac{-9\phi}{4(1-\phi)}\right)\right]t \qquad (41)$$

DISCUSSION

Comparison of equations (20), (25), (28), (31), (35), (38) and (41) leads to the conclusion that the same shape of the dependence of R on t can result from different assumptions about the mobility of the interface and the driving force for coalescence. It is apparent that no decision about interface mobility and driving force for coalescence should be based on the shape of the dependence of R vs. t only. It should be pointed out that for $\tau = R/2$, our equations for systems with mobile, partially mobile and immobile interfaces, and using the gravitational force, differ from van Gisbergen's and Meijer's results[4] only by the probability p, which in turn is dependent on ϕ only. For $\phi = 0.2$, p achieves the value 0.4302. For this reason, unrealistic (too high) rates of coalescence are predicted by this theory if the same parameters as in ref. 4 are used for calculation.

Therefore, we compare rates of coalescence calculated for systems with different interface mobility and driving force for coalescence. Parameters similar to the parameters for polystyrene/polyethylene (PS/PE) blends used in ref. 4 are used for calculation. These parameters are collected in *Table 1*. The critical distance for film rupture, h_c, is not a measurable quantity. Therefore, we also study its effect. We believe that there are two reasonable assumptions about the critical distance for the origin of film drainage, τ. The first assumption is that τ is proportional to the droplet radius R. This assumption is frequently used in the literature[4,11]. The second assumption is that τ is a parameter independent of R. This assumption is supported by the fact that the critical concentration of the dispersed phase for the yield stress effect increases with increasing size of the dispersed particles[15]. This fact leads to the conclusion that the range of the interparticle forces does not increase proportionally to the particle radius. For this reason, calculations of the functions $R(t)$ for $\tau = R/2$ and $\tau = R_0/2$ are compared.

It can be seen in *Figure 1* that the increase in R with increasing t is substantially smaller for constant τ than for τ proportional to R. The increase in h_c leads to higher velocity of coalescence. The curve R vs. t, calculated for $\tau = R_0/2$ and $h_c = 5\,\text{nm}$, seems to be the most realistic one, but the rate of coalescence is still about one order of magnitude higher than the experimental one for uncrosslinked PS/PE blend[4]. In *Figure 1* also the effect of concentration of the dispersed phase on coalescence can be seen (cf. curves 4, 5 and 6).

Table 1 The parameters used in calculation of $R(t)$ dependences

Quantity	Symbol	Used values
Temperature	T	473 K
Volume fraction of dispersed phase	ϕ	0.1–0.5
Droplet radius at the origin	R_0	10^{-6} m
Critical distance at the origin	τ	see text
Critical distance for film rupture	h_c	5×10^{-9} to 5×10^{-8} m
Viscosity of dispersed phase	η_d	1000 Pa s
Viscosity of matrix	η_m	1000 Pa s
Interface tension	σ	0.005 N m^{-1}
Difference of densities between matrix and dispersed phase	$\Delta\rho$	150 kg m^{-3}
Acceleration due to gravity	g	9.81 m s^{-2}
Boltzmann constant	k	1.38×10^{-23} J K^{-1}
Hamaker constant	A	10^{-20} J

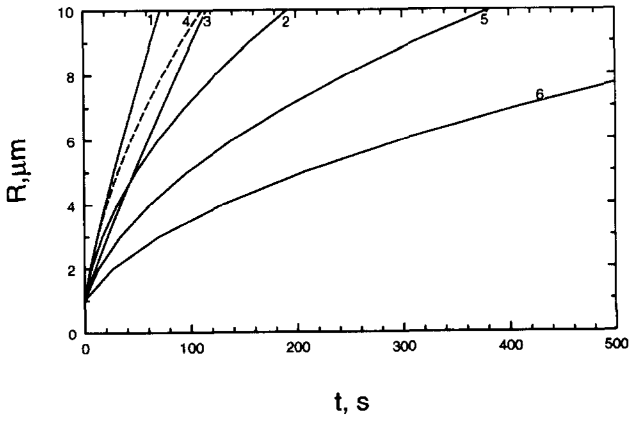

Figure 1 The time dependence of the droplet radius $R(t)$ for a *mobile* interface. Curves: (1) and (2) $h_c = 5 \times 10^{-8}$ m, $\phi = 0.2$, $\tau = R/2$ (1), $\tau = R_0/2$ (2); (3) $h_c = 5 \times 10^{-9}$ m, $\phi = 0.2$, $\tau = R/2$; (4), (5) and (6) $h_c = 5 \times 10^{-9}$ m, $\tau = R_0/2$, $\phi = 0.5$ (4), $\phi = 0.2$ (5), $\phi = 0.1$ (6). For other parameters, see *Table 1*

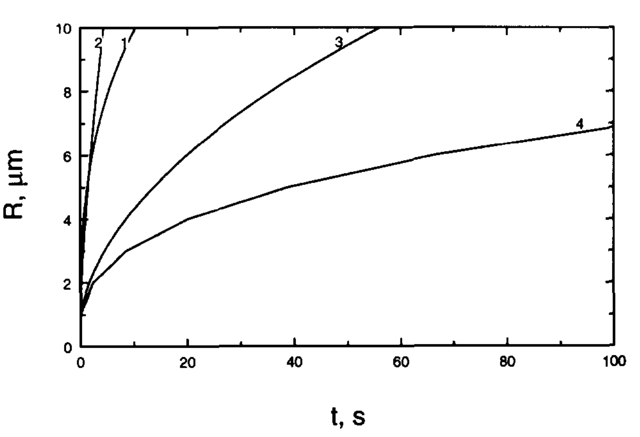

Figure 2 The time dependence of the droplet radius $R(t)$ for a *partially mobile* interface, for $h_c = 5 \times 10^{-9}$ m and $\phi = 0.2$. Curves: (1), (2) and (3) $\tau = R/2$; (4) $\tau = R_0/2$; (1) gravity driving force; (2) Brownian motion driving force; (3) and (4) van der Waals driving force. For other parameters, see *Table 1*

For systems with partially mobile interface, an unrealistic steep growth of the droplet size with increasing time is predicted for all the considered driving forces (see *Figure 2*). A higher rate of coalescence than for systems with fully mobile interface was obtained even for the system with $h_c = 5\,\text{nm}$, $\tau = R_0/2$ and the van der Waals driving force (see *Figures 1* and *2*).

For the systems with immobile interface, too steep increase in R with t is predicted for all driving forces, if $h_c = 50\,\text{nm}$ is taken into account. In the case of $h_c = 5\,\text{nm}$, both the gravity- and Brownian motion-induced coalescences lead to a substantially steeper increase of R than the experimentally determined one. However, the rate of coalescence, calculated by using equation (40), is comparable with the experimentally determined one (see *Figure 3*). In this case, the function $R(t)$ is very sensitive to the value of h_c (cf. equation (41) and *Figure 3*).

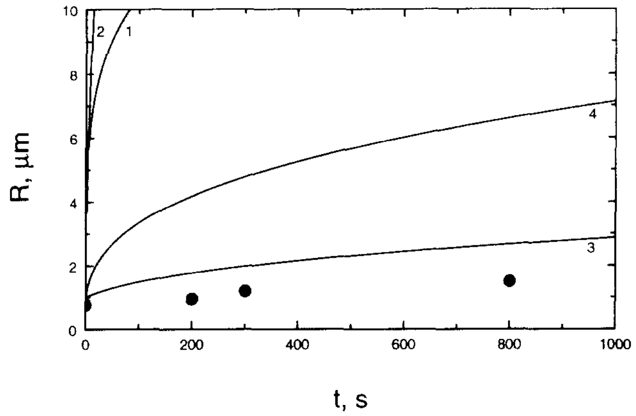

Figure 3 The time dependence of the droplet radius $R(t)$ for an *immobile* interface, for $\tau = R/2$ and $\phi = 0.2$. Curves: (1), (2) and (3) $h_c = 5 \times 10^{-9}$ m; (4) $h_c = 10^{-8}$ m; (1) gravity driving force; (2) Brownian motion driving force; (3) and (4) van der Waals driving force. (●) Experimental points according to ref. 4. For other parameters, see *Table 1*

It follows from the above discussion that for $h_c \geq 5$ nm values of $R(t)$ comparable with experimental ones are predicted only for a system with immobile interface on the assumption that coalescence is induced by the van der Waals force. A suitable choice of h_c can lead to a good agreement of the time dependence of R with experimental results from ref. 4. However, a satisfactory model should correctly describe also the dependence of particle size on the viscosity of the dispersed phase and of the matrix. Theories for systems with fully mobile and immobile interfaces predict a decrease in the rate of coalescence with increasing viscosity of the matrix and its independence on the viscosity of the dispersed phase. On the other hand, the theory for systems with partially mobile interface predicts for the coalescence rate a decrease with increasing viscosity of the dispersed phase and independence on the viscosity of the matrix. The decrease in the rate of coalescence with increasing viscosity of the dispersed phase was verified for coalescence in the quiescent state[4] and in a flow field[16]. So far, a dependence of the coalescence rate on the viscosity of the matrix has been neither confirmed nor refuted. It is apparent that any investigated expression for the time evolution of the droplet size does not describe experiments satisfactorily. In a discussion of the results for systems with various mobility of the interface, it should be remembered that equations (9)–(11) are derived only in an approximate manner for a sufficiently strong driving force. For systems with partially mobile and immobile interfaces, non-physical expressions are obtained for the time of coalescence t_c in the case of very weak driving forces. If the driving force for coalescence F goes to 0, t_c also goes to 0, i.e. the rate of coalescence goes to infinity (see equations (21) and (32)). This leads to the paradox that the weakest force causes the quickest coalescence in systems where several driving forces exist simultaneously. It is apparent that the non-physical behaviour of equations (10) and (11) (or (21) and (32)) represents a much more serious limitation of their applicability in this theory than in the theory of flow-induced coalescence. In the latter case, an unrealistic low t_c for low F, i.e. low shear rates, is fully compensated by a very low probability of droplet collision[6,11] under these conditions. We believe that an adequate description of film drainage in systems with partially mobile and immobile interfaces is the most important condition for further improvement of the theory of coalescence in polymer blends at rest.

In spite of the trouble associated with the description of film drainage in systems with partially mobile and immobile interfaces, we believe that this theory gives a reasonable description of coalescence in quiescent polymer blends. Although the rate of coalescence is somewhat overestimated by the theory, the results for systems with mobile, partially mobile and immobile interfaces and van der Waals driving force are in better agreement with experiments than the results of the preceding theories[3,8]. It seems that the van der Waals force is the driving force for coalescence at rest for most polymer blends.

CONCLUSIONS

A theory of coalescence in molten quiescent polymer blends with a higher content of the dispersed phase was derived. The theory gives a reasonable dependence of the rate of coalescence on the content of the dispersed phase. Its results agree with experiments better than the results of the preceding theories.

It was shown that it is impossible to decide about interface mobility and driving force for coalescence from knowledge of the dependence of R vs. t only.

A more adequate description of film drainage between droplets, caused by a weak force, is necessary for further improvement of the theory.

ACKNOWLEDGEMENTS

The authors would like to thank the Grant Agency of the Academy of Sciences of the Czech Republic for its support by Grants No. 45055 and 450102.

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