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Theoretical description of steady droplet size in polymer blends containing a compatibilizer

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Abstract

A theory was derived which describes the dependence of the size of dispersed droplets on the composition of compatibilized polymer blends in steady shear flow. The effect of droplets breakup and coalescence on the interfacial area available for molecules of a compatibilizer and, hence, on interfacial tension has been considered. Dependences of the droplet size on the volume fraction of the dispersed phase has been determined for the following cases: (i) constant density of a compatibilizer on the interface; (ii) all compatibilizer molecules are localized on the interface; (iii) maximum density of a compatibilizer on the interface exists which is characteristic of the system under study. The shapes of the dependences of the droplet size on the amount of dispersed phase for these cases are different. They strongly differentiate if the total amount of a compatibilizer or the ratio of the amount of compatibilizer to that of dispersed phase is constant during an increase in volume fraction of the dispersed phase. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Breakup; Coalescence

1. Introduction

It is well known that most polymer pairs form blends with coarse phase structure and bad mechanical properties. Fine phase structure and improvement in mechanical properties can be achieved by the addition of block and graft copolymers with blocks, which are identical or miscible with the blend components. An effect of amount and molecular properties of copolymers on the phase structure and mechanical properties of polymer blends was studied intensively [1–5]. A number of important results have been obtained; however, discrepancies still exist in views on the effect of copolymer architecture on its compatibilization efficiency [4,5].

Also interrelations between the effect of a compatibilizer and mixing conditions on the phase structure development in polymer blends was studied experimentally [6–8].

Substantially smaller attention was paid to the theoretical analysis of the phase structure development at mixing. Tang and Huang [9] tried to describe the effect of a compatibilizer on the size of dispersed droplets in polymer blends. They assumed that the interfacial tension of compatibilized polymer blends decreases exponentially with increasing concentration of a compatibilizer (relative to the content of a dispersed phase) from the value for uncompatibilized blend to the value related to saturation of the interface by the compatibilizer. The particle size is calculated from the Taylor equation for the critical droplet size at breakup. This approach is justified only for blends containing very small fractions of the dispersed phase because coalescence, which has a significant effect on the particle size starting from blends containing only few per cent of the dispersed phase [10–13], is fully neglected. Milner and Xi [14] considered the effect of a compatibilizer on both breakup and coalescence of dispersed droplets. They made the conclusion that the decrease in interfacial tension due to a compatibilizer is small and, therefore, it does not affect breakup of the droplets. However, this conclusion is in strong disagreement with the results of other experimental and theoretical studies where substantial effect of a compatibilizer on interfacial tension was found [15–19]. They assumed that a compatibilizer suppresses mobility of the interface thus lowering the probability of coalescence. The probability of coalescence was calculated for undeformed droplets. At flow induced coalescence, however, substantial flattening of droplets occurs [20–22].

Recently, the breakup by stepwise and transient mechanisms and coalescence of dispersed droplets in polymer blends containing a compatibilizer were analyzed [23,24]. In these blends, the droplet breakup and coalescence are affected by a change in interfacial tension due to the

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Nomenclature

C	Function of the mobility of the interface (Eq. (10))
c_ϕ	Number of copolymer molecules per volume unit
Ca	Capillary number
Ca_c	Critical capillary number for droplet breakup
f	Function of rheological properties of the dispersed phase and matrix (Eq. (11))
F	Driving force of the coalescence
g	Function of molecular parameters of the copolymer (Eq. (1))
g'	$g/27$
h_0	Distance between droplets at the beginning of the coalescence
h_c	Distance at which matrix film trapped between droplets bursts
l	Ratio of the circulation length and the distance of droplets (Eq. (6))
n	Number of droplets in the volume unit
P_c	Probability that collision of the droplets will be followed by their fusion
q	Density of the copolymer molecules on the interface
q_m	Maximum density of the copolymer on the interface
Q	Total number of copolymer molecules on the interface
Q_e	Total amount of a copolymer in the volume unit of a blend
R	Radius of the droplet
R_c	Radius of the droplet in infinitely diluted system
R_m	Droplet radius relating to $q = q_\mathrm{m}$
S	Interfacial area in the system
t	Time
t_B	Breakup time of the droplet
t_c	Time necessary for the approach of the droplets from h_0 to h_c
t_i	Interaction time (Eqs. (4) and (5))
$\dot{\gamma}$	Shear rate
η_d	Viscosity of the dispersed phase
η_m	Viscosity of the matrix
λ	Ratio of the viscosities of the dispersed phase and matrix
σ	Interfacial tension
σ_0	Interfacial tension of the blend without a compatibilizer
σ_e	Interfacial tension at $q = \mathrm{const.}$
ϕ	Volume fraction of the dispersed phase
$\partial\sigma/\partial r$	Interfacial tension gradient at the periphery of the film between coalescing droplets

presence of a compatibilizer and its migration along the interface and between the interface and bulk phases. For the stepwise mechanism, a lowering of the interfacial tension due to the presence of a compatibilizer causes easier droplet breakup. The breakup is enhanced also by convection of a compatibilizer towards the stagnant points, which leads to a local decrease in interfacial tension. It is suppressed by dilution of a compatibilizer on the droplet surface caused by the droplet deformation. The magnitude of these effects depends on the rate of compatibilizer migration along the interface and between the interface and bulk phases.

The breakup time of highly stretched droplet by the transient mechanism is inversely proportional to the interfacial tension [23,24]. It follows from an analysis of the breakup of a long viscoelastic cylinder in a system containing a compatibilizer that its breakup is slower than in an uncompatibilized system with the same interfacial tension and rheological properties [24,25]. It should be considered that the presence of a compatibilizer leads to easier droplet deformation and that the interfacial tension of highly elongated droplet is substantially larger than that of the spherical droplet covered by the same amount of a compatibilizer.

The probability that the droplets collision will be followed by their fusion is lowered in a compatibilized system due to a lower interfacial tension and a decrease in the interface mobility [23,24]. For description of a competition between breakup and coalescence of the droplets, not only the effect of a compatibilizer on the breakup and coalescence should be considered but also the fact that the droplet breakup leads to an increase and coalescence causes a decrease in the interfacial area of a system. A change in the interfacial area induces a change of the interfacial tension. The aim of the contribution is derivation of a theory of the phase structure development, which takes into account changes in the interfacial tension. The theory is focused namely on the description of a dependence of the size of dispersed droplets in steady flow on the content of the dispersed phase in a blend.

2. Theory

A number of relations for a decrease in the interfacial tension caused by the presence of a compatibilizer (block or graft copolymer) on the interface have been derived [15–18]. We use the equation derived by Lyatskya et al. [15] which expresses interfacial tension as an explicit function of the interfacial area. The equation for the interfacial tension, σ, can be written as

$$\sigma = \sigma_0 - gQ^3/S^3 = \sigma_0 - gq^3 \tag{1}$$

where σ_0 is the interfacial tension of the blend without a compatibilizer, g a function of molecular parameters of the polymer, Q the total number of the copolymer molecules on the interface, S the whole interfacial area and q is the density of the copolymer molecules on the interface. In analysis of the phase structure development, it must be considered that Q is not the number of copolymer molecules added to a system. A part of the copolymer can be localized in one or both of bulk phases.

A system of monodisperse spheres with the radius R, which remains monodisperse also during breakup and coalescence of the droplets, will be studied. The breakup leads to a decrease and coalescence to an increase in R. This assumption is a rough approximation of the real events. However, the results for the average droplet size during coalescence [26] and in dynamic equilibrium between breakup and coalescence [13,27] for this model are in qualitative agreement with models considering changes in the droplet distribution. For a volume unit of the system of monodisperse spheres, Eq. (1) can be rewritten as

$$\sigma = \sigma_0 - g\frac{Q^3}{27\phi^3}R^3 \tag{2}$$

where ϕ is the volume fraction of the dispersed phase. Q in Eq. (2) generally can be a function of R.

The droplet size will be calculated for simple shear flow. We believe that the results can be used for qualitative discussion of the phase structure development during mixing of polymer blends, namely in batch mixers. For a change in the number of particles, n, in time unit due to coalescence, $(\mathrm{d}n/\mathrm{d}t)_\mathrm{c}$, the following equation is valid [10,11,13,27]

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{c} = -\frac{4}{\pi}\dot{\gamma}\phi P_\mathrm{c} n \tag{3}$$

where $\dot{\gamma}$ is the shear rate and P_c the probability that collision of the particles will be followed by their fusion. P_c is a function of σ and R. Calculation of P_c is a complex problem which has been solved only approximately [10–13]. We will use the procedure suggested by Janssen and Meijer [28], where

$$P_\mathrm{c} = \exp(-t_\mathrm{c}/t_\mathrm{i}) \tag{4}$$

where t_i is the interaction time which is given by the equation

$$t_\mathrm{i} = \dot{\gamma}^{-1} \tag{5}$$

t_c is the time necessary for the approach of the droplets from the distance at the beginning of the collision, h_0, to the distance h_c at which the matrix film trapped between droplets bursts. The equation derived by Jeelani and Hartland [29] will be used for t_c

$$t_\mathrm{c} = \frac{3\eta_\mathrm{m}R^2F}{16\pi\sigma^2h_\mathrm{c}^2}\left[1 + \frac{3l}{\lambda}\left(1 + \frac{R^{3/2}F^{1/2}}{2^{5/2}\pi^{1/2}h_0\sigma^{3/2}}\cdot\frac{\partial\sigma}{\partial r}\right)\right]^{-1} \tag{6}$$

where η_m is the viscosity of the matrix, $\lambda = \eta_\mathrm{d}/\eta_\mathrm{m}$ the ratio of the viscosities of the dispersed phase and matrix, l the ratio of the circulation length and the distance of droplets, $\partial\sigma/\partial r$ the interfacial tension gradient at the periphery of the film and F is the driving force of the coalescence which can be expressed as [28]

$$F = 6\pi\eta_\mathrm{m}\dot{\gamma}R^2 \tag{7}$$

Substitution of Eqs. (5)–(7) into Eq. (4) leads to

$$P_\mathrm{c} = \exp\left\{-9Ca^2R^2/8h_\mathrm{c}^2\left[1 + \frac{3l}{\lambda}\left(1 + \frac{\sqrt{3}Ca^{1/2}R^2}{4h_0\sigma}\cdot\frac{\partial\sigma}{\partial r}\right)\right]\right\} \tag{8}$$

where capillary number, Ca, is defined as

$$Ca = \frac{\eta_\mathrm{m}\dot{\gamma}R}{\sigma} \tag{9}$$

Eq. (8) can be expressed in the form

$$P_\mathrm{c} = \exp\left\{-\frac{9Ca^2R^2}{8h_\mathrm{c}^2(1 + 3C/\lambda)}\right\} \tag{10}$$

where C is a function of the mobility of the interface. For a system without a compatibilizer $C = l$ and for a system with immobile interface $C = 0$. More detailed discussion of P_c can be found in Refs. [23,24].

It is commonly assumed that droplets burst by the transient mechanism at Ca substantially higher than the critical capillary number Ca_c. For Ca not much greater than Ca_c, droplets burst in two halves (stepwise mechanism) [28,30,31]. Therefore, we assume that the average droplet size in steady shear flow is controlled by the stepwise mechanism. This assumption is undoubtedly realistic for systems with the average droplet radius not much higher than the critical radius R_c (related to Ca_c). In examination of the validity of the assumption for the steady state in a batch mixer, relations between residence times in places with very different stresses and characteristic times of the breakup and coalescence must also be considered. For a change in the number of droplets in a time unit, due to breakup, $(\mathrm{d}n/\mathrm{d}t)_\mathrm{B}$, the following equation is used [13,27]

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{B} = f(Ca - Ca_\mathrm{c})n \tag{11}$$

where f is a function of rheological properties of the dispersed phase and matrix. f and Ca_c are not functions of R and σ. They can be different for systems with and without compatibilizer and with the same rheological properties and interfacial tension. Eq. (11) relates to the assumption $t_\mathrm{B}^{-1} = f(Ca - Ca_\mathrm{c})$ where t_B is the droplet breakup time. The reasons for using Eq. (11) are discussed in Ref. [27].

In a steady state, the following equation is valid:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{B} + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{c} = 0 \tag{12}$$

Substitution from Eqs. (11), (9), (10) and (3) into Eq. (12) leads to

$$f\left(\frac{\eta_\mathrm{m}\dot{\gamma}R}{\sigma} - Ca_\mathrm{c}\right) = \frac{4}{\pi}\dot{\gamma}\phi \exp\left\{-\frac{9\eta_\mathrm{m}^2\dot{\gamma}^2R^4}{8h_\mathrm{c}^2\sigma^2(1 + 3C/\lambda)}\right\} \tag{13}$$

It is necessary to specify dependences of σ and C on R and on the total amount of a copolymer in the blend. During further study, we shall assume that C is independent of R and σ. We believe that the assumption is quite realistic and does not affect strongly the following results. Because general relations between the size of interfacial area and distribution of the copolymer between the interface and bulk phases are not available, several cases will be studied separately.

2.1. Constant density of a copolymer on the interface

This case relates to the situation where the interface is fully occupied by copolymer molecules and a sufficient amount of a copolymer, which can quickly migrate to the interface if its area increases, is in the bulk phases. For $q =$ const., it follows from Eq. (1) that

$$\sigma = \sigma_\mathrm{e} = \text{const.} \tag{14}$$

Eq. (13) passes to

$$R = R_\mathrm{c} + \frac{4\sigma_\mathrm{e}}{\pi\eta_\mathrm{m}f}\phi \exp\left\{-\frac{9\eta_\mathrm{m}^2\dot{\gamma}^2R^4}{8h_\mathrm{c}^2\sigma_\mathrm{e}^2(1 + 3C/\lambda)}\right\} \tag{15}$$

where

$$R_\mathrm{c} = \frac{\sigma_\mathrm{e}}{\eta_\mathrm{m}\dot{\gamma}}Ca_\mathrm{c} \tag{16}$$

Eq. (15) is the same as for a blend without a compatibilizer with σ_e. Eq. (15) is a transcendent one and it is generally solvable only numerically. For $P_\mathrm{c} = 1$ (it relates, e.g. to very small $\dot{\gamma}$), Eq. (15) reduces to

$$R = R_\mathrm{c} + \frac{4\sigma_\mathrm{e}}{\pi\eta_\mathrm{m}f}\phi \tag{17}$$

Eq. (17) relates to the equation derived for the system without a compatibilizer and for $P_\mathrm{c} =$ const. in Ref. [27] (in this reference, factor $4/\pi$ is omitted due to misprint). For $P_\mathrm{c} = 0$, Eq. (15) passes to

$$R = R_\mathrm{c} \tag{18}$$

Because R_c is the smallest radius of the droplet at which breakup can occur, the average droplet radius should lie between R_c and $R_\mathrm{c}/\sqrt[3]{2}$ (see Refs. [32,33]). The difference between the real value of R for $\phi = 0$ and the value from Eq. (18) is a consequence of approximations used under the study. For a small argument, the exponential function in Eq. (15) can be expanded in a Taylor series. In the first approximation, an algebraic equation of fourth degree in R is obtained. For small P_c, Eq. (15) can be solved by iteration using $R_0 = R_\mathrm{c}$.

2.2. All copolymer molecules are localized on the interface, $Q/\phi =$ const.

This case relates to the situation where the total amount of a copolymer is localized on the interface and the ratio of the amount of the copolymer and that of the dispersed phase is kept constant. During changes in the blend composition, Eq. (2) can be rewritten as

$$\sigma = \sigma_0 - g'c_\phi^3R^3 \tag{19}$$

where $g' = g/27$ and c_ϕ is a number of copolymer molecules per volume unit of the dispersed phase which is independent of ϕ.

After substitution of Eq. (19), Eq. (13) passes to

$$f\frac{\eta_\mathrm{m}\dot{\gamma}R}{\sigma_0 - g'c_\phi^3R^3} - fCa_\mathrm{c} = \frac{4}{\pi}\dot{\gamma}\phi \exp\left\{-\frac{9\eta_\mathrm{m}^2\dot{\gamma}^2R^4}{8h_\mathrm{c}^2(1 + 3C/\lambda)(\sigma_0 - g'c_\phi^3R^3)^2}\right\} \tag{20}$$

Generally, Eq. (20) is solvable only numerically. For $P_\mathrm{c} = 1$, Eq. (20) reduces to the equation of the third degree

$$R^3 + \frac{f\eta_\mathrm{m}\dot{\gamma}}{g'c_\phi^3(fCa_\mathrm{c} + (4/\pi)\dot{\gamma}\phi)}R - \frac{\sigma_0}{g'c_\phi^3} = 0 \tag{21}$$

Eq. (21) has the following real positive solution

$$R = \left(\frac{\sigma_0}{2g'c_\phi^3}\right)^{1/3} \times\left(\left\{1 + \left[1 + 4/27\frac{\sigma_0}{g'c_\phi^3}\left(\frac{\sigma_0}{\eta_\mathrm{m}\dot{\gamma}}Ca_\mathrm{c} + \frac{4}{\pi}\frac{\sigma_0}{\eta_\mathrm{m}f}\phi\right)^{-3}\right]^{1/2}\right\}^{1/3} + \left\{1 - \left[1 + 4/27\frac{\sigma_0}{g'c_\phi^3}\left(\frac{\sigma_0}{\eta_\mathrm{m}\dot{\gamma}}Ca_\mathrm{c} + \frac{4}{\pi}\frac{\sigma_0}{\eta_\mathrm{m}f}\phi\right)^{-3}\right]^{1/2}\right\}^{1/3}\right) \tag{22}$$

For $P_c = 0$, Eq. (20) passes to

$$R^3 + \frac{\eta_m \dot{\gamma}}{g' c_\phi^3 Ca_c} R - \frac{\sigma_0}{g' c_\phi^3} = 0 \tag{23}$$

with the solution

$$R = \left(\frac{\sigma_0}{2g' c_\phi^3}\right)^{1/3} \left\{ \left[1 + \left(1 + \frac{4}{27} \frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0}{g' c_\phi^3} \right)^{1/2} \right]^{1/3} + \left[1 - \left(1 + \frac{4}{27} \frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0}{g' c_\phi^3} \right)^{1/2} \right]^{1/3} \right\} \tag{24}$$

In the limit for

$$\frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0}{g' c_\phi^3} \to 0,$$

Eq. (24) passes to

$$R = \left(\frac{\sigma_0}{g' c_\phi^3}\right)^{1/3} \tag{25}$$

Eq. (25) relates to the condition $\sigma = 0$. In the limit for

$$\frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0}{g' c_\phi^3} \to \infty,$$

the following equation is valid

$$R = \frac{\sigma_0}{\eta_m \dot{\gamma}} Ca_c \tag{26}$$

For small arguments, the exponential function on the right-hand side of Eq. (20) can be expanded in a Taylor series. In the first approximation, an algebraic equation of the sixth degree in R is obtained. For small P_c, Eq. (20) can be solved by iterations using Eq. (24) for R_0.

2.3. All copolymer molecules are localized on the interface, $Q = \mathrm{const}$.

This case relates to the situation when a constant amount of a copolymer, independent of the blend composition, is added to the blend components. In Eq. (2), $Q = Q_e$ is a constant and ϕ is an independent variable. Eq. (13) can be rewritten as

$$f \frac{\eta_m \dot{\gamma} R}{\sigma_0 - g'(Q_e^3/\phi^3) R^3} - f Ca_c - \frac{4}{\pi} \dot{\gamma} \phi \exp\left\{ - \frac{9 \eta_m^2 \dot{\gamma}^2 R^4}{8 h_c^2 (1 + 3C/\lambda)(\sigma_0 - g'(Q_e^3/\phi^3) R^3)^2} \right\} = 0 \tag{27}$$

For $P_c = 1$, Eq. (27) passes to the equation

$$R^3 + \frac{f \eta_m \dot{\gamma} \phi^3}{g' Q_e^3 (f Ca_c + (4/\pi) \dot{\gamma} \phi)} R - \frac{\sigma_0 \phi^3}{g' Q_e^3} = 0 \tag{28}$$

Eq. (28) has the solution

$$R = \left(\frac{\sigma_0 \phi^3}{2g' Q_e^3}\right)^{1/3} \times \left(\left\{ 1 + \left[1 + 4\phi^3/27 \frac{\sigma_0}{g' Q_e^3} \left(\frac{\sigma_0}{\eta_m \dot{\gamma}} Ca_c + \frac{4}{\pi} \frac{\sigma_0}{\eta_m f} \phi \right)^{-3} \right]^{1/2} \right\}^{1/3} + \left\{ 1 - \left[1 + 4\phi^3/27 \frac{\sigma_0}{g' Q_e^3} \left(\frac{\sigma_0}{\eta_m \dot{\gamma}} Ca_c + \frac{4}{\pi} \frac{\sigma_0}{\eta_m f} \phi \right)^{-3} \right]^{1/2} \right\}^{1/3} \right) \tag{29}$$

For $P_c = 0$, Eq. (27) passes to

$$R^3 + \frac{\eta_m \dot{\gamma} \phi^3}{Ca_c g' Q_e^3} - \frac{\sigma_0 \phi^3}{g' Q_e^3} = 0. \tag{30}$$

The solution of Eq. (30) is

$$R = \left(\frac{\sigma_0 \phi^3}{2g' Q_e^3}\right)^{1/3} \left\{ \left[1 + \left(1 + \frac{4}{27} \frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0 \phi^3}{g' Q_e^3} \right)^{1/2} \right]^{1/3} + \left[1 - \left(1 + \frac{4}{27} \frac{\eta_m^3 \dot{\gamma}^3}{\sigma_0^3 Ca_c^3} \frac{\sigma_0 \phi^3}{g' Q_e^3} \right)^{1/2} \right]^{1/3} \right\} \tag{31}$$

It follows from Eq. (31) that in this case, the droplet size increases with increasing ϕ also in the case in which coalescence is not operative.

Also Eq. (27) can be solved by the expansion of the exponential function in a Taylor series for small arguments of the function. First approximation leads to the equation of the sixth degree. For small values of the last term on the right-hand side, Eq. (27) can be solved by iterations. Eq. (31) should be used as the zeroth approximation.

2.4. System with the maximum density of a copolymer on the interface

It is assumed that the whole amount of a copolymer is localized on the interface if its density is lower than the maximum density, q_m. A further addition of a copolymer on the interface preserves its density q_m. Further copolymer is localized in the bulk phases. For a system with a certain composition, maximum droplet radius, R_m, exists at which $q = q_m$.

For a system with constant ratio of the amount of copolymer and dispersed component, c_ϕ, R_m can be expressed as

$$R_m = \frac{3 q_m}{c_\phi} \tag{32}$$

For a system with $R < R_m$, the competition between the breakup and coalescence is described by Eq. (20). For $R \geq R_m$, Eq. (15) is valid with σ_e given by the equation

$$\sigma_e = \sigma_0 - g q_m^3 \tag{33}$$

For $R < R_m$, Eq. (22) at $P_c = 1$ and Eq. (24) at $P_c = 0$ are

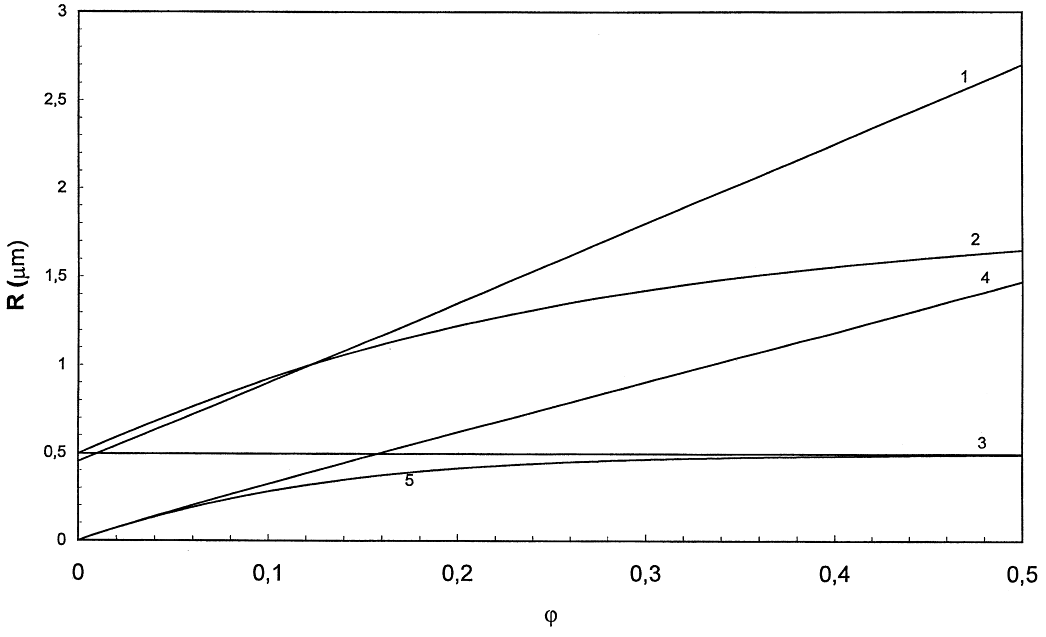

Fig. 1. Dependence of the radius R on the volume fraction ϕ of the dispersed phase. Curves: 1—cf. Eq. (17), 2—cf. Eq. (22), 3—cf. Eq. (24), 4—cf. Eq. (29), 5—cf. Eq. (31). Constants used: $\sigma_0 Ca_c/(\eta_m \dot{\gamma}) = 0.5$ μm, $4\sigma_0/(\pi\eta_m f) = 5$ μm, $\sigma_0/(g' c_\phi^3) = 10$ μm, $\sigma_0/(g' Q^3) = 50$ μm^3.

valid. For $R_m \geq R$, Eq. (17) at $P_c = 1$ and Eq. (18) at $P_c = 0$ are valid.

For a system with a constant amount of a copolymer Q_e, R_m can be expressed as

$$R_m = \frac{3q_m}{Q_e}\phi \tag{34}$$

It follows from Eq. (34) that R_m is proportional to ϕ. For $R < R_m$, the competition between the droplet breakup and coalescence is described by Eq. (27). Eqs. (29) and (31) are valid for $P_c = 1$ and $P_c = 0$, respectively. For $R \geq R_m$, Eq. (15) describes the dependence of R on ϕ.

3. Discussion

It can be seen from Eq. (17) and Fig. 1 that a linear dependence of R on ϕ has been found for $q =$ const. and $P_c = 1$. The same result was found for blends without a compatibilizer [27]. Generally, for P_c given by Eq. (10), the growth of R with ϕ is slower than linear (see Fig. 2). For most blends without a compatibilizer, the growth of R with ϕ is steeper than linear [13,34]. This difference is caused by approximations used in the derivation of Eqs. (3) and (11), mostly by neglecting simultaneous collisions of three and more droplets [13,32,33].

In a system where the total amount of a compatibilizer is localized on the interface and the ratio of the amount of compatibilizer, Q_e/ϕ, is kept constant at variable ϕ, the dependences of R on ϕ qualitatively differ from the related dependences for blends without a compatibilizer. Only for $P_c = 0$, R is independent of ϕ equally to the system without a compatibilizer. In this case, the interfacial tension is independent of ϕ at a constant R. For $P_c > 0$, the growth of R with ϕ is slower than for the related blends without a compatibilizer (see Eq. (22) and Figs. 1 and 2). The growth of R causes a decrease in the interfacial tension which leads to an increase in $(\mathrm{d}n/\mathrm{d}t)_B$ and a decrease in $(\mathrm{d}n/\mathrm{d}t)_c$.

If a constant amount of a compatibilizer is added to the system and it is localized on the interface, i.e. $Q = Q_e =$ const., R is a function of ϕ also for $P_c = 0$ (see Eq. (31) and Fig. 1). In this case, there is an excess of a copolymer in the system at small ϕ and $\sigma = 0$ is achieved for $\phi \to 0$. At a constant droplet size, the density of a copolymer on the interface decreases with increasing ϕ. For $P_c = 0$, the slope of R vs. ϕ dependence gradually decreases with increasing ϕ. The growth of R is steep in the whole range of ϕ (see Eq. (29) and Fig. 1). It can be seen that for the whole amount of a compatibilizer localized on the interface, the shape of R vs. ϕ curves is very sensitive regarding the fact that Q_e or Q_e/ϕ is kept constant at variable ϕ.

The assumption that the limit density of a compatibilizer on the interface, q_m, exists is quite realistic. If the ratio of the total amount of a compatibilizer and of the interfacial area is higher than q_m, only a part of the compatibilizer related to q_m is localized on the interface. The rest of the compatibilizer is localized in the bulk phases. In the opposite case, the whole amount of the compatibilizer is localized on the interface ($Q = Q_e$). The dependences of R on ϕ for these systems are plotted in Fig. 3. If Q_e/ϕ is constant, the whole amount of a compatibilizer is localized on the interface for small ϕ. R of the droplets and, hence, also q increase with increasing ϕ due to the growing coalescence. For a certain ϕ, q achieves the value q_m. In blends with constant Q_e, the

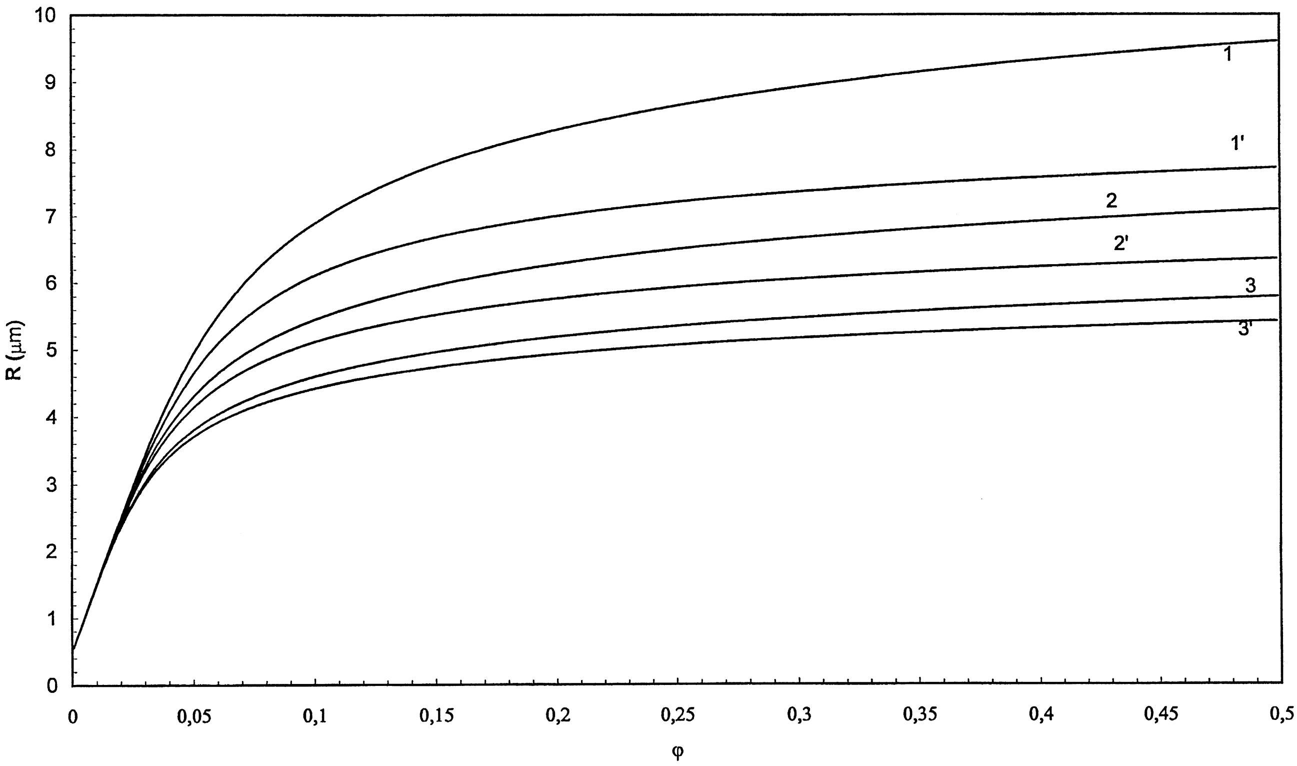

Fig. 2. Dependence of the radius R on the volume fraction ϕ of the dispersed phase. Calculation was performed numerically using Eq. (20) with $C = 0$ in the following form

$$R = (1 - F_R R^3)\left(K_0 + K_1 \exp\left\{-K \frac{R^4}{(1 - F_R R^3)^2}\right\}\right), \text{ where } K = \frac{9}{8h_c^2}\left(\frac{\eta_m}{\sigma_0}\right)^2 \dot{\gamma}^2,\ K_0 = \frac{\sigma_0}{\eta_m} \cdot \frac{Ca_c}{\dot{\gamma}},\ K_1 = \frac{\sigma_0}{\eta_m} \cdot \frac{4}{\pi f}$$

and $F_R = g' c_\phi^3/\sigma_0$.Values of constants: $K_0 = 5 \times 10^{-7}$ m, $K_1 = 10^{-4}$ m, Curves: 1 and 1′—$K = 2 \times 10^{20}$ m^{-4}, 2 and 2′—$K = 8 \times 10^{20}$ m^{-4}, 3 and 3′—$K = 2 \times 10^{21}$ m^{-4}, 1, 2 and 3—without compatibilizer ($F_R = 0$). 1′, 2′ and 3′—with compatibilizer ($F_R = 7 \times 10^{14}$ m^{-3}).

density of a compatibilizer on the interface is q_m for small ϕ. The amount of a compatibilizer localized in the bulk phases decreases with increasing ϕ and, for a certain ϕ, the whole amount of a compatibilizer is localized on the interface and q is smaller than q_m.

It has been assumed that C in Eq. (10) and Ca_c in Eq. (11) are independent of ϕ. The exact evaluation of this assumption needs information about the rate of the migration of a copolymer along the interface and between the interface and bulk phase [23,24]. Unfortunately, these data are not available now. However, we believe that these assumptions are satisfactorily fulfilled for many systems. In the first approximation, we can apparently assume $C = 0$, i.e. droplets have immobile interface, if q is not too small. When droplets burst by the stepwise mechanism, Ca_c depends on the rate of migration between the bulk phase and the interface and along the interface [23,24]. Using Ca_c for the uncompatibilized blend with the same rheological properties and interfacial tension can be used as a first rough estimation. We believe that using the mentioned approximations can affect values of the function $R(\phi)$ but not the qualitative trends of R vs.ϕ dependence.

Qualitative conclusions of the theory are apparently valid also in the case when Eq. (2) is substituted by another equation predicting a decrease in interfacial tension with an increasing amount of a copolymer localized on the interface. The same qualitative conclusions can be assumed also in the case when Eq. (10) for P_c and/or Eq. (11) for $(dn/dt)_B$ are substituted by other expressions for the probability of droplets fusion and the rate of the breakup by the stepwise mechanism.

Due to the problems discussed above, only qualitative comparison of results of the proposed theory with experiment is reasonable. The basic conclusions of the theory, i.e. that the addition of a compatibilizer leads to a decrease in R for $\phi \to 0$ and suppresses an increase in R with ϕ, are in agreement with experiment [3,35,36]. However, also almost no effect of a compatibilizer on R at $\phi \to 0$ was found in the literature [37]. Tentative explanation of this fact is that other than the stepwise mechanism of breakup was operative. The theory should be verified by a comparison of predicted shapes of R vs. ϕ curves with experimental data. In spite of the fact that the effect of a compatibilizer is well documented in the literature, we found only a very limited number of experimental dependences suitable for comparison, i.e. R vs. ϕ dependences for blends with and without compatibilizer determined at steady shearing or mixing. Available data for blends with a constant ratio of the amount

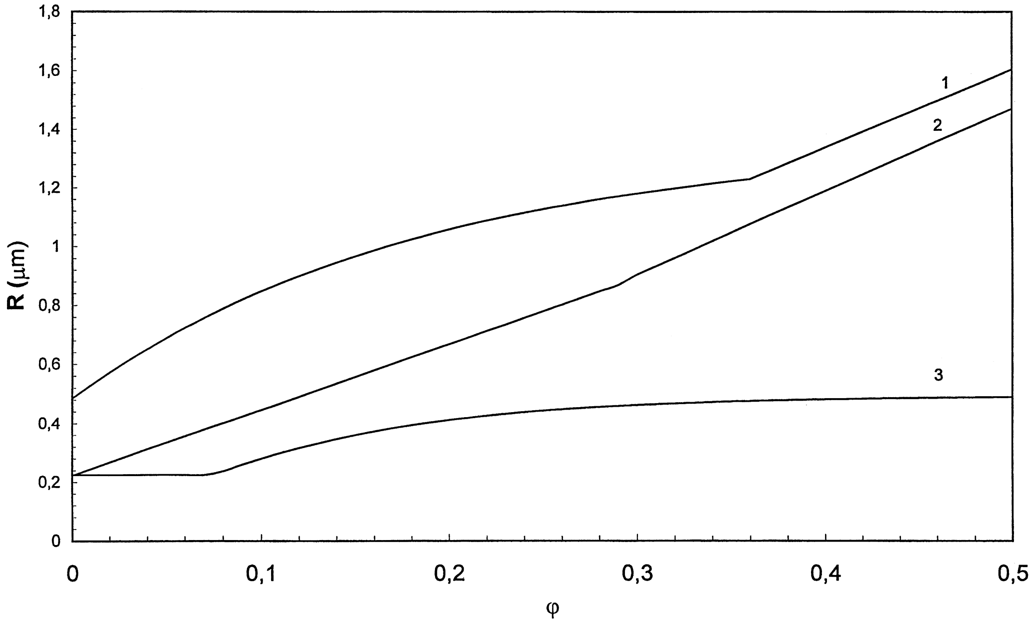

Fig. 3. Dependence of the radius R on the volume fraction ϕ of the dispersed phase in the case of existence of limit density q_m on the interface. Curves: 1—for $\phi \le \phi_m = 0.36$ Eq. (22) is used, for $\phi > \phi_m$ Eq. (17) with σ according to Eq. (19) is valid. 2—for $\phi \le \phi_m = 0.29$ Eq. (17) with σ according to Eqs. (33) and (34) is used, while for $\phi > \phi_m$ general Eq. (29) is valid. 3—For $\phi \le \phi_m = 0.074$ Eq. (18) with σ according to Eqs. (33) and (34) is used, while for $\phi > \phi_m$ Eq. (31) is valid.

of a compatibilizer and dispersed phase show a similar shape of the dependence of R on ϕ. For this case and $P_c =$ const., a straight line and a slightly downward curve are predicted for blends without and with a compatibilizer, respectively (see Fig. 1). The steeper growth of R than linear with ϕ was found for all blends under experimental study [35,37]. The reason for this discrepancy was discussed above. Qualitatively, the upward curvature of the R vs. ϕ curve for compatibilized blends should be smaller than for the related uncompatibilized ones. However, quantitative difference between these curves cannot be estimated because the influence of a compatibilizer on the effects neglected in derivation of the theory is unknown. Due to the reasons mentioned above and a certain scatter of experimental results, the comparison of the theoretical and available experimental shapes of the R vs. ϕ curves for the related blends with and without a compatibilizer gives only very limited information about plausibility of the proposed theory.

The theory of the competition between the droplet breakup and coalescence can be used also in the calculation of the dependence of the droplet size on other parameters than ϕ, e.g. on $\dot{\gamma}$. In this case, the dependences of all quantities from Eq. (13) on this variable must be specified.

4. Conclusions

A theory describing the dependence of the size of dispersed droplets on their concentration in polymer blends containing a compatibilizer was derived.

The shapes of the dependence of droplet radius, R, on the volume fraction of the dispersed phase, ϕ, generally differ for blends with and without a compatibilizer.

The distribution of a compatibilizer between the interface and bulk phases has a fundamental effect on the R vs. ϕ curves.

The dependences of R on ϕ which were found for a constant ratio of the amounts of a copolymer and dispersed phase and for a constant total amount of the copolymer are qualitatively different.

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