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Competition between Breakup and Coalescence of Droplets in Polymer Blends Containing a Compatibilizer

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SUMMARY: In description of the effect of a compatibilizer on the phase structure development in molten polymer blends, the following processes must be considered: (i) a decrease in the interfacial tension, (ii) the effect of a compatibilizer on the course of droplet breakup and coalescence, (iii) the effects of the droplet breakup and coalescence on the interfacial area. The dependence of the average droplet size in steady flow on the blend composition can be calculated if distribution of a compatibilizer between the interface and bulk phase is assumed. The effect of compatibilizer migration along the interface and between the interface and bulk phase are estimated. The shapes of the dependence strongly varied depending on whether the total compatibilizer amount or the ratio compatibilizer/dispersed phase is constant during an increase in volume fraction of the dispersed phase.

Introduction

It is well known that most polymer blends contain a compatibilizer (Refs. 1,2). Up to the present time, rather small attention was paid to theoretical analysis of the phase structure development of these blends in mixing. Tang and Huang (Ref. 3) 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 compatibilizer (relative to the content of the 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 negligible fractions of the dispersed phase because of coalescence, which has a significant effect on the particle size (Ref. 4), is fully neglected. Milner and Xi (Ref. 5) 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 compatibilizer is small and, therefore, it does not affect the breakup of droplets. However, this conclusion is in strong disagreement with the results of other experimental and theoretical studies, where a substantial effect of compatibilizer on interfacial tension was found (Ref. 6). They assumed that the compatibilizer suppresses

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mobility of the interface and, therefore, it lowers the probability of coalescence. Therefore, we try to analyze the phase structure development in compatibilized polymer blends considering a decrease in interfacial tension, the effect of a compatibilizer on the course of the droplet breakup and coalescence, and changes in interfacial area in the droplet breakup and coalescence.

Decrease in Interfacial Tension

A number of relations for a decrease in interfacial tension caused by the presence of a compatibilizer (block or graft copolymer) on the interface have been derived in the literature (Refs. 6-8). We use the equation derived by Lyatskaya et al. (Ref. 6) 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 is a function of molecular parameters of the polymer, Q is the total number of the copolymer molecules on the interface, S is 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 the system. A part of copolymer molecules can be localized in one or both bulk phases. For a volume unit of the system of monodisperse spheres, Eq. (1) can be rewritten as

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

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

Compatibilizer Effect on the Droplet Breakup and Coalescence

The breakup by stepwise and transient mechanisms and coalescence of dispersed droplets in polymer blends containing a compatibilizer were analyzed in Refs. 9,10. In these blends, the droplet breakup and coalescence are affected by a change in interfacial tension due to the presence of a compatibilizer and its migration along the interface and between the interface and bulk phases. The stepwise mechanism is controlled by the capillary number Ca which for shear flow is defined as

$$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma} \quad (3)$$

where η_m is the viscosity of the matrix and $\dot{\gamma}$ is the shear rate. The breakup occurs when Ca is higher than critical capillary number, Ca_c, which is a function of rheological properties of the components. A decrease in σ leads to an increase in Ca and, hence, to an easier droplet breakup. The breakup is enhanced also by convection of a compatibilizer towards the stagnant points, especially in elongational flow, which leads to a local decrease in interfacial tension. The breakup 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 (Refs 9,10). Therefore, Ca_c for a blend containing a compatibilizer is not necessarily identical with Ca_c for a blend with the same rheological properties and σ. Unfortunately, parameters needed for calculation of Ca_c in compatibilized blends are not available in the literature. A commonly accepted dependence of the breakup time, t_B, on Ca and rheological properties of the components has not been determined so far. For $Ca < Ca_c$, the relation $t_B \rightarrow \infty$ is valid. For Ca slightly greater than Ca_c, the following equation was derived based on general assumptions (Ref. 11)

$$t_B^{-1} = f(Ca - Ca_c) \quad (4)$$

where f is a function of rheological properties of the components. Other dependences of t_B on Ca, e.g., t_B independent of Ca, were used in the literature.

The breakup time of a highly stretched droplet by the transient mechanism is inversely proportional to the interfacial tension (Refs. 9,10). It follows from analysis of the breakup of the 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 (Ref. 11). It should be considered that the presence of a compatibilizer leads to an easier droplet deformation and that the interfacial tension of a highly elongated droplet is substantially larger than that of the spherical droplet covered by the same amount of a compatibilizer.

A change in the number of particles, n, related to a time unit due to coalescence, $(dn/dt)_c$, is described by the equation (Ref. 4)

$$\left(\frac{dn}{dt}\right)_c = -\frac{4}{\pi}\dot{\gamma}\varphi P_c n \quad (5)$$

where $\dot{\gamma}$ is the shear rate and P_c is the probability that collision of the particles will be followed by their fusion. P_c is a function of σ and R. For blends containing a compatibilizer, P_c is lower due to a lower interfacial tension and a decrease in mobility of the interface (Refs. 9,10). Using the Janssen and Meijer procedure (Ref. 12) for calculation of P_c, and the Jeelani and Hartland expression for the time necessary for the droplets approach at the critical distance, h_c, at which the matrix film trapped between droplets bursts, we found (Ref. 9,10)

$$P_c = \exp\left\{-\frac{9Ca^2R^2}{8h_c^2\left(1+\frac{3C}{\lambda}\right)}\right\} \tag{6}$$

where λ is the ratio of the viscosities of the dispersed phase and matrix and C is a function of the mobility of the interface. For a system without a compatibilizer, $C = l$, where l is the ratio of the circulation length and the distance of droplets; for a system with immobile interface, $C = 0$.

Competition between Breakup and Coalescence

In description of competition between breakup and coalescence of droplets, there should be considered not only the effect of a compatibilizer on the breakup and coalescence but also the fact that the droplet breakup leads to an increase whereas coalescence to a decrease in the interfacial area of a system. The change of the interfacial area induces a change in the interfacial tension and, hence, in the distribution of a compatibilizer between the interface and bulk phase, i. e., in Q. The problem is treatable if reasonable assumption about the distribution of a compatibilizer can be made and Q or q can be considered as known parameters.

We studied the dependence of the average droplet radius on the content of the dispersed phase in steady flow (Ref. 13). The assumption was made that a system also remains monodisperse during the breakup and coalescence. It is apparent that in steady flow, the breakup of droplets with the radius slightly larger than the average one is decisive. It is commonly accepted that for Ca substantially larger than Ca_c, breakup by the transient mechanism prevails whereas for Ca not too much greater than Ca_c, the stepwise mechanism predominates. Therefore, it was assumed that the steady droplet size is controlled by the stepwise mechanism. This assumption is correct if the average R is not much greater than R_c related to Ca_c.

A change in the number of droplets in a time unit due to breakup, $(\mathrm{d}n/\mathrm{d}t)_\mathrm{B}$, can be expressed as

$$(\mathrm{d}n/\mathrm{d}t)_\mathrm{B} = t_\mathrm{B}^{-1}n \qquad (7)$$

In steady state, the following equation is valid

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{B} + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_\mathrm{c} = 0 \qquad (8)$$

Substitution from Eqs (7), (4), (5) and (6) into Eq. (8) leads to

$$f\left(\frac{\eta_m \dot{\gamma} R}{\sigma} - Ca_c\right) = \frac{4}{\pi}\dot{\gamma}\varphi \exp\left\{-\frac{9\eta^2\dot{\gamma}^2R^4}{8h^2\sigma^2\left(1+\frac{3C}{\lambda}\right)}\right\} \qquad (9)$$

where σ is given by Eq. (2). Generally, Ca_c and C are also functions of R and Q. However, we believe that the assumption that Ca_c and C are independent of R and σ is quite realistic and it does not change the results qualitatively. Equation (9) was solved with the one of the following assumptions:

Constant density of copolymer on the interface

This case relates to the situation where the interface is fully occupied by copolymer molecules and a sufficient amount of the 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 also σ is a constant. Therefore, the shape of the dependence of R on φ is the same as for blends without compatibilizer using the same σ and P_c. It should be mentioned that the presence of compatibilizer leads to a decrease in σ and P_c and hence to a slower increase in R with φ.

All copolymer molecules are localized on the interface, Q/φ = const

This case relates to the situation where the total amount of a copolymer is localized on the interface and the ratio amount of the copolymer/dispersed phase is kept constant. The increase in R with φ is suppressed in comparison with uncompatibilized blends due to the fact that an increase in interfacial area leads to a decrease in σ.

All copolymer molecules are localized on the interface, Q = const

This case relates to the situation when a constant amount of the copolymer, independent of the blend composition, is added to the blend components. In Eq. (2), Q is a constant and φ is an independent variable. There is an excess of the copolymer in the system at small φ and $\sigma = 0$

is reached for $\varphi \rightarrow 0$. R increases with φ (with decreasing slope) also for $P_c = 0$. Generally, the growth of R with φ is rather steep.

System with the maximum density of copolymer on the interface

It is assumed that the whole amount of the 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, (related to the limit volume fraction of the dispersed phase, φ_m) exists at which $q=q_m$. If a constant ratio of the amount of a compatibilizer and dispersed phase is maintained in the system, the R vs. φ dependence related to Q/φ = const describes the system at $\varphi < \varphi_m$. For $\varphi \geq \varphi_m$, the system is described by the dependence for q = const. If a constant total amount of a compatibilizer is added to the system, the R vs. φ dependence for q = const describes the system at $\varphi < \varphi_m$. The dependence for Q = const relates to the system for $\varphi \geq \varphi_m$.

Proposed theory leads to the conclusion that the addition of a compatibilizer causes a decrease in droplet size in dilute blends as well as in the growth of the droplet size with σ. The ratio of R's of blends with and without compatibilizer need not be equal to the ratio of their corresponding σ's. It is in agreement with experimental results (Ref. 14). On the other hand, Milner and Xi (Ref. 10) do not predict any effect of a compatibilizer on R for $\varphi \rightarrow 0$.

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