Block Copolymers Suppressing Droplet Coalescence through Stopping Film Rupture

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ABSTRACT: It has been assumed that the block copolymers suppress droplet coalescence in immiscible polymer blends by preventing droplets from approaching each other. However, recent measurements of the minimum block copolymer coverage for suppressing coalescence did not support this mechanism. In this paper, we assume that the block copolymers suppress coalescence by preventing the rupture process of the matrix film between the droplets. By using stability analysis, the minimum block copolymer coverage was calculated. It has been shown that the minimum coverage is independent of the shear rate that is applied to the polymer blends but decreases with an increasing molecular weight. Such results qualitatively agree with the experimental observations.

Introduction

It has been demonstrated that block copolymers can suppress droplet coalescence in immiscible polymer blends. Coalescence is a dynamic process in which two droplets move close to each other, the matrix film between the droplets ruptures, and the two droplets merge into a larger one.[1−6] Recent experiments with a polystyrene/polyethylene blend by Lyu et al.[6] have shown that the minimum block copolymer coverage ($\Sigma_{\min}$) for suppressing coalescence was independent of, or very weakly correlated with, the shear rate ($\dot{\gamma}$). However, this minimum coverage decreased as increasing the molecular weight of the block copolymers. In the case that the block copolymers were asymmetric, e.g., where the size of the blocks that stay in the matrix side (outside) was different from that of the blocks that stay in the droplet side (inside), those copolymers with larger outside blocks had stronger suppression effects.

Sundararaj et al. proposed that the steric interaction between block copolymers balanced the force that drives the droplets to approach each other and the coalescence of the droplets was prevented.[1] The minimum block copolymer coverage was predicted to be independent of the shear rate but decrease as increasing the molecular weight of the block copolymers. The original theory was proposed for static coalescence where the driving force was van der Waals attraction. In the case of dynamic coalescence, the shear force drives droplets to approach each other. On the basis of this theory, the minimum block copolymer coverage for suppressing coalescence is expected to increase with the shear rate, which disagrees with the experimental observations.

Milner and Xi assumed that the block copolymers at droplet surfaces resisted the droplets to approach each other, and then the coalescence between droplets was suppressed. The resistant force occurred when the block copolymers in the gap between droplets were brought out by the squeezing flow of the matrix and a concentration gradient formed in the droplet surfaces as the droplets moved close to each other.[7] This force is called the Marangoni force. The minimum block copolymer coverage for suppressing coalescence was calculated to be proportional to the shear rate. Obviously, this prediction did not agree with the experiments either. Cristini et al. proposed a similar theory that gave a similar result.[8]

On the basis of a similar concept, Blawzdziewicz et al. proposed another mechanism and did predict the minimum block copolymer coverage to be independent of shear rate.[9] In this mechanism, the ratio of Marangoni force to shear force, or the so-called Marangoni number, was assumed to be much greater than 1, which was different from Milner and Xi's mechanism where Marangoni number was smaller so that the block copolymer concentration gradient was significant. This large Marangoni number assumption in Blawzdziewicz et al.'s mechanism led to a situation in which the block copolymer layers at droplet surfaces were incompressible and the droplet surfaces were essentially immobile. Then the coalescence efficiency was calculated to depend on the mobility and coverage of the block copolymers but not on the shear rate. However, Blawzdziewicz et al. could not explain the effects of the symmetry of block copolymers on the droplet coalescence, e.g., why the block copolymers with larger outside blocks suppressed coalescence more efficiently than the block copolymers with smaller outside blocks and even the total molecular weights and the mobility were similar.

To explain these effects of block copolymers on coalescence, we propose in the this paper that the block copolymers suppress droplet coalescence by preventing the rupture process of the matrix film between droplets. Van der Waals interaction between the droplets compresses the film. The compression force increases when there is a fluctuation in the facing surfaces of the droplets. Thus, the fluctuation tends to grow. However, as the surfaces fluctuate, the interfacial energy increases due to the increase in surface area, which damps the fluctuation. When the film is thick, the compression force is negligible; the surface fluctuation is always damped. However, when the film thickness is smaller than a critical value (h_c), the van der Waals compression force exceeds the damping force, the fluctuation grows, and the film becomes unstable and ruptures (Figure 1, parts a and b).[10] Obviously, the external shearing has no effect on the onset of the rupture.

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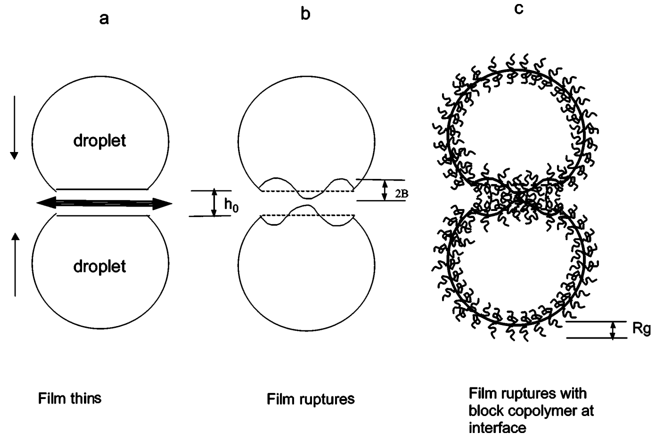

Figure 1. Schematics of the rupture processes of the film of the matrix between two droplets. Rupture was suppressed if there were block copolymers at the interfaces of droplets.

When block copolymers are attached to the droplets' surfaces, the steric interaction between block copolymers adds to damping force and delays the rupture process to a new and smaller critical thickness (H_C). However, more important effects lie in the following process: as the matrix film is compressed, more and more matrix molecules move out of the gap; the volume fraction of the block copolymers in the gap increases. When the gap thickness reaches a certain value (H_B), the block copolymer volume fraction reaches 100% and the film is essentially incompressible. If H_B is greater than H_C, film rupture is impossible (Figure 1c). Then, the coalescence is prevented. In the following sections, we will quantify this speculation.

Film Rupture without Block Copolymer

According to Vrij[10] the free energy (E) of the matrix film includes the energy due to van der Waals attraction (E_v) and interfacial energy (E_S). They are

$$E_v = \iint_{\text{surface}} -\frac{A}{12\pi h^2}\,ds \tag{1}$$

$$E_S = 2\iint_{\text{surface}} \gamma\,ds \tag{2}$$

$$E = E_S + E_v \tag{3}$$

where A is the Hamaker constant, h is the face to face distance between the two droplets, γ is the interfacial tension, and s is the surface area. When there is surface fluctuation, both E_v and E_S change. To calculate these changes, we approximate the circular facing surfaces of two approaching droplets as rectangles with a length of r and a fixed width of W just as Vrji did.[10] We randomly take one branch of the Fourier series of the surface fluctuation as indicated in the following equation

$$h = h_0 + 2B\sin\left(2\pi\frac{r}{\lambda}\right) \tag{4}$$

where λ is the wavelength of the fluctuation with its maximum value equal to the diameter of the facing surfaces of the droplets. Then the change in free energy is

$$\Delta E_S = 2\int_0^\lambda \gamma\left(\left(1+\left(\frac{d(h/2)}{dr}\right)^2\right)^{1/2}-1\right)W\,dr = \frac{2\pi^2 W B^2\gamma}{\lambda} \tag{5}$$

$$\Delta E_v = \int_0^\lambda (E_v(h)-E_v(h_0)W\,dr = \int_0^\lambda\left(\frac{dE_v}{dh}\Delta h + \frac{1}{2}\frac{d^2E_v}{dh^2}\Delta h^2 + ...\right)W\,dr = -\frac{AWB^2\lambda}{2\pi h_0^{\,4}} \tag{6}$$

$$\Delta E = \Delta E_S + \Delta E_v = W\lambda B^2\left(\frac{2\pi^2\gamma}{\lambda^2} - \frac{A}{2\pi h_0^{\,4}}\right) \tag{7}$$

In the above calculation, all the terms higher than second order were neglected. In order for an instability to occur, ΔE must be negative, or

$$\frac{4\pi^2\gamma}{\lambda^2} - \frac{A}{\pi h_0^{\,4}} < 0$$

Then the film thickness at rupture is

$$h_c < \left(\frac{A\lambda^2}{4\pi^3\gamma}\right)^{1/4} \tag{8}$$

Typically, A [1,10] is equal to thermal energy at room temperature or $kT = 10^{-21}$ J, $\lambda = 10^{-7}$ m, $\gamma = 0.0053$ J/m. We have $h_c \sim 2$ nm.

Film Rupture Process with Block Copolymer at Interface

The block copolymers at two droplet interfaces repulse each other like two springs[1] when the distance between the interfaces is smaller than the twice of the radius of gyration of the outside block of the copolymers. The energy increase due to such interaction is

$$E_B = \left(\frac{\Sigma}{\Sigma_0}\right)^2 \int_0^\lambda 2\Sigma\frac{3kT}{R_g^{\,2}}(R_g - h/2)^2\,dr \tag{9}$$

where Σ is the block copolymer coverage or surface concentration, kT is the thermal energy, R_g is the radius of gyration of the outside block of the block copolymers, and $3kT/R_g^2$ is the elastic constant of a polymer chain coil. The factor $(\Sigma/\Sigma_0)^2$ accounts for the probability that one block in one droplet surface interacts with another block in the other droplet. Σ_0 is the maximum coverage. When the film surface fluctuates, the changes in free energy due to block copolymers can be calculated in the same way as that for van der Waals energy, or

$$\Delta E_B = \int_0^\lambda\left(\frac{dE_B}{dh}\Delta h + \frac{1}{2}\frac{d^2E_B}{dh^2}\Delta h^2 + ...\right)W\,dr = \frac{1}{2}\int_0^\lambda \frac{d^2E_B}{dh^2}\Delta h^2\,dr = \frac{3kT\Sigma^3 WB^2\lambda}{\Sigma_0^{\,2}R_g^{\,2}} \tag{10}$$

Adding this energy to eq 7, we have

$$\Delta E = \Delta E_v + \Delta E_S + \Delta E_B = W\lambda B^2\left(\frac{2\pi^2\gamma}{\lambda^2} - \frac{A}{2\pi h_0^{\,4}} + \frac{3kT\Sigma^3}{\Sigma_0^{\,2}R_g^{\,2}}\right) \tag{11}$$

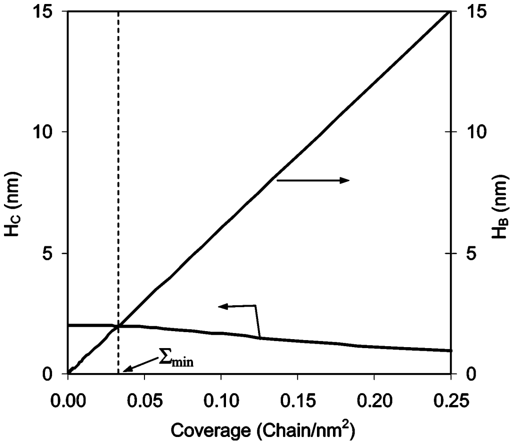

Figure 2. Critical film rupture thickness (H_c) and densely packed block copolymer thickness (H_B) as a function of block copolymer coverage. The film rupture is prevented when $H_c < H_B$ and is delayed otherwise.

The new critical film thickness at which rupture occurs is reduced by the presence of block copolymers to H_C:

$$H_C = \left(A/\left(2\pi\left(\frac{2\pi^2\gamma}{\lambda^2} + \frac{3kT\Sigma^3}{\Sigma_0^{\ 2}R_g^{\ 2}}\right)\right)\right)^{1/4} = h_c\left(\frac{1}{1+\alpha}\right)^{1/4} \quad (12)$$

where

$$\alpha = \frac{3kT\Sigma^3\lambda^2}{2\pi\gamma\Sigma_0^{\ 2}R_g^{\ 2}} \quad (13)$$

Substituting $kT = 7 \times 10^{-21}$ J (at 220 °C), $\Sigma = 0.2/\text{nm}^2$, $\lambda = 0.1\ \mu\text{m}$, $\gamma = 0.0053\ \text{J/m}^2$, $\Sigma_0 = 0.25/\text{nm}^2$, $R_g^2 = Na^2$, $N = 192$, and $a = 0.67$ nm (see ref 6 for these data), we have $H_C \sim 0.7h_C \sim 1.4$ nm. This result tells that the addition of block copolymers causes a decrease in the critical thickness for film to rupture (Figure 2). When applying a constant compression force to a film, the thinning rate of the film is proportional to the cube of its thickness.[11] These mean that the addition of block copolymers increases the film rupture time by about $(1/0.7)^3 \sim 3$ times. Therefore, the presence of block copolymer makes it more difficult for the film to reach the rupture thickness. Notice that $R_g \sim 9.5\ \text{nm} > H_C$. The condition of eq 9 was met.

Thickness of Densely Packed Block Copolymers

As the droplets approaching together, more and more matrix molecules are squeezed out from the gap. As a result, the volume percentage of the block copolymers in the gap increases until it reaches 100%. At this point, the thickness of the block copolymer layer is

$$H_B = Na^3\Sigma \quad (14)$$

Take the same values for the parameters as the above, we have $H_B \sim 12$ nm which is greater than H_C. This suggests the gap is filled with 100% block copolymers first (Figure 2). When this condition is reached, the film becomes incompressible; its thickness cannot be further reduced to H_C for the rupture to occur. As a result, the film rupture is prevented. The critical condition for film rupture to occur is $H_B = H_C$, or

$$\left(A/\left(2\pi\left(\frac{2\pi^2\gamma}{\lambda^2} + \frac{3kT\Sigma_{\min}^{\ 3}}{\Sigma_0^{\ 2}R_g^{\ 2}}\right)\right)\right)^{1/4} = h_c\left(\frac{1}{1+\alpha}\right)^{1/4} = Na^3\Sigma_{\min} \quad (15)$$

This equation determines the minimum block copolymer coverage for completely suppress the coalescence between droplets. Substituting all the parameters with the values gave above, by numerical calculation, we obtained $\Sigma_{\min} = 0.034$, 0.014, and 0.007 chain/nm² for the PS−PE with molecular masses of 20−20, 50−50, and 100−100 kg/mol, respectively.

Equation 15 can be simplified. Substituting the calculated $\Sigma_{\min}$ into eq 13, we have $\alpha = 0.014$, 0.001, and 0.0001 for PS−PE with molecular masses of 20−20, 50−50, and 100−100 kg/mol, respectively. Such a small α suggests that the contribution of the block copolymers to the reduction of H_c can be neglected. Then we have

$$\Sigma_{\min} = \left(\frac{h_c}{Na^3}\right) \quad (16)$$

Using the above equation, we calculate $\Sigma_{\min} = 0.035$, 0.014, and 0.007 chain/nm² for the PS−PE with molecular masses of 20−20, 50−50, and 100−100 kg/mol, respectively. These values are almost the same as those calculated with eq 15. Therefore, the simplification was valid. The simplified equation not only allows us to easily calculate the minimum coverage but also explicitly indicates that (1) the minimum block copolymer coverage for completely suppress droplet coalescence is independent of shear rate and (2) the minimum coverage is reciprocal to the molecular weight of the outside blocks. Obviously, these results qualitatively agree with what have been observed in the experiments in ref 6. The reason that $\Sigma_{\min}$ is independent of shear rate is that the block copolymers suppress coalescence by preventing the film rupture process that is driven by the van der Waals interaction rather than delaying the droplet approaching process that is driven by the shear force.

In the above calculation, we have made two assumptions. First, we assumed that the squeezing flow of the matrix in the gap between the droplets did not significantly reduce the block copolymer coverage. Shear force drives the block copolymers to move out of the droplets' gap. However, as long as some block copolymers move out, a concentration gradient forms, yielding a Marangoni force. This force, in return, resists to the further outward moving (or convection) of the block copolymers. Blawzdzwicz et al. estimated that the change in block copolymer coverage due to external shear flow is about[9]

$$\frac{\Delta\Sigma}{\Sigma} \sim \frac{1}{M} \quad (17)$$

where

$$M = \frac{\frac{\Sigma_{\min}}{\lambda}\frac{\partial\Gamma}{\partial\Sigma}}{\eta\dot{\gamma}} \sim \frac{\frac{\Gamma}{\lambda}}{\eta\dot{\gamma}} \quad (18)$$

is the Marangoni number, measuring the competition between Marigoni force and shear force. Obviously, if M is much greater than 1, the change in the coverage of block copolymers is negligible. The Marigoni number for the PS/HDPE/PS−PE (20−20 kg/mol) system was estimated to be 883, 88, and 8.8 for a shear rate of 0.1, 1, and 10 s^{-1}, respectively (where the viscosity of PS was 600 Pa s). Therefore, within the shear rate range from 0.1 to 10 s^{-1} the change in block copolymer coverage was not significant. The first assumption is valid. However, the shear rate 10 s^{-1} was probably close to the upper limit for the change in block copolymer coverage to be negligible. At a shear rate of 100 s^{-1}, M would be less than 1 and the outward moving of block copolymers is expected to be significant. Indeed, when the shear rate was 100 s^{-1}, it was observed that the droplets of HDPE coalesced in the PS matrix and even the block copolymer loading was the same.[6] This set the limit to the current theory: it is valid when the Marangoni number is much greater than 1. Such a condition was similar to that of Blawzdziewicz et al.'s theory.

The second assumption we made was that block copolymer was insoluble in homopolymers. For a block copolymer molecule to be dissolved in a homopolymer phase, the energy penalty is $N\chi kT$, where χ is the Flory−Huggins interaction parameter which is about 0.07 for PS−PE.[6] Then, the ratio of the concentration of PS−PE (20−20 kg/mol) in the PS phase to that in the interfacial region is proportional to $\exp(-N_{PE}\chi) \sim 10^{-22}$. The ratio of the concentration of PS−PE in the HDPE phase to that in the interfacial region is proportional to $\exp(-N_{PS}\chi) \sim 10^{-6}$. Therefore, the 20−20 kg/mol block copolymer essentially was not dissolved in either PS or HDPE phase. The solubility of higher molecular weight PS−PE in homopolymers was even lower. Therefore, the present assumption is valid.

It should be pointed out that although the present theory qualitatively agrees with the experimental measurements, the calculated Σ_{min} was smaller than the experimental values, 0.2, 0.1, and 0.05/nm^2 for PS−PE of 20−20, 50−50, and 100−100 kg/mol, respectively, by 6 to 7 times. There are a few possible reasons for the difference. The first reason may be the rough approximations we made all through the paper such as $H_B = Na^3\Sigma_0$, $R_g{}^2 = Na^2$, and $A = 10^{-21}$ J. A second reason might be that some of the block copolymers were consumed by aggregating into micelles. Micelles (including swollen micelles) were observed in certain blends and they preferred to stay in specific phases.[3,6] A third possible reason might be that the block copolymers in the gap between two droplets may diffuse out to the backside of the droplets, leading to a larger apparent coverage. However, for a block copolymer molecule to diffuse a distance of a particle size (1 μm) within processing time frame (1/shear rate = 1/1 = 1 s), diffusion coefficient needs to be greater than 10^{-8} cm^2/s. This number is significantly greater than a typical diffusion coefficient, 10^{-12} cm^2/s, of polymers. Thus, diffusion may not be a major reason.

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