Interfacial Tension Reduction and Coalescence Suppression in Compatibilized Polymer Blends

Jean-Christophe Lepers and Basil D. Favis
Centre de Recherche Appliquée sur les Polymères (CRASP), Dept. of Chemical Engineering,
Ecole Polytechnique de Montréal, Montréal, P.Q. Canada H3C 3A7

This work examines the influence of well-defined diblock copolymers on the interfacial tension and morphology of an immiscible polymer blend. The system studied is a blend of 80% polystyrene and 20% ethylene propylene copolymer compatibilized by diblock copolymers of poly(styrene-hydrogenated butadiene). The diblocks differed in that one contained 53% styrene (symmetric diblock) and the other 30% styrene(asymmetric diblock). The interfacial tension was performed using the breaking-thread technique, and the results were compared to both the theoretical predictions of Noolandi and Hong, and Leibler. The morphology was tracked using an emulsification curve, comparison of which with the interfacial tension results made it possible to estimate the relative role of interfacial tension and coalescence reduction in particle-size reduction phenomena.

Introduction

It is widely known that suitably chosen block copolymers can play the role of compatibilizing agents in immiscible polymer blends (Fayt et al., 1981, 1986; Favis, 1991). An effective copolymer is able to decrease the interfacial tension and the dispersed phase size, provide stabilization against coalescence, and improve the adhesion between both phases. The influence of the architecture, chemical composition, and molecular weight of the modifier are important considerations and their role in the emulsification process needs to be clarified.

In a recent study, Cigana et al. (1996) examined the effect of the architecture, chemical composition, and molecular weight of styrene (PS)-hydrogenated butadiene (EB) diblock copolymers on its emulsification capacity for a polystyrene (PS)/ethylene-propylene copolymer (EPR) blend. In another study Matos et al. (1995) considered the influence of styrene-hydrogenated butadiene−styrene triblock copolymers on the same blend system. They used the emulsification curve (Favis, 1994) as a tool to compare the efficacy of the different copolymers. That approach, which has been used for classic emulsions (Gopal, 1968), has been shown to be applicable to polymer blends (Willis and Favis, 1988, 1990), and essentially tracks the evolution of the dispersed phase size as a function of the copolymer concentration. This morphological approach to characterizing the interface displays a sharp decrease in the dispersed phase size up to a critical concentration in copolymer, after which a plateau is reached. The plateau indicates the maximum possible saturation of the interface by the modifier for that particular system under melt processing conditions. In the studies on diblock copolymers (Cigana et al., 1996; Favis et al., 1997), it was shown that the more symmetrical the copolymer, the better the emulsification. It was also demonstrated that the nature of the junction between the blocks of copolymer—pure or tapered—does not influence the emulsification ability of the copolymer. The molecular weight of the diblock copolymers had an effect on emulsification below the critical concentration for interfacial saturation; however, all the data converged at the C_{crit}, and an identical plateau diameter was obtained in all three cases. These results indicated that the molecular weight of the interfacial modifier had a much more limited role in emulsification than had been expected. In the study on triblock copolymers (SEBS), Matos et al. (1995) clearly showed that the molecular weight of the triblock copolymer did not affect the critical concentration or the equilibrium particle size. In that case, even below the critical concentration for interfacial

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Correspondence concerning this article should be addressed to B. D. Favis.

saturation, the triblock copolymers displayed similar emulsification behavior.

Numerous authors have studied the effect of the addition of a copolymer on the interfacial tension between two homopolymers. Elemans et al.(1990) have shown that when 1% of a block copolymer polystyrene-*b*-polyethylene was added to a high-density polyethylene/polystyrene system, the interfacial tension was reduced by a factor 4.8. Chen and White (1993) and Mekhilef et al. (1997) studied the decrease in the interfacial tension between a PS and a high-density polyethylene made compatible by a triblock SEBS copolymer using the pendant drop and the breaking thread method, respectively. They observed a sharp decrease in the interfacial tension until a leveling off was reached. It is interesting to note that the plateau interfacial tension obtained by Mekhilef et al. is similar to the value obtained by Chen and White. Anastasiadis et al. (1989), in a study on the interfacial tension between the PS and a polybutadiene (PB), found a similar decrease when a diblock copolymer P(S-*b*-B) was added to their blends. Finally, in studies on PS/poly(dimethylsiloxane) (PDMS) blend, Hu (1995) reported a decrease in the interfacial tension through the addition of a PS/PDMS diblock copolymer. A reactive copolymer also seems to be very effective at reducing the interfacial tension. Recently, Chapleau et al. (1998) have shown that a polyethylene-*co*-isobutyl acrylate-*co*-methacrylic acid was able to decrease the interfacial tension between polyamide-6 and polypropylene. Similar behavior for an *in situ* reactive blend was obtained by Lepers (Lepers et al., 1997; Lepers and Favis, 1999), where a triblock copolymer of SEBS grafted with maleic anhydride was successfully used to decrease the interfacial tension in a PP/polyethylene terephthalate blend. Finally, using modifier designs based on acid−base considerations, Liang et al. (1997, 1999) demonstrated that the LLDPE/polyvinyl chloride interfacial tension was decreased when a poly(isoprene-4-vinylpyridine) or a hydroxyl-terminated polystyrene were used as interfacial modifiers.

In the present work, the breaking-thread technique is used to measure the interfacial tension between PS and EPR in the presence of a symmetric and asymmetric diblock copolymer. The effect of the symmetric copolymer on the interfacial tension will be compared with the theories of Noolandi and Hong (1982, 1984) and Leibler (1988). The relative role of interfacial tension reduction and coalescence suppression on particle-size reduction is also studied by comparing the emulsification curves generated by the two interfacial modifiers.

Experimental Studies

Materials

The polymers used as matrix and dispersed phase in the present study are a PS and an EPR. The PS used was a styron 667 supplied by Dow Chemical. That styrene was preferred for the interfacial tension measurement to the PS styron D685 used by Cigana et al. (1996) because it possesses a lower viscosity but approximately the same molecular weight. The EPR, a random copolymer of ethylene and propylene containing 54% ethylene, was supplied by Exxon (Vistalon V-504). That EPR was chosen with a molecular weight low enough so that a Newtonian plateau was apparent at low shear. Both copolymers used as interfacial modifiers are pure diblocks of styrene and hydrogenated butadiene. The symmetrical copolymer used (PD1) was synthesized at the Center for Education and Research on Macromolecules (CERM) at the University of Liège, Belgium. Details concerning its synthesis were given previously (Cigana et al., 1996). That copolymer contains 53% styrene. The two asymmetrical copolymers (CAP 4741 and CAP 4745) were obtained from Shell and contain 30% and 26% styrene, respectively. Some properties of these materials are shown in Table 1.

Table 1. Molecular Weight of the Polymers

Materials	M_n (g/mol)	M_w (g/mol)	Degree of Polymerization	
PS	100,000	215,000	2,067	
EPR	69,000	173,000	5,230	
PD1	63,000	64,900	$S = 330$	$EB = 544$
CAP 4741	67,000			
CAP 4745	187,000			

Blend preparation

a) Blends Used in the Breaking-Thread Measurement. For each interfacial modifier, a series of blends was produced by varying the concentration from 0% to 10% interfacial modifier (wt %). The EPR and modifier were blended in a Brabender internal mixer for 8 min at 50 rpm at a temperature of 200°C under nitrogen. The Brabender mixer is predominantly a shear mixing device. A small amount (0.2 wt %) Irganox B-225 from Ciba-Geigy was added to the mixture to reduce the thermal oxidation of the polyolefins.

b) Blends Used in the Morphology Experiments. Blends were prepared using a Brabender internal mixer for 8 min at 50 rpm and at a temperature of 200°C under nitrogen. The matrix, dispersed phase, and interfacial agent were added simultaneously (one-step mixing). After mixing, the material was quenched in cool water to freeze-in the morphology.

Morphology

Cryogenic microtomy was performed in order to obtain a planar surface on the sample for scanning electron microscope observation. Between 250 and 300 diameter measurements were made for each sample, from which the volume average diameter, d_v, and number average diameter, d_n, were obtained. A procedure was applied to correct for polydispersity and the fact that the knife does not cut through the diameter. Further details are given in a previous paper from this laboratory (Cigana et al., 1996).

Rheological measurement

The polymers were pressed at 200°C in order to obtain the disks used for the rheological measurement. Rheological characterization of the polymers was carried out using a Bohlin constant-stress rheometer (CSM) in the dynamic mode at 200°C under nitrogen. A parallel-plate configuration was used with a gap size between 1 and 1.5 mm. Time sweeps were performed to study the stability of the polymers. Stress sweeps were also carried out to define the region of linear

Table 2. Interfacial Tension Parameters: Zero Shear Viscosity, Viscosity Ratio, and Omega Function (PS Thread in EPR and/or EPR/SEB Matrix)

Materials	Zero-Shear Viscosity (Pa·s)	Viscosity Ratio $\eta_{thread}/\eta_{matrix}$	$\Omega(\lambda_m, p)$
PS	6,150	—	—
EPR	5.29×10^4	0.116	0.205
EPR/PD1 90/10	7.01×10^4	0.088	0.233
EPR/CAP 4741 90/10	8.79×10^4	0.070	0.266

viscoelasticity. Both a frequency sweep and creep-test mode were used to obtain the zero shear viscosity of the PS, EPR, and EPR/SEB blends. Those values are given in Table 2 for the principal polymer systems, and their rheological curves are shown in Figure 1. A low molecular-weight EPR was chosen to ensure that it displays Newtonian behavior at low shear.

Breaking-thread technique

The breaking-thread technique was used to measure the interfacial tension of the blends and is based on the theory of Tomotika (1935) for Newtonian fluids.

When a thin thread is embedded in a matrix, small sinusoidal distortions appear at the surface of the fiber. These distortions are caused by temperature microgradients that create amplitude differences in the Brownian movements. The small distortions grow exponentially with time when the distortion wavelength (λ) becomes larger than the initial circumference of the thread ($2\pi R_o$). The distortion grows in time at a growth rate q that is directly proportional to the interfacial tension. It is possible to obtain the interfacial tension by measuring the evolution of the radius of the fiber over time. Details about the experimental and theoretical procedures were reported previously by Lepers et al. (1997). Preblended resins were pressed between two metal plates on a Carver laboratory press at 200°C to produce films of EPR. The PS threads were produced by drawing PS pellets on a hot plate. Thread diameters ranged from 15 to 30 μm. The PS thread was inserted between two films of EPR/SEB. This sample was then enclosed between two glass slides and inserted in a Mettler hot-stage model FP 82 HT connected to a FP90 Central Processor. The distortion amplitude was then observed by a Nikon transmission optical microscope. The theoretical function $\Omega(\lambda_m, p)$ is given in Table 2. Figure 2 shows the dependance of the distortion amplitude with time of a PS thread embedded in a matrix of EPR/copolymer. Five breaking-thread measurements were undertaken for each copolymer concentration, except for the plateau region, where 10 measurements were used.

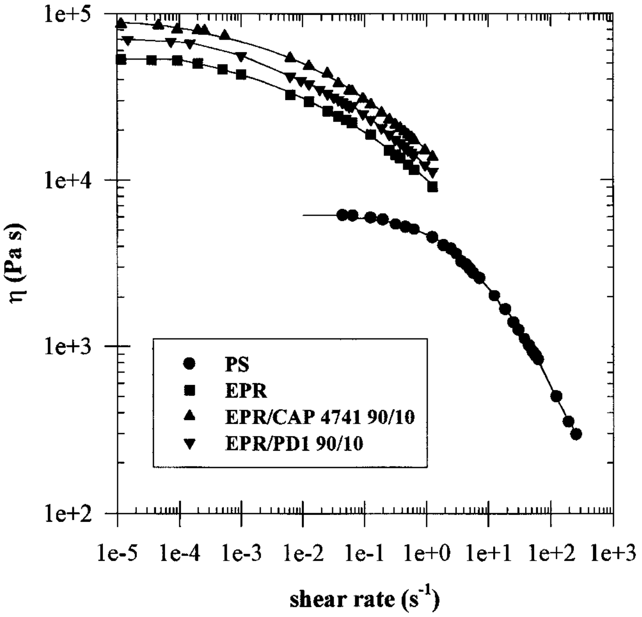

Figure 1. Rheological curves at 200°C for PS, EPR, EPR/PD1 and EPR/CAP 4741 90/10 blends.

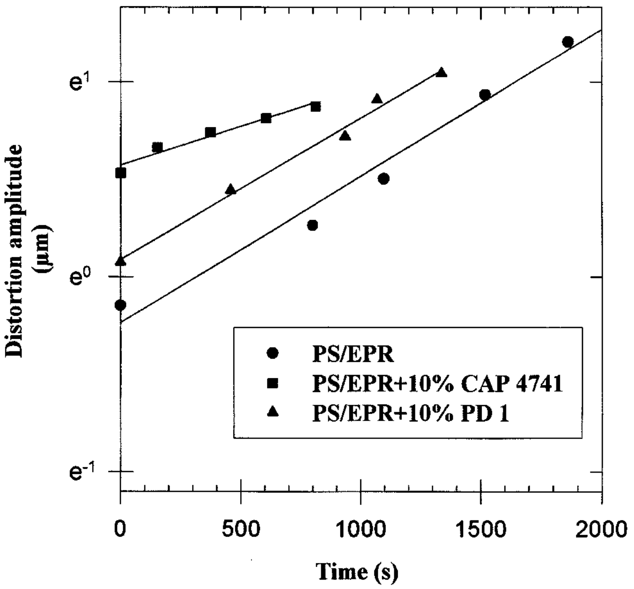

Figure 2. Distortion amplitude vs. time in a PS thread embedded in a matrix of EPR/copolymer.

Three cases are shown: PS/EPR; PS/EPR/CAP 4741; and PS/EPR/PD1.

Results and Discussion

Interfacial tension of the binary blend

The interfacial tension between the PS and the EPR performed at 200°C gave an average value of 6.5 mN/m. This is in good agreement with the results reported by other authors working on similar blends, such as PS/PE. In fact, the PE and the EPR are both polyolefins with a similar structure. Mekhilef et al. (1997) measured a value of 5.6 mN/m for a PS/HDPE blend using the breaking-thread method, while Chen and White (1993) measured a value of 5.2 mN/m for the same blend using a pendant-drop analysis.

Compatibilization by the symmetrical diblock copolymer

Effect of the Modifier on the Interfacial Tension. The interfacial tension data for the PS/EPR/PD1 system is plotted as a function of the copolymer concentration in Figure 3. The copolymer concentration is expressed as the weight of copolymer per weight of EPR. As described in the Introduction, the addition of the copolymer results in a decrease of the interfacial tension, illustrating the surfactant-like behavior of the diblock copolymer. The interfacial tension levels off as the concentration is increased. The saturation concentration is found to be 7.5% for that blend, with a 1.6-fold reduction (37%) in the interfacial tension as compared to that of the binary blend.

The leveling of the interfacial tension indicates that the interface is saturated by the copolymer. As mentioned earlier, twice the number of measurements (10) were taken at each copolymer concentration in the plateau region in order to describe this behavior with confidence. Any further addition of the copolymer will not influence the interface, but will result in the formation of micelles of the copolymer dispersed in the EPR homopolymer, as observed by Cigana and Favis (1998).

Comparison with Theory. Noolandi and Hong (1982, 1984) and Leibler (1988) have developed theories based on statistical thermodynamics that can be used to describe the emulsifying effect of a copolymer interfacial modifier on polymer blends.

Noolandi and Hong (1982, 1984) developed a general theory of inhomogeneous systems where two homopolymers *A* and *B* are dissolved in a solvent *S* and are compatibilized by a copolymer *A-B*. Their theory is applicable to nondilute polymer blends by letting the total polymer volume fraction, ϕ_c, go to 1. In this case, for a symmetrical copolymer, the decrease in interfacial tension can be reduced to the following expression:

$$\Delta\gamma \simeq d\phi_c\left\{\frac{1}{2}\chi + \frac{1}{Z_c} - \frac{1}{Z_c}\exp\frac{Z_c\chi}{2}\right\}. \tag{1}$$

In Eq. 1, d is the width at the half-height of the copolymer profile in units of b; χ is the Flory Huggins interaction parameter, Z_c is the degree of polymerization of the copolymer; and ϕ_c is the volume fraction of the copolymer. As shown by the equation, an exponential dependance of the interfacial tension reduction on the block copolymer molecular weight is predicted, as is a linear dependence of the interfacial tension reduction on the copolymer volume fraction.

In order to compare our results to the theory of Noolandi and Hong, the decrease in the interfacial tension as a function of the copolymer volume fraction in the EPR is presented in Figure 4. The value of d was taken as 63.5 monomer units. This value was used by Anastasiades et al. (1989) for a similar copolymer. According to Van Krevelen and Holtgzen (1972), the value of χ was estimated to be 0.154 at 200°C. As described by the theory, a linear decrease in the interfacial tension as a function of the copolymer content is observed until a plateau is reached. This seems to indicate that the theory is in good agreement with the observed behavior of the blend. However, estimation of the decrease of the slope from the experimental data (-24 mNm^{-1}/100% copolymer) and that obtained from the theoretical calculations (-1.38×10^{28} mNm^{-1}/100% copolymer) are very different.

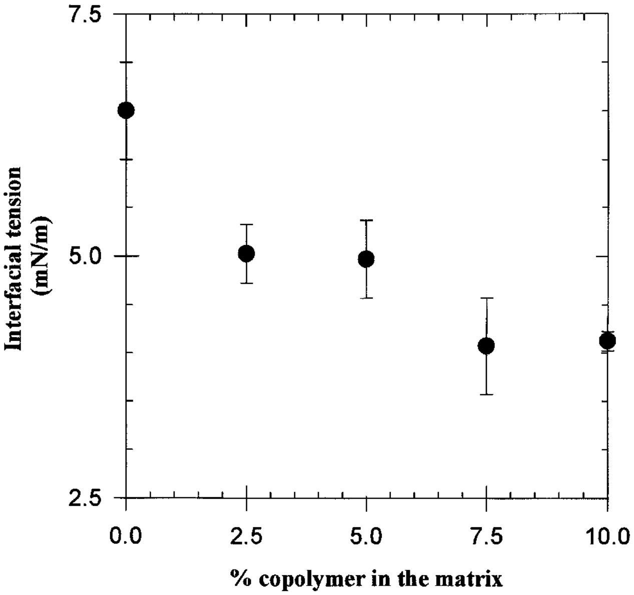

Figure 3. Dependence of the interfacial tension between EPR (matrix) and PS (thread) as a function of the wt. % of PD1 copolymer in the matrix.

The source of the deviation from theory is likely related to two factors: difficulty in diffusing copolymer to the interface, and the inability of the theory to estimate the influence of copolymer molecular weight on interfacial tension in the high molecular-weight range. In fact, it is the latter parameter that

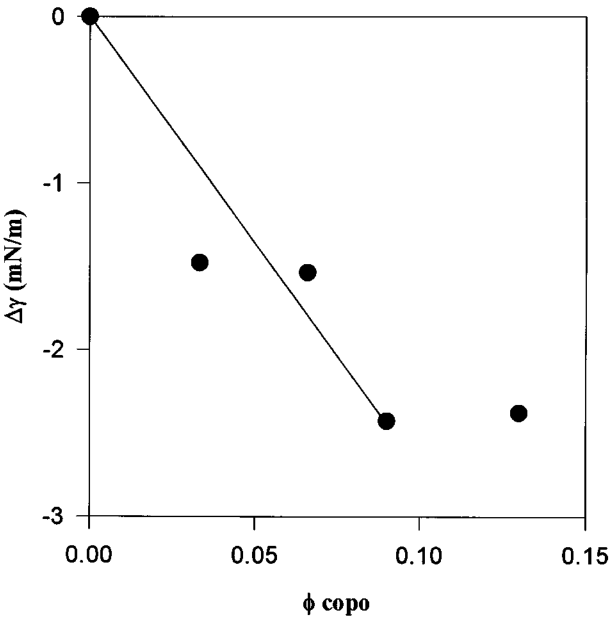

Figure 4. Dependence of the interfacial tension reduction between EPR (matrix) and PS (thread) as a function of the volume fraction of copolymer in the matrix, comparison with the Noolandi theory.

is by far the most important of the two. Note that in Noolandi and Hong's theory there is an exponential dependance of degree of polymerization on interfacial tension reduction. Simply increasing the Z_c from 200 to 800 [the former is the case of Anastasiadis et al. (1989), and the latter is approximately our case] results in a reduction of a factor of 10^{22} in the concentration of copolymer necessary for a given interfacial tension reduction. It is certainly reasonable to assume that a limiting molecular weight of the modifier exists beyond which a further increase in molecular weight has little influence on interfacial tension, and so beyond that point any theoretical expression will greatly overestimate the effect of molecular weight on interfacial tension. Anastasiadis et al. (1989) studied the interfacial tension between PS and polybutadiene blends compatibilized by a PS-PB copolymer and reported good agreement between their data and the Noolandi and Hong theory, including the predicted and actual copolymer concentrations. Nevertheless, the homopolymers they used had molecular weights of between 2200 g/mole and 7800 g/mole and a copolymer molecular weight of 18,800 g/mole.

In order to confirm these findings, the results were also compared to a recent and more refined theoretical development by Leibler (1988). Leibler used a scaling argument to predict the interfacial tension reduction in an A/B immiscible polymer blend in the presence of an A-B copolymer. In such a system, the copolymer is located at the interphase in the form of a brush, with each block of the copolymer oriented in the direction of the corresponding homopolymer. That brush can be in the form of two different regimes: a wet-brush or a dry-brush regime. When the interfacial area occupied per copolymer molecule is relatively large and the homopolymers have a lower molecular weight as compared to that of the copolymer, homopolymer chains will penetrate into the brush. This is the so-called wet brush case. In contrast, a small area occupied per copolymer chain and a homopolymer having a relatively high molecular weight compared with that of the copolymer leads to the formation of a dense copolymer brush in which the homopolymers are not able to penetrate. That case is called the dry-brush case. For both cases, the reduction of the interfacial tension is a function of a power of $\ln(\phi)$. That decrease is expressed in Eq. 2 for the wet brush, and in Eq. 3 for the dry brush:

$$\frac{\Delta\gamma}{\gamma_0} = \left(\frac{256}{3125}\right)^{1/2} \left(\ln(\Phi_A) + \chi N_B\right)^{5/2} \times \left(N_A P_A^{-2/3} + N_B P_B^{-2/3}\right)^{-3/2} \chi^{-1/2} \tag{2}$$

$$\frac{\Delta\gamma}{\gamma_0} = \left(\frac{48^{1/2}}{9}\right)\left[\ln(\Phi_A) + \chi N_B\right]^{3/2} N^{-1/2} \chi^{-1/2}, \tag{3}$$

where P_a and P_b represent the degree of polymerization of A and B homopolymers; N_a and N_b are the degree of polymerization of the A and B blocks of the copolymer, and ϕ_A represents the volume fraction of the copolymer in the A homopolymer. The criteria for the dry brush are $N_i < P_i^{3/2}$ and $\Sigma < N_i^{1/2} a^2$, with Σ representing the interfacial area occupied per molecule and a the length of the monomer; the criterion for the wet brush is $N_i > P_i^{3/2}$.

Prior to comparing the data with theory, it is important to determine whether these interfaces are in the dry-brush or wet-brush regime. From the degree of polymerization given in Table 1, it can be seen that, based on the molecular weight criterion, the interface corresponds to the dry-brush case. However, comparing $N_i^{1/2} a^2$ ($N_{PS} = 330$ and $a = 0.306$ nm results in a surface coverage value of 1.706 nm^2/molecule) with the interfacial area/molecule obtained by the morphological measurement [7 nm^2/molecule (Cigana, 1996)], it can be seen that the measured interfacial area occupied per interfacial modifier molecule is much higher than the coverage predicted by the theory. Furthermore, the finite plateau value obtained for the interfacial tension in Figure 3 is indicative of homopolymer penetration. Pure diblock copolymer at the interface would be expected to result in close to zero interfacial tension. In addition, the homopolymers used in the present study are polydisperse, and some of the smaller chains may be able to wet this interface. For these reasons, it is likely that the blend studied here is in a state between the wet and dry case.

In order to compare the experimental data with the model, the dependence of the decrease of the interfacial tension is presented as a function of $\ln(\phi_{\text{copolymer in EPR}})$ for both the wet-brush and the dry-brush predictions. In order to compare theory and data on the same figure, the x-axis scales for the copolymer concentration are different for each. As observed in the comparison to Noolandi theory, the Leibler theory also shows a large discrepancy between the predicted copolymer concentration for a given decrease in interfacial tension and that observed experimentally. As mentioned earlier, one of the principal reasons for the discrepancy between the interfacial tension reduction and the predicted and actual copolymer concentrations is likely due to the inability of the theory to estimate the influence of copolymer molecular weight on interfacial tension in the high molecular-weight range. In Leibler theory, the interfacial tension reduction is dominated by $\ln(\phi) + \chi N$. As estimated for the Noolandi equation, this term results in a similar high theoretical underestimation of the concentration of copolymer for a given interfacial tension reduction in this high molecular-weight range. Experimental support of this hypothesis is given at the end of the article.

It is also possible that some of the difference in predicted vs. actual copolymer concentrations for a given interfacial tension reduction could be due to difficulties in diffusing the modifier to the interface. This can be dealt with in a couple of ways. In an earlier article (Chapleau et al., 1998), a novel preparation technique for the breaking thread method, based on coextrusion, was shown to result in higher levels of modifier at the interface. This was demonstrated by X-ray photoelectron spectroscopy. Second, in studying the interfacial tension in the presence of an interfacial modifier in systems of this type, one should likely restrict themselves to discussions related to the plateau value, where one can reasonably expect interfacial saturation and that kinetic effects due to migration to the interface have been minimized. This latter approach is applied to the study of coalescence phenomena described in the next subsection.

In Figure 5, the decrease in the interfacial tension appears to be better described by the dry-brush theory. The fit is certainly better than in the wet-brush case. As discussed earlier, however, given the nonzero plateau value of the interfacial

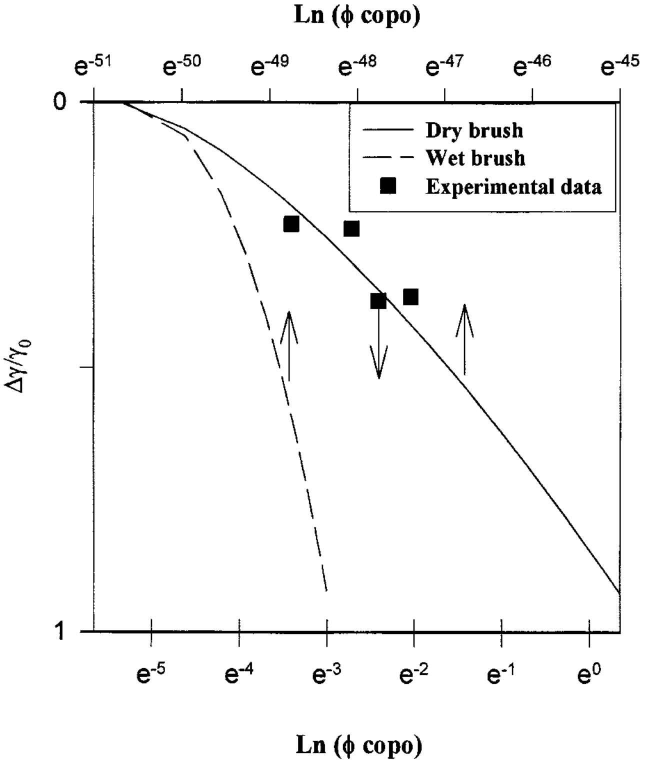

Figure 5. Dependence of the interfacial tension reduction between EPR (matrix) and PS (thread) as a function of Ln of copolymer (volume fraction) in the matrix.

Comparison with the Leibler theory.

tension and the high value of the area occupied by each molecule, the system studied here is more likely in an intermediate dry–wet brush case. In a recent study on interfacial tension reduction in polystyrene/poly(dimethylsiloxane) blends by the addition of poly(styrene-*b*-dimethylsiloxane), Hu et al. (1995) showed that the dry-brush theory was able to correctly predict the decrease in the interfacial tension of blends as a function of copolymer concentration. The interfacial tension was measured by the pendant-drop method, and the copolymer was added in the PDMS matrix. However, the polymers they used had a very low molecular weight, as well as low polydispersity, as in the work with Anastasiades et al. (1989).

(c) Effect of Interfacial Tension and Coalescence on the Morphology. The effect of adding the PD1 copolymer on the dispersed phase size for PS/EPR 20/80 blends has been studied in detail by Cigana et al. (1996). The emulsification curve obtained for that system is presented in Figure 6. As observed for the decrease of the interfacial tension, the morphology data displays a decrease in the particle size, followed by a reduction to a plateau value at a certain critical concentration. The volume average diameter drops from 2.7 μm for the binary blend to 0.4 μm after interfacial saturation (20% interfacial agent based on the minor phase). The diameter values are summarized in Table 3.

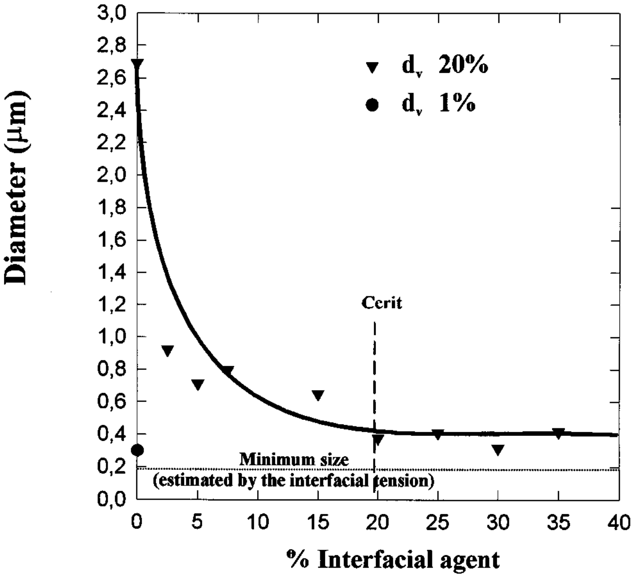

Figure 6. Emulsification curve for the system 80% PS/20% EPR, modified with the interfacial agent PD1.

The interfacial agent concentration is given in wt. % based on the minor phase.

Earlier studies on polypropylene/polyethylene terephthalate blends, made compatible by a SEBS copolymer grafted with maleic anhydride (Lepers and Favis, 1997, 1999), concentrated on the relative role of coalescence and interfacial tension in reducing the particle size. This was accomplished by comparing the decrease in the dispersed phase size at 10% and 1% of dispersed phase (after the addition of an interfacial modifier) with the decrease in the interfacial tension. A direct relationship was found between the interfacial tension reduction and the dispersed phase-size reduction (see also Liang et al., 1999).

That same analysis applied earlier to a PP/PET system was also carried out on the EPR/PS/PD1 system in order to separate the relative contribution of the coalescence and interfacial tension on the morphology of the blend. Starting from the plateau phase size of the uncompatibilized 1% EPR/PS blend (see Table 3), and assuming a direct dependence between phase size and interfacial tension, as observed previ-

Table 3. Dispersed Phase Size (d_v) and Interfacial Tension Data for the EPR/PS Blends

	At 0% Compatibilizer	At Saturation by PD1	At Saturation by CAP 4741
d_v (EPR/PS 20/80) (μm)	2.73	0.40	0.64
d_v (EPR/PS 1/90) (μm)	0.31	0.19*	0.16*
Interfacial Tension (mN/m)	6.5	4.1	3.5

*Estimated by the interfacial tension.

Table 4. Relative Reduction of the Interfacial Tension, Dispersed Phase Size and Coalescence of the EPR/PS 80/20 Blends at Interfacial Saturation with Diblock Copolymers

Copolymer	Reduction of d_v (%)	Reduction of Interfacial Tension (%)	Reduction of d_v Due to Coalescence Suppression (%)
PD1	85	37	48
CAP 4741	76	46	30

ously (Lepers and Favis, 1997, 1999), one can estimate the minimum diameter resulting from both full coalescence suppression and full interfacial tension reduction for this system. That estimated value is 0.19 μm, and is also given in Table 3. Comparing that minimum value to the diameter value of the uncompatibilized 20% EPR blend, it can be seen that the particle size is reduced by 85%. The coalescence suppression contribution to particle-size reduction for the 20% EPR system can then be calculated by subtracting the decrease of the interfacial tension in percent (using the plateau value from Figure 3) from 85%. For 20%EPR/80%PS compatibilized by a symmetrical pure diblock copolymer, the relative contribution of coalescence suppression to particle-size reduction is 48%, and that due to interfacial tension reduction is 37% (Table 4). It is interesting to note that, as observed previously for the *in situ* compatibilized PP/PET system (Lepers and Favis, 1999), both interfacial tension and coalescence suppression contribute significantly to particle-size reduction phenomena upon addition of a premade diblock copolymer.

Comparison of symmetrical vs. asymmetrical diblock copolymer

The effect of the relative chemical composition of the interfacial agent was investigated by comparing the decrease in interfacial tension obtained with interfacial agent PD1 and CAP 4741. Both copolymers are pure diblocks of nearly equal molecular weight, but CAP 4741 contains only 30% styrene by weight, whereas PD1 is a symmetrical diblock (53% styrene by weight).

The decrease in the interfacial tension for both copolymers is given in Figure 7. For the entire range of concentrations studied, CAP 4741 reduces the interfacial tension somewhat more effectively than PD1 (48% reduction, 1.9-fold). The plateau interfacial tension value measured for the blend compatibilized by the PD1 is 4.1 mN/m and that compatibilized by the CAP 4741 is 3.4 mN/m. According to Leibler theory (1988), a symmetrical copolymer should be more effective at reducing the interfacial tension than an asymmetrical one. The argument put forward is that a symmetrical copolymer will be less severely constrained at a plane interface (the interface between a thread and a matrix is planar on a molecular scale) than in a spherical micelle. In contrast, the asymmetrical copolymer will be less severely constrained in a spherical micelle configuration. The theory predicts a more significant drop in the interfacial tension for the symmetrical interfacial modifier, an effect not noted here even when comparing the plateau interfacial tension values. Clearly, more pronounced micelle formation for the asymmetrical diblock does not occur here.

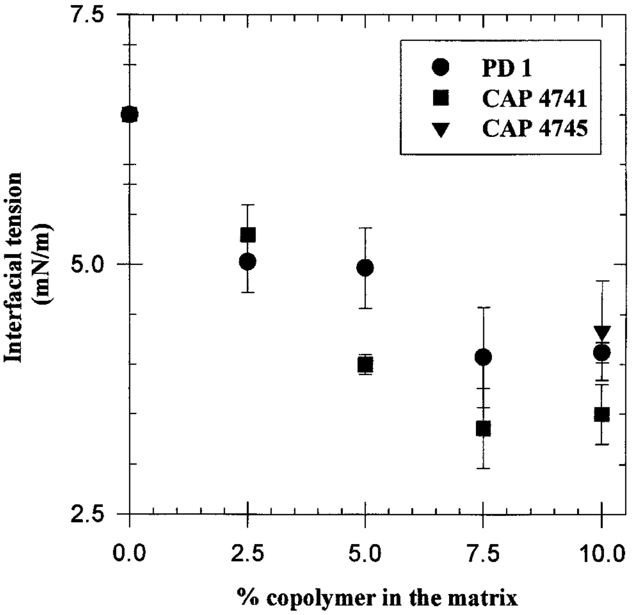

Figure 7. Effect of interfacial-agent block symmetry on the interfacial tension between EPR (matrix) and PS (thread) as a function of the wt. % of copolymer in the matrix.

PD1 is a symmetrical diblock; CAP 4741 and CAP 4745 are asymmetrical diblocks.

The effect of the block symmetry of the interfacial agent on morphology has been investigated by Cigana et al. (1996) by comparing the emulsification curves obtained with both interfacial modifiers. The results are presented in Figure 8. Both curves have the typical shape of the emulsification curve; nevertheless, throughout the entire range of modifier concentrations, PD1 reduces the particle size more significantly than CAP 4741. That result goes in the opposite sense to that of the interfacial tension data. It is clear that if the plateau interfacial tension is slightly lower for the CAP 4741 copolymer, then the superior effect of reducing particle size shown in Figure 8 for PD1 must be due to more effective coalescence suppression. Using the same approach as applied earlier in this article for PD1, the relative role of interfacial tension and coalescence suppression in contributing to particle-size reduction was also estimated for the CAP copolymer. The relevant data are given in Table 4. Interfacial tension reduction accounts for about 46% of the particle-size reduction, and coalescence suppression accounts for about 30%.

Even though the CAP 4741 and PD1 block copolymers display a similar efficacy at reducing interfacial tension, the PDI is more effective at reducing the dispersed phase particle size because of increased coalescence suppression (Figure 8). This can be understood by examining the coalescence phenomenon itself. Coalescence occurs when two drops of dispersed phases meet each other. There will be a flattening of the drops in the contact zone, and a thin film of matrix remains between the drops (Elemendorp and Van Der Vegt, 1986). This film decreases its thickness in a drainage process until a critical size is reached. At the critical size, van der Waals attraction is sufficient to provoke the rupture of the film, and the two drops fuse into a new and larger drop. When

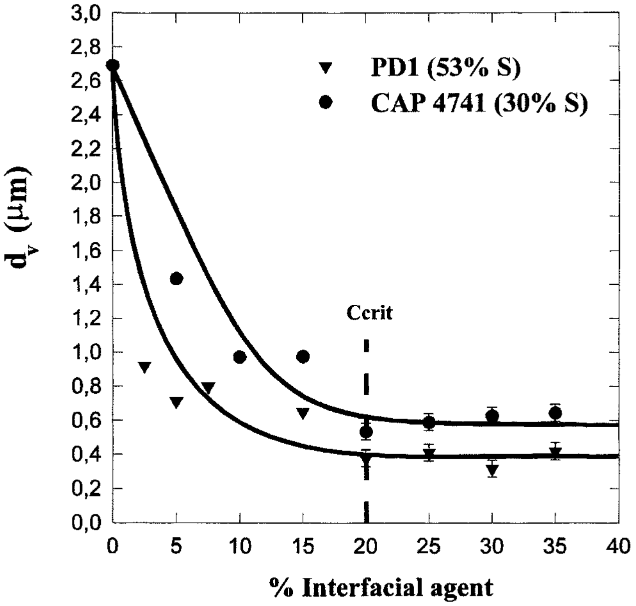

Figure 8. Effect of interfacial agent chemical composition on emulsification as studied by dispersed phase-size evolution as a function of the wt. % copolymer (based on the weight of dispersed phase).

PD1 is a symmetrical diblock; CAP 4741 is an asymmetrical diblock.

a copolymer is added to the blend, it stays at the interface, creating a shell around the drop. When two compatibilized drops approach each other, the presence of the copolymer chains outside the drop will tend to reduce the drainage process, thus increasing the time necessary to coalesce. In addition, during the approach of the particles, the copolymer chains will be compressed (Elemendorp and Van Der Vegt, 1986). Both of these phenomena will render coalescence more difficult. In the case studied here, the dispersed phase is the EPR and the copolymer block forming the outer shell is the styrene block. Because the PD1 possesses a longer styrene block than does the CAP 4741, the shell of the symmetrical copolymer created outside the dispersed phase is thicker. These results demonstrate that the length of the block forming the outer shell is particularly critical to coalescence suppression.

Interfacial tension/molecular-weight dependence

As mentioned earlier, the wide difference between the predicted and actual copolymer concentrations resulting in a given interfacial tension reduction appears to be related to the inability of the theory to accurately predict interfacial tension reduction for interfacial modifiers in the high molecular-weight range. Both the theories of Noolandi and Hong, and Leibler discussed earlier predict an exponential relationship between the molecular weight of the copolymer and the concentration needed to reduce the interfacial tension. In order to test the dependence on molecular weight, a scouting experiment was carried out using a higher molecular weight copolymer (CAP 4745, M_n 187,000 g/mol). This copolymer has a composition similar to the CAP 4741 (M_n 67,000 g/mol). A high enough quantity of the modifier was used to ensure that it was in the interfacial tension plateau range, and that point is shown in Figure 7. The scouting experiment shows that essentially identical interfacial tension values are obtained for CAP 4741 and CAP 4745. This result, although only preliminary, supports the hypothesis that the theory overestimates the influence of the modifier molecular-weight on interfacial tension reduction in this high molecular-weight range. This is further confirmed by earlier emulsification studies (Matos et al., 1995; Cigana et al., 1996) on this same system in a melt mixing environment where the results indicate only a limited role for the molecular weight of the interfacial modifier on dispersed phase size reduction.

Conclusions

This study has shown that symmetric and asymmetric diblock copolymers reduce the interfacial tension in ethylene-propylene/polystyrene blends in a similar fashion, with the latter displaying a slightly lower interfacial tension plateau. Comparison of the interfacial tension reduction resulting from the addition of the symmetrical diblock copolymer with theoretical predictions indicates that the trends are well described by the theory of Noolandi and Hong, and the dry brush theory of Leibler. However, the corresponding experimental copolymer concentration associated with a given interfacial tension reduction is very different from that predicted by theory. It is proposed that the principal cause of the discrepancy between experiment and theory is that the theory overestimates the influence of the modifier molecular-weight on interfacial tension reduction in this high molecular-weight range. It is also suggested that in systems of this type, using the interfacial tension data should be restricted to the plateau values where one can reasonably assume interfacial saturation and that kinetic effects such as migrating the modifier to the interface have been minimized.

The relative role of interfacial tension and coalescence suppression on dispersed phase size reduction for these PS/EPR blends was estimated quantitatively by a comparison of the interfacial tension reduction at the plateau value with the emulsification curve as derived from morphology studies. It is shown that, for the symmetrical and asymmetrical diblock copolymers, both interfacial tension and coalescence suppression play an important role in particle-size reduction phenomena. However, the level of coalescence suppression achieved by the symmetric diblock was more pronounced. This is seen as an indication of the particular importance of the block length of the outer shell of the modifier in coalescence phenomena.

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