PII: S0032-3861(97)10041-6

Polymer Vol. 39 No. 15, pp. 3373–3378, 1998

0032-3861/98/$19.00+0.00

The relative efficacy of diblock and triblock copolymers for a polystyrene/ethylene–propylene rubber interface

Patrick Cigana and Basil D. Favis*
Centre de recherche appliquée sur les polymères, Department of Chemical Engineering, Ecole Polytechnique de Montréal, P.O. Box 6079, Stn 'Centre-Ville', Montréal, Québec H3C 3A7, Canada
(Received 18 July 1997; accepted 18 August 1997)

Blends of polystyrene and ethylene–propylene rubber are compatibilized by different block copolymer interfacial modifiers using melt processing. The emulsification curve, which relates the minor phase particle average diameter to the concentration of emulsifier, is used to compare the efficacy of these modifiers for the interface. Blends containing 90% PS/10% EPR and 80% PS/20% EPR were modified by diblock and triblock copolymers of equal molecular weight and chemical composition. At 10% minor phase, the triblock copolymer acts as a more efficient emulsifier than the diblock, as evidenced by the lower equilibrium diameter (0.35 μm for the triblock, as opposed to 0.6 μm for the diblock) and the lower critical concentration for emulsification. At 20% minor phase, the emulsification curve demonstrates a shift in both critical concentration for emulsification and equilibrium particle diameter, which suggests strong evidence of micellar formation for the triblock copolymer. Even at concentrations lower than the critical concentration for emulsification (C_{crit}), micelle formation is suggested by the low values of interfacial area occupied per molecule for the triblock copolymer in the 80:20 blends, although a transmission electron microscopic study performed on a similar system did not detect any micelle formation at subcritical concentrations. The blends compatibilized by the diblock copolymer, however, show the same equilibrium diameter and critical concentration for emulsification for both blend compositions, indicating that even at 20% minor phase, all the diblock modifier migrates to the interface. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blends; morphology; block copolymer interfacial modifiers)

INTRODUCTION

For many years now, block copolymers have been used as compatibilizing agents in blends of immiscible polymers. It is widely accepted that by localizing at the polymer–polymer interface, block copolymers reduce the interfacial tension between phases and provide steric stabilization against phase structure coarsening[1,2]. However, block copolymers also have a tendency to form micelles in one or both of the phases[3,4], a form under which they seem to be ineffective at compatibilizing the blend. Their propensity to form micelles depends upon several factors, including: chemical interactions with the matrix and/or minor phase, molecular architecture, and molecular weight[3,4].

Physically analysing the specific location of these interfacial agents in the blend remains a problem, since interfacial modifiers are used in very small concentrations, and are usually chemically similar to at least one of the blend components. Transmission electron microscopy (TEM) has been traditionally used to localize the block copolymer in a blend after selective staining of one of the blocks[5–7]. Recently, in this group[8], TEM was used in combination with electron energy-loss spectroscopy (EELS) to localize a dimethylaminoethanol (DMAE) modifier in a blend of polystyrene (PS) and bromobutyl rubber (BB). Nitrogen atoms (from the DMAE) were only detected in the minor phase particles by EELS, unambiguously indicating the presence of interfacial modifier at this location.

In this work, the emulsification curve will be used to evaluate the efficacy of various modifiers for the polystyrene/ethylene–propylene rubber interface. This curve relates minor phase particle diameter to interfacial agent concentration. Long known in classical systems[9], its use has more recently been extended to polymer melts[10]. It displays a characteristic shape, namely a sharp drop at low concentrations of interfacial agent, followed by a leveling off to a quasi-equilibrium value once a certain critical concentration [not to be confused with the critical micelle concentration (CMC) which will be discussed later] has been attained. In recent years, this curve has been used to characterize the relative emulsification efficacies of different interfacial agents. Matos *et al.*[11] studied a system of 90% PS and 10% ethylene–propylene rubber (EPR), compatibilized by different triblock and star-shaped copolymer modifiers. It was found that the molecular weight of saturated triblock copolymers of styrene/ethylene–butylene/styrene (SEBS) did not have a significant effect on their emulsification capacity for this blend. However, the efficacy of the modifier is strongly influenced by its chemical composition and molecular architecture. Thus, star-shaped copolymers did not perform as well as triblock copolymers of similar composition. Saturation of the middle block of the triblock copolymer also has an important effect: the SEBS copolymers were better emulsifiers than a copolymer of similar molecular weight but with a butadiene central block.

---

*To whom correspondence should be addressed

Cigana *et al.*[12] used a series of diblock copolymers of styrene/ethylene–butylene (SEB) to modify an 80% PS/20% EPR blend. An effect of modifier molecular weight on the critical concentration for emulsification was observed in this case (contrary to what was shown in the triblock work), but there was no effect on the equilibrium particle diameter. Also, symmetrical diblock copolymers (containing 50% styrene by weight) were shown to be more effective than asymmetrical copolymers (30% styrene) of similar molecular weight. Finally, inserting a taper between the blocks did not affect the emulsification capacity of the modifier.

Lomellini *et al.*[13] developed an expression to estimate the minimum amount of block copolymer needed to saturate the interface for the case of dispersed spherical particles under melt mixing conditions. The model was based on geometrical considerations and was tested against the results of the two previous PS/EPR studies performed in this group[11,12].

This work will compare the emulsification capacities of diblock and triblock copolymers of similar molecular weight and chemical composition, at two different blend compositions.

EXPERIMENTAL

Materials

The blends investigated consist of a matrix of Dow Styron D685 polystyrene (PS) and a dispersed phase of Dexco Vistalon V-504 ethylene–propylene rubber (EPR). Three interfacial agents were used to compatibilize the blends: a styrene/ethylene–butylene diblock copolymer (SEB), supplied by Shell (CAP 4741); a styrene/ethylene–butylene/styrene triblock copolymer (SEBS), also supplied by Shell (Kraton 1650); and a styrene/butadiene/styrene triblock copolymer (SBdS), supplied by Dexco (Vector 6241D). Some properties of these materials are given in *Tables 1* and *2*. The rheological properties have been measured and reported in previous work[11]. It should be noted that although hydrogenated polybutadiene is not purely compatible with EPR, it was chosen over hydrogenated polyisoprene as the polyolefin segment of the compatibilizer, since it is very difficult to obtain complete hydrogenation of polyisoprene. A previous study[11] has shown that the presence of double bonds hinders emulsification significantly in this system.

Blend preparation

The materials were blended using a Brabender internal mixer under a nitrogen blanket at 50 rpm. The temperature was set at 200°C and the blending time was 8 min. All components were added simultaneously (one-step mixing). After mixing, the blend was quenched under cold water to freeze in the morphology. A previous study[14] has demonstrated that the most important deformation/disintegration processes take place within the first 2 min of mixing. Thus, the mixing time is sufficiently long to attain a quasi-equilibrium or steady-state morphology.

The interfacial agent concentration in the blends is expressed in terms of the minor phase volume. Thus, a blend of 90% PS/10% EPR with 10% interfacial modifier added contains 90 parts PS, 10 parts EPR and 1 part modifier (10% of EPR content), whereas a blend of 80% PS/20% EPR with 10% interfacial modifier added contains 80 parts PS, 20 parts EPR and 2 parts modifier (10% of EPR content).

Table 1 Physical properties of materials

Material	Commercial name	M_n (g/mol)	M_w (g/mol)	Density (g/ml)	T_g (°C)
PS	Styron D685 (Dow)	125000	275000	1.05	108
EPR	Vistalon V-504 (Dexco)	69000	173000	0.85	− 38

Table 2 Properties of interfacial modifiers

Modifier	Commercial name	$M_n \cong M_w$ (g/mol)	% PS (wt.%)	Description
SEBS	Kraton 1650 (Shell)	70000	29	Saturated triblock copolymer
SEB	CAP 4741 (Shell)	67000	30	Saturated diblock copolymer
SBdS	Vector 6241D (Dexco)	66000	45	Unsaturated triblock coplymer

Transmission electron microscopy

Since the butadiene block in the SBdS modifier is unsaturated, the samples containing SBdS were suitable for TEM observation in order to localize the modifier and detect possible micelle formation. Those samples were stained with osmium tetroxide for 60 h. 70 nm thick slices were cut from the samples using an RMC model MT-7 ultramicrotome, equipped with a diamond knife. The slices were then observed under a Philips model CM-30 microscope, operating at 300 keV.

Scanning electron microscopy

The emulsification curves shown in *Figures 1*, *3* and *4* were obtained using the scanning electron microscope. Prior to observation, samples were microtomed under a jet of liquid nitrogen with a Leica Jung RM 2065 microtome equipped with a glass knife. The samples were then coated with a gold–palladium alloy. Jeol models 820 and T300 scanning electron microscopes (SEM), operating at 10 kV, were used to examine the surfaces.

The semi-automatic image analyser used to measure the diameters of the dispersed phase was developed in-house.

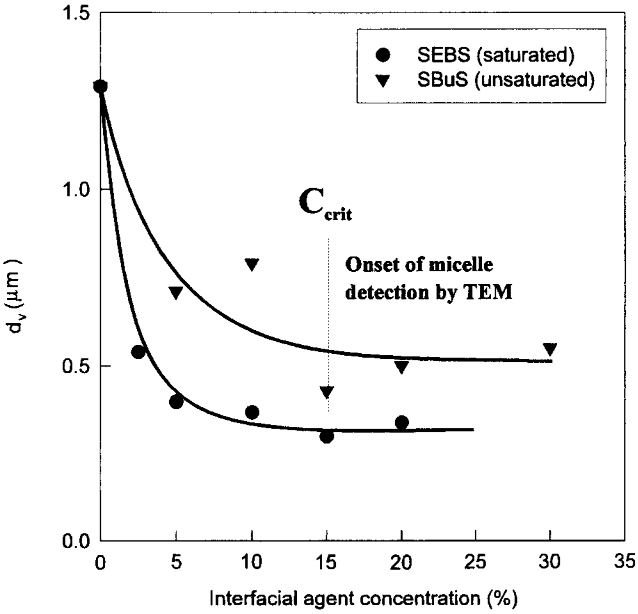
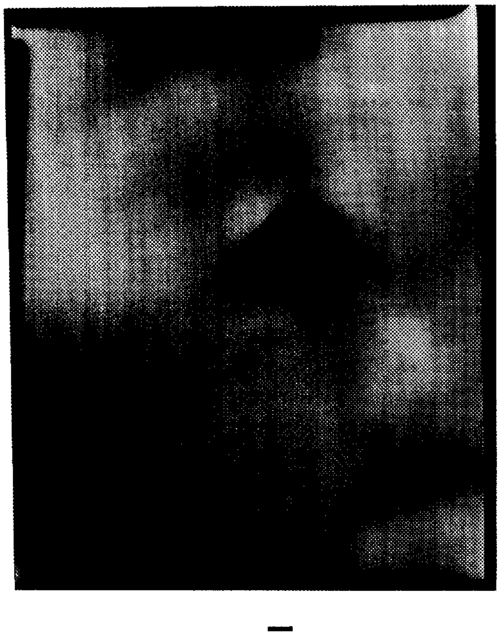
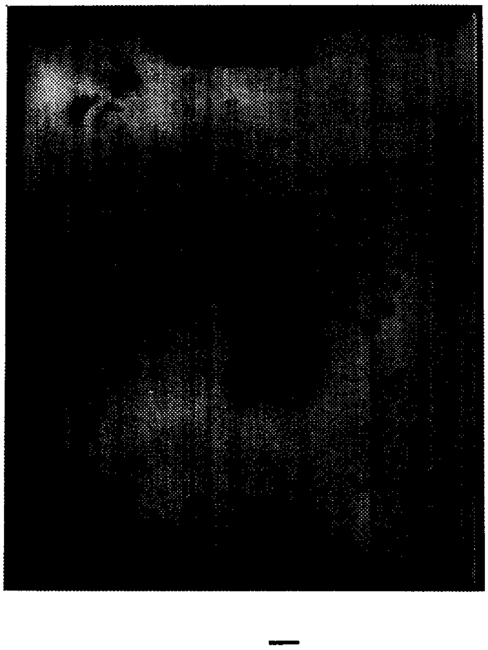


Figure 1 Emulsification curves for blends containing 90 vol% PS/10 vol% EPR, modified by unsaturated SBdS (▼) and saturated SEBS (●) triblock copolymers. The interfacial modifier concentration is based on the volume of the dispersed phase

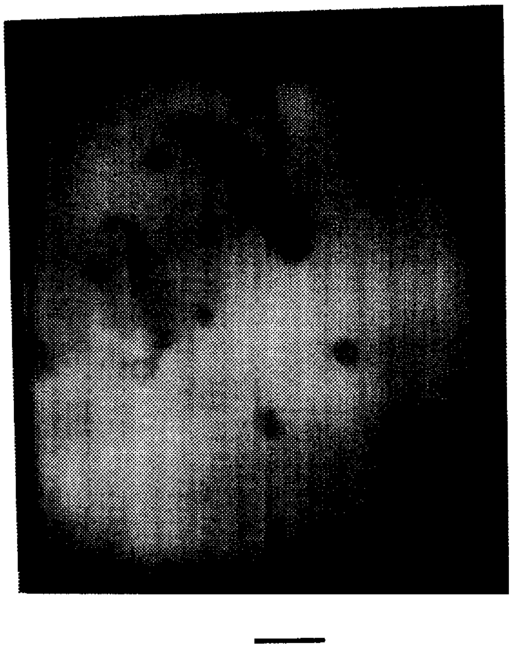


a) 100 nm



b) 100 nm

Figure 2 Transmission electron microscope micrographs of the blend 90% PS/10% EPR modified by (a) 10% and (b) 15% SBdS modifier (based on the dispersed phase volume). The periodic structure of the dark spots is visible in (c)



c) 100 nm

Figure 2c

The operation of this instrument has been described elsewhere[15]. SEM photomicrographs were analysed for each sample to calculate the number average diameter, d_n, and the volume average diameter, d_v. A correction factor[15] was applied to the diameters determined from SEM micrographs of microtomed surfaces. On average, 200–300 diameter measurements were taken per blend preparation.

RESULTS AND DISCUSSION

Observation of micelles

One of the main questions to be answered concerning the emulsification process is to what extent the interfacial modifier finds its way to the interface in the melt mixing process. In previous studies[11,12], a series of emulsification curves was generated to show the influence of a variety of molecular parameters of the modifier on its capacity to emulsify. In one of those papers[11], it was shown that using a saturated (EB) or unsaturated (Bd) middle block, in SEBS and SBdS, respectively, had a significant influence on the emulsification capability of the modifier. The results of this study are shown in *Figure 1*, and it can be seen that the unsaturated triblock interfacial modifier is only a fair modifier, as evidenced by its higher equilibrium diameter value. More scatter in the data is also a typical feature for systems which are not highly emulsified. A direct conclusion arising from that work is that the unsaturated SBdS is not as specific for the interface as its saturated counterpart.

In this study, it was decided to examine the unsaturated system by TEM to determine the onset of micelle formation. Examination of the unsaturated system is ideal for two main reasons. Firstly, it represents a system that is only fairly emulsified, and hence, of any of our previous studies, represents the case where micelle formation would likely be occuring. Secondly, the double bonds are readily stained by osmium tetroxide for unambiguous visualization of that segment of the copolymer molecule. *Figure 2* shows TEM micrographs of the 90% PS/10% EPR blends compatibilized with 10% (a) and 15% (b) SBdS modifier, based on the minor phase volume. Many dark spots are clearly visible on *Figure 2b*, but not on *Figure 2a*. Close observation of these dark zones (*Figure 2c*) reveals their periodic structure, with alternating dark (butadiene, stained) and light (styrene) zones, confirming that they are indeed microphases of interfacial agent. So-called 'onion' and 'ribbon' structures, previously reported in the literature[7], can be observed.

The sizes of these domains of interfacial agent are in the 20–400 nm diameter range. The period size (measured from the middle of a dark zone to the middle of the next dark zone) varies from 13 to 27 nm, with an average near 20 nm. The radius of gyration of such a molecule in the unperturbed state can be estimated by:

$$R_g^2 = \frac{C_\infty N_A L^2}{6}$$

where N_A is the number of main skeletal bonds in a chain of type A, C_∞ is the characteristic ratio of the chain, and L is the length of a skeletal bond. Using average literature values for the last two parameters[17–19], the radius of gyration is estimated at about 12 nm. Given that the molecular arrangement in the microphase probably imposes conformation restrictions on the chains (i.e. stretching of the blocks into their respective microphases), this value is consistent with the observed period.

Several other authors have observed such micellar forms by TEM, but most of these studies were performed on solvent-cast films of binary blends (A/A–B)[20–22]. For these reasons, the micelles observed in those studies were in the micron rather than the nanometer range. The present work is one of the first which examines micelles formed by melt mixing, and in the presence of a minor phase. These conditions more closely simulate an actual blending situation, where the block copolymer is added in small quantities (1.5% based on the total blend, in this case, as compared to 15–30% concentration in previous studies) as a compatibilizer rather than a minor phase in itself.

This raises an important point regarding much of the theoretical and experimental work in this field. Many studies have been carried out to determine, for example, the critical micelle concentration (CMC) for homopolymer/block copolymer blends. In that situation, the CMC, defined as the concentration of block copolymer at which the weight fraction of block copolymer in a micellar conformation increases abruptly[23], would be extremely low. In a case such as the one examined here, however, there is a matrix/minor phase interface towards which the block copolymer is strongly drawn. This has the effect of drastically increasing the CMC as compared to the binary blend case.

No micelles of SBdS were detected by TEM at modifier concentrations lower than the critical concentration for emulsification for this system. This may mean that micelle formation is negligible below the critical concentration for emulsification in a ternary system; however, this would seem surprising, since SBdS is only a fair emulsifier for this system. Instead, it may be possible that the TEM detecting limit is already at a point where micelle formation is advanced. This point will be addressed in the following section.

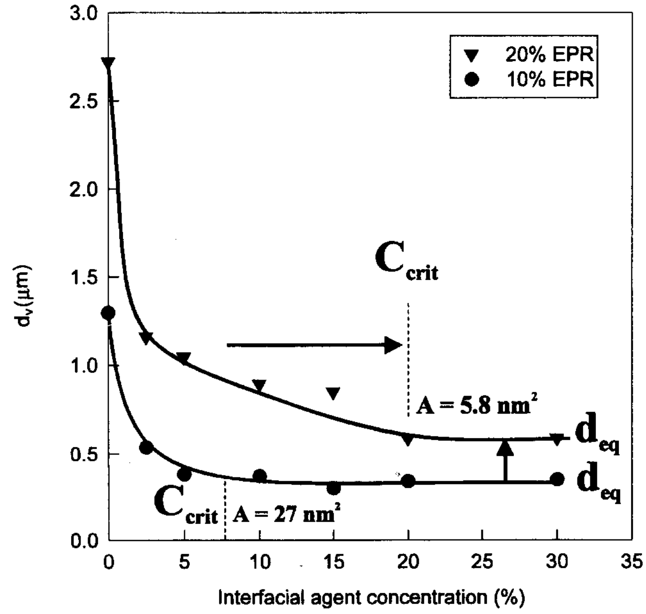


Figure 3 Effect of blend composition on emulsification by the SEBS triblock copolymer. Interfacial agent concentration is based on the volume of dispersed phase. Note the shift in critical concentration for emulsification and in equilibrium diameter, and the resulting change in interfacial area occupied per molecule

Emulsification curves and composition study

Direct comparisons of diblock and triblock copolymer efficacy were made on systems comprising 90% PS/10% EPR (volumetric), and 80% PS/20% EPR, modified by SEBS (triblock) and SEB (diblock) interfacial agents. The emulsification curves are shown in *Figures 3 and 4*. For comparison purposes, it is useful to express the interfacial agent concentration based on the minor phase volume instead of the total volume of the blend. This takes into account the fact that more dispersed phase requires larger quantities of interfacial modifier to achieve interfacial saturation, due to the higher total interfacial area.

For the triblock copolymers (*Figure 3*), the critical concentration shifts from about 7.5% to 20% interfacial agent (or 0.75% to 4%, based on the total blend volume) when going from 10% to 20% minor phase. The equilibrium diameter also increases from about 0.35 μm to 0.6 μm. Variations in both the critical concentration for emulsification and the equilibrium particle diameter are accounted for when one calculates the interfacial area occupied per molecule of interfacial modifier. This value is obtained by dividing the number of molecules of interfacial agent in the blend by the total blend interfacial area (which can be estimated by the mean particle size). This calculation assumes that all the interfacial agent added to the blend migrates to the interface, and this assumption is only meaningful at concentrations of interfacial agent less than or equal to the critical concentration for emulsification. The triblock copolymer (SEBS), in a 90% PS/10% EPR blend, occupies an interfacial area of about 27 nm²/molecule at the critical concentration. If micellar formation is negligible in this system, then the interfacial area occupied per molecule

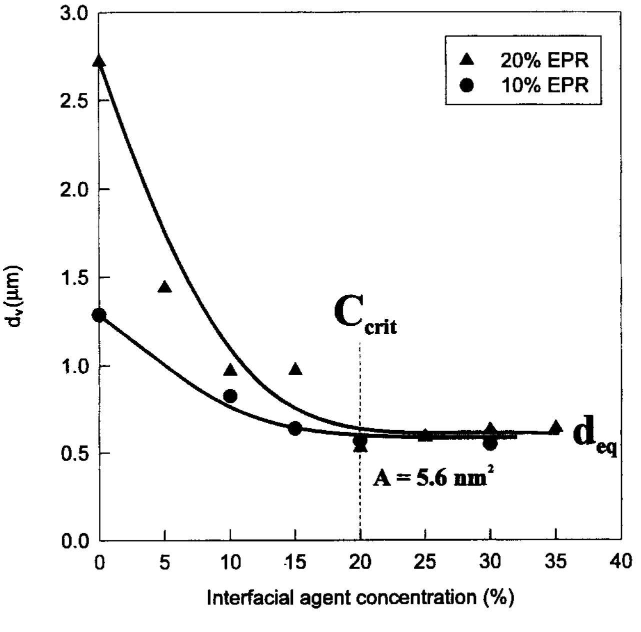


Figure 4 Effect of blend composition on emulsification by the SEB diblock copolymer. Interfacial agent concentration is based on the volume of dispersed phase

should remain constant when going from a 90/10 to an 80/20 system, because the state of the interface should be similar. However, the apparent interfacial area occupied per molecule for the 80/20 blend (which contains twice the amount of modifier at a given concentration than the 90/10 case), at the critical concentration, is 5.8 nm^2/molecule. Since this value is much smaller, it can be assumed that much of the SEBS in the 80/20 blend is either lost in the form of micelles or monomolecularly dispersed in one or both of the phases. Even at 10% interfacial modifier based on the minor phase, the calculated interfacial area occupied is around 8 nm^2/molecule, indicating that micellar formation is an important phenomenon even well below the critical concentration for this system.

In *Figure 4*, the effect of the composition of the blend on the emulsification by diblock copolymers is shown. It must be kept in mind that since the concentration of interfacial modifier is based on the minor phase volume, at a given concentration of modifier, the 80/20 blend contains twice as much block copolymer, in absolute value, as the 90/10 blend. It is remarkable that both the 90/10 and the 80/20 systems achieve interfacial saturation at the same concentration of interfacial modifier (20%, based on the dispersed phase volume), and the same equilibrium diameter. The interfacial area occupied is therefore equal in both cases, at around 5.6 nm^2. This value is much lower than that obtained for the triblocks at 10% minor phase, and intuitively, this would be expected[12]. Indeed, a diblock copolymer can assume a conformation that extends away from the interface, thus occupying less area than a triblock copolymer, whose central block separates the two end blocks, forcing a looping in and out of the minor phase, or at least flattening it at the interface. More importantly, the diblock interfacial area value does not depend on the blend composition, which leads to the astounding conclusion that up to the critical concentration for emulsification, all the diblock modifier goes to the interface.

These findings suggest a new, unforeseen application of the emulsification curve: it may be used as a sensitive tool to track micelle formation. Already, in this group, it has been suspected in a recent study[24] that dynamic effects were responsible for the poorer impact strength of 80% PS/20% EPR blends compatibilized by a high molecular weight triblock compatibilizer ($M_n = 174\,000$) as compared to a lower molecular weight triblock compatibilizer ($M_n = 50\,000$). The emulsification curves obtained for those blends (see original paper) indicated that much of the high molecular weight compatibilizer did not migrate as efficiently to the interface. This was suggested by the equilibrium diameter on the emulsification curve, which was twice as high as that obtained with the low molecular weight interfacial agent. Annealing studies confirmed this by demonstrating markedly high coalescence for the high molecular weight material, which apparently was not finding its way to the interface, perhaps due to micelle formation. It is indeed well known that a block copolymer's propensity for micelle formation strongly increases with its molecular weight[4].

It is interesting to note that the diblock copolymers in this study demonstrate a higher efficacy for the interface than their triblock counterparts, at a given molecular weight and chemical composition, when the modifier is present in high absolute quantities. This finding may seem surprising at first. Indeed, it contradicts the results obtained by Horák *et al.*[25], which constitute, to our knowledge, the only published comparison of diblock and triblock copolymers as emulsifiers of polymer blends in the melt phase. Horák *et al.* compared the efficacy of diblock, triblock and pentablock copolymers of styrene and butadiene at compatibilizing blends of polypropylene (PP) and high impact polystyrene (HIPS). They observed, by TEM, a large number of microphases of diblock copolymers dispersed in the matrix. In addition, the black layer (stained copolymer) surrounding the dispersed phase droplets was more clearly developed in the case of the tri- and pentablock copolymers as in the case of the diblock copolymers. This seemed to indicate that the diblock copolymer was inefficient at migrating to the interface; mechanical tests confirmed this. However, in that study, the molecular weight of the diblock copolymer used was more than twice that of the tri- or pentablock copolymer. This does not allow for a fair comparison between the different interfacial modifiers, since, as stated earlier, the tendency of a block copolymer to form micelles increases rapidly with its molecular weight. Furthermore, the polybutadiene segment, with its double bonds, significantly diminshes the emulsification capability of the compatibilizer for a system with a PP minor phase[11].

Thermodynamic arguments can be invoked to explain the superiority of diblocks over triblocks in compatibilizing this system at higher concentrations of modifier. Although simple, well-defined molecules with a sharp demarcation in chemical structure tend to form micelles more easily than more complex molecules with a certain degree of randomness in their chemical structure[22], complex, multiblock copolymers must also overcome important entropic constraints to situate themselves at the interface and assume a minimal free energy conformation. Thus, though diblocks form micelles more easily than triblocks in a binary system[26], in the ternary blend case, diblocks may also be more strongly driven to the interface than triblocks, and therefore act more efficiently as emulsifiers. One must also bear in mind that thermodynamic models predicting micellar formation assume 'ideal' spherical micelles, with sharply defined cores and coronas. Though such 'model' micelles may be obtained in well-controlled conditions, such as solvent-cast films (which has been the chosen method for most of the experimental work in this field), it is questionable whether this approach is relevant in industrial melt-mixing processes.

One last point to be addressed is the lower equilibrium diameter achieved with the triblock copolymers at 10% minor phase, which is around 0.35 μm (*Figure 3*), compared to 0.6 μm with the diblock copoylmers at the same composition (*Figure 4*). Assuming that at 10% minor phase all the interfacial modifier migrates to the interface at modifier concentrations up to the critical concentration, the difference in equilibrium particle diameter between the diblock- and triblock-modified systems can be attributed either to a difference in interfacial tension or to coalescence effects. Leibler[27] has shown theoretically that diblocks were slightly more effective than triblocks at reducing the interfacial tension in a ternary blend; the explanation of the results shown here therefore likely lies in the suppression of coalescence effects.

It is possible that the interweaving of the triblock copolymer molecules across the interface renders the triblock more effective than the diblock copolymer at immobilizing the interface. The spacing between the polystyrene blocks of the copolymer may allow penetration of polystyrene matrix chains into the interfacial area, again stabilizing the interface. The lower interfacial area occupied per molecule obtained with the diblock copolymers

(5.6 nm^2, as compared to 27 nm^2 for the triblock copolymers at 10% minor phase) indicates that the diblocks are more densely packed at the interface, and that they tend to extend away from the interface more than the triblocks. The impact of these phenomena on minor phase particle coalescence is not yet clear.

CONCLUSIONS

These results show that at 90% PS/10% EPR and at 80% PS/20% EPR, a diblock copolymer attains a similar critical concentration for interfacial saturation and equilibrium particle size on the emulsification curve. The area occupied per molecule of diblock modifier is identical at 5.6 nm^2 despite the fact that the 80/20 system contains twice as much modifier, based on the total blend volume, as the 90/10 blend at the critical concentration. This indicates that almost all of the diblock modifier finds its way to the interface. The triblock copolymer is a better emulsifier than the diblock at 90% PS/10% EPR as shown by the lower C_{crit} and equilibrium particle size. However, when the amount of triblock modifier is doubled in the 80/20 blend, the C_{crit} and d_{eq} values increase considerably with the apparent interfacial area decreasing from 27 to 5.8 nm^2. This indicates that modifier is not reaching the interface and strongly suggests micellar formation even though TEM performed on a similar system modified by an unsaturated compatibilizer does not indicate the presence of micelles.

These results strongly indicate that micelle detection by TEM is limited and that, in fact, the emulsification curve, although an indirect approach, may be used as a sensitive tool to detect the onset of molecular aggregation.

ACKNOWLEDGEMENTS

The authors would like to thank the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support of this project, as well as Mr Alain Tremblay and Ms Valérie Benoit for their experimental work.

REFERENCES

1. Paul, D. R. and Newman, S., *Polymer Blends*. Academic Press, New York, 1978.
2. Favis, B. D., *Can. J. Chem. Eng.*, 1991, **69**, 619.
3. Leibler, L., *Makromol. Chem. Macromol. Symp.*, 1988, **16**, 1.
4. Whitmore, M. D. and Noolandi, J., *Macromolecules*, 1985, **18**, 657–665.
5. Fayt, R., Jérôme, R. and Teyssié, Ph., *J. Polym. Sci., Polym. Phys. Ed.*, 1986, **24**, 25.
6. Polance, R., Nichols, K. L. and Jayaraman, K., *Polymer*, 1994, **35**, 5051.
7. Jannasch, P., Hassander, H. and Wesslén, B., *J. Polym. Sci., Polym. Phys. Ed.*, 1996, **34**, 1289.
8. Tremblay, A., Tremblay, S., Favis, B. D., Selmani, A. and L'Espérance, G., *Macromolecules*, 1995, **28**, 4771.
9. Djakovic, L., Dokic, P., Radivojevic, P., Sefer, I. and Sovilj, V., *Coll. Polym. Sci.*, 1987, **265**, 993.
10. Favis, B. D., *Polymer*, 1994, **35**, 1553.
11. Matos, M., Favis, B. D. and Lomellini, P., *Polymer*, 1995, **36**, 3899.
12. Cigana, P., Favis, B. D. and Jérôme, R., *J. Polym. Sci., Polym. Phys. Ed.*, 1996, **34**, 1691.
13. Lomellini, P., Matos, M. and Favis, B. D., *Polymer*, 1996, **37**, 5689.
14. Favis, B. D., *J. Appl. Polym. Sci.*, 1990, **39**, 285.
15. Favis, B. D. and Chalifoux, J. P., *Polym. Eng. Sci.*, 1987, **27**, 1591.
16. Saltikov, S. A., *Stereometric Metallography*. Metallurgizdat, Moscow, 1958.
17. Graessley, W. W. and Edwards, S. F., *Polymer*, 1981, **22**, 1329.
18. Aharoni, S. M., *Macromolecules*, 1983, **16**, 1722.
19. Wu, S., *J. Polym. Sci., Polym. Phys. Ed.*, 1989, **27**, 723.
20. Koizumi, S., Hasegawa, H. and Hashimoto, T., *Macromolecules*, 1994, **27**, 6532.
21. Braun, D., Fischer, M. and Hellmann, G. P., *Makromol. Chem. Macromol. Symp.*, 1994, **83**, 77.
22. Jiang, M., Huang, X. and Yu, T., *Polymer*, 1983, **24**, 1259.
23. Leibler, L., Orland, H. and Wheeler, J. C., *J. Chem. Phys.*, 1983, **79**, 3550.
24. Cigana, P., Favis, B. D., Albert, C. and Vu-Khanh, T., *Macromolecules*, 1997, **30**, 4163.
25. Horák, Z., Fořt, V., Hlavatá, D., Lednický, F. and Večerka, F., *Polymer*, 1996, **37**, 65.
26. Noolandi, J., *Makromol. Chem. Theory Simul.*, 1992, **1**, 295.
27. Leibler, L., *Macromolecules*, 1982, **15**, 1283.