

# Strategies to measure and optimize the migration of the interfacial modifier to the interface in immiscible polymer blends

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## Abstract

A family of emulsification curves has been systematically prepared in order to determine the extent of interfacial modifier migration to the high density polyethylene (HDPE)/polystyrene (PS) interface. Through an examination of the evolution of the equilibrium dispersed phase size after interfacial saturation, as well as a comparison of the apparent interfacial area occupied per modifier molecule ( $A_{app}$ ) at the different dispersed phase concentrations, it is possible to detect the onset of micelle formation and to estimate the extent of interfacial coverage. This approach has been applied to HDPE/PS blends, using a variety of triblock and diblock copolymer interfacial modifiers for that system. It is shown quantitatively that it is the affinity of the block copolymer for the matrix material that dominates migration efficacy to the interface. Asymmetrical block copolymers (30PS/70EB) show a strong tendency to form micelles when HDPE is the matrix. This effect is virtually eliminated when PS is the matrix material or when symmetrical block copolymers (50PS/50EB) are used. In these latter cases all the interfacial modifier finds its way to the interface. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Emulsification curve; Interfacial area per copolymer molecule; Micelle formation

## 1. Introduction

The addition of an appropriately tailored block copolymer to an incompatible polymer blend can have a profound effect on both the morphology and on the mechanical properties of that blend [1–11]. The morphology of the blend is mainly related to the effects of the block copolymer in reducing the interfacial tension [12–14] and suppressing particle–particle coalescence [15–17]. This leads to a significant reduction in dispersed phase size [5,9,18–21]. The efficacy of a copolymer, as an interfacial modifier, for the interface of polymer blend is often characterized by an emulsification curve, which essentially follows the evolution of the dispersed phase size with copolymer composition. The shape of the emulsification curve is highly dependent on interfacial modifier type and on the processing conditions [22]. The emulsification curve has been studied for several polymer blend systems [23–25] and it displays a key characteristic, an initial significant drop in the size of the dispersed phase with the addition of copolymer followed

by the obtention of an equilibrium value at high concentration of copolymer. A detailed discussion of the fundamentals of the emulsification curve is given in Section 3.

In previous work from this laboratory, Matos et al. [5] studied blends of 90% polystyrene (PS)/10% ethylene–propylene rubber (EPR) compatibilized by commercial triblock copolymers of styrene–ethylene butylene–styrene (SEBS), styrene–butadiene–styrene (SBdS) and a star-shaped copolymer. They noted that the molecular weight of the interfacial agents did not have an effect on the critical concentration for emulsification, nor did it influence the equilibrium particle diameter. They reported that a 30PS/70 ethylene butylene triblock copolymer of 50, 70, and 174 kg/mol occupied interfacial areas of 13, 27, and 45 nm<sup>2</sup>/molecule, respectively. They also established that triblock copolymers were more effective as compatibilizers than star-shaped copolymers.

Cigana et al. [7–9] investigated the efficacy of various diblock interfacial modifiers for the PS/EPR interface using the emulsification curve. Their results showed that at 90% PS/10%EPR and 80%PS/20% EPR, a diblock copolymer attains a similar critical concentration for interfacial saturation and equilibrium particle size on the emulsification curve [9]. The interfacial area occupied per molecule of

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diblock modifier of molecular weight 67 kg/mol and composition 30%PS/70% ethylene butylene is identical in both cases ( $5.6 \text{ nm}^2$ ), despite the fact that the 80%PS/20%EPR blend system contains twice as much modifier based on the total blend volume, as the 90%PS/10%EPR blend at the critical concentration. Considering the above interesting phenomenon, they proposed that almost all of the diblock modifier finds its way to the interface during melt blending. At 90%PS/10%EPR they found that a triblock copolymer is a better emulsifier than the diblock [9]. However, when the amount of triblock copolymer is doubled in the 80%PS/20% EPR blend, the equilibrium diameter of the dispersed phase increases considerably from 0.35 to 0.55  $\mu\text{m}$  and the apparent interfacial area per molecule decreases from 13 to 5.6  $\text{nm}^2$  [5,8]. This strongly suggested that much of the SEBS in the 80%PS/20%EPR blend was either lost in the form of micelles or was monomolecularly dispersed in one or both of the phases. They concluded that micelle formation below the critical concentration was the key factor for lowering the emulsification efficacy of triblock copolymer. From the earlier work they suggested that a family of emulsification curves, prepared at different levels of dispersed phase concentration, could be used as a tool to detect the efficacy of an interfacial modifier to migrate to the interface.

Some research work has already considered micelle formation in interfacially modified melt blended systems. Fayt et al. [1] observed the location of block copolymers at the interface of LDPE and PS by transmission electron microscope (TEM). The block copolymer formed layers with a seemingly regular thickness around the dispersed phase of either PS or LDPE. Block copolymer micelles were also observed in the LDPE phase. Dai et al. [26] investigated the segregation of a poly [(2-vinylpyridine)-*b*-styrene-*d*<sub>8</sub>-*b*-(2-vinylpyridine)] (PVP-dPS-PVP) triblock copolymer and dPS-PVP diblock copolymer to a planar interface between the PS and PVP by forward recoil spectrometry. In their experiment, they prepared a series of laminate samples (one layer is pure PVP and the other layer, PS mixed with various volume fractions of triblock copolymer) and then annealed the samples to allow the block copolymer to segregate to the interface between the PS and PVP homopolymers. They compared the interfacial excess for triblock and diblock copolymer and found that triblock copolymer has a larger critical micelle concentration than the diblock copolymer. Polance et al. [27] demonstrated that under the influence of a dynamic melt environment, the micelles tend to be significantly smaller than those generated in solution. Jannasch et al. [28] studied the macro- and microphase separation of compatibilizing graft copolymers in melt-mixed PS/polyamide 6 blends. In their work the TEM was used to relate the onset of micelle formation to concentrations higher than the critical concentration as defined by the emulsification curve.

Cigana et al. [9] carried out a TEM study to analyze micelle formation in the 90%PS/10%EPR blend containing

15%SBdS (based on the dispersed phase). SBdS was chosen because it had been shown to be only a fair emulsifier for that system and should have a tendency therefore to readily demonstrate micelle formation. Furthermore the butadiene part of the block was readily stained using osmium tetroxide. In their work micelle detection was only observed at values equal to or greater than the critical concentration even though the emulsification curve clearly indicated that a significant portion of that modifier was not effectively migrating to the interface. It was concluded that the TEM is limited in its ability to demonstrate the onset of micelle formation. A possible explanation for this effect is that the onset of micelle formation is characterized by a molecular dispersion with a large interparticle distance between micelles. Since the limiting thickness of sections for the TEM is about 100 nm it is likely that these initially formed micelles escape detection.

The objective of this work is to systematically prepare a family of emulsification curves at various levels of dispersed phase concentration in order to detect the micelle formation of copolymer below and at the critical concentration level. Since the amount of added copolymer is calculated based on the quantity of dispersed phase, increasing the dispersed phase concentration also increases the concentration of modifier in the mixing bowl at a given stated level of copolymer. The variation in the observed behaviors will be analyzed to explore the potential of the emulsification curve as a tool to quantify the efficacy of migration of the modifier to the interface. A number of interfacial modifier copolymers of varying architecture and chemical composition will be studied.

## 2. Experimental

### 2.1. Materials

Both the PS and the high density polyethylene (HDPE) used in this study were obtained from Dow Chemical of Canada. The antioxidant used was Irganox 1010 from Ciba-Geigy. Two types of interfacial agents of well characterized molecular weight and composition were chosen. The first type of modifier consists of two styrene-ethylene-butylene diblock copolymers of similar molecular weight and different %styrene, referred to as SEB1 and SEB2, respectively. The second type of modifier consists of two SEBS triblock copolymers of different %styrene referred to as SEBS1 and SEBS2, respectively. Some properties of these materials are given in Table 1.

### 2.2. Blend preparation

The materials were blended using a Brabender internal mixer under a nitrogen blanket at 50 rpm. The temperature was set at 195 °C and the blending time was 5 min. Prior to blending, all the components were dry mixed and 0.2% of Irganox 1010 was added as an antioxidant. All components

Table 1  
Characteristic properties of materials

	PS	HDPE	SEBS1	SEBI	SEBS2	SEB2
$M_w$	215 000	79 000				
$M_n$	100 000	24 000	$S = 7500$ ; EB = 35 000; composition: 30% styrene	$S = 20 000$ ; EB = 47 000; composition: 30% styrene	$S = 22 000$ ; EB = 44 000; composition: 50% styrene	$S = 33 390$ ; EB = 29 610; composition: 53% styrene
Density (20 °C) (g/ml)	1.04	0.962	0.910	0.910	0.910	0.910
Density (195°C) (g/ml)	0.974	0.754	0.820	0.820	—	—
Supplier	Dow	Dow	Shell	Shell	Synthesized	Synthesized

were then added into the internal mixer simultaneously (one step mixing). After mixing, the blend was quenched under liquid nitrogen to freeze in the morphology.

The effect of the sequence of addition of interfacial modifier was tested on 10%PS/90%HDPE blends. No difference in the morphology was observed when the copolymer interfacial modifier was initially premixed with the PS phase followed by blending with HDPE.

The copolymer concentration in the blends is expressed in terms of the minor phase volume. Thus, a blend of 10%PS/90%HDPE with 10% added copolymer contains 10 parts PS, 90 parts HDPE and one part copolymer (10% of PS content), whereas a blend of 30%PS/70%HDPE with 10% added copolymer contains 30 parts PS, 70 parts HDPE and three parts of copolymer (10% of PS content).

### 2.3. Matrix dissolution

In the cases where PS is the matrix, matrix dissolution was carried out to isolate the dispersed phase for subsequent microscopic observation. The extraction of the PS matrix was performed followed by centrifugation. Initially the sample (about 1 g) was placed into a centrifuge tube filled with 50 ml tetrahydrofuran (THF) at room temperature. The tube containing the sample was then placed on a shaker and shaken for 48 h. After that, the sample was centrifuged for 1 h. The precipitated HDPE was situated at the bottom of the tube and the solution was poured away. To purify the precipitated HDPE, fresh THF solvent was added and the sample was shaken for another 48 h. This process was repeated three times, which was sufficient to separate the HDPE dispersed phase from PS matrix in the HDPE/PS blend. Finally, all the dispersed phase samples were carefully collected and dried in a vacuum oven at 40 °C for 72 h.

### 2.4. Microtomy and scanning electron microscopy

For the samples with PS as dispersed phase, blends with and without copolymer were microtomed under a jet of liquid nitrogen (−150 °C) to create a plane face with a Leica Jung RM 2065 microtome equipped with a glass knife. The samples were then subjected to solvent extraction with a Soxhlet extraction apparatus to remove the dispersed PS phase. This serves to improve the contrast during subsequent microscopic observation. The selective solvent extraction of dispersed PS and copolymer in THF was performed in a Soxhlet extractor for 36 h and was then dried in a vacuum oven for 72 h at 40 °C.

All the samples (with PS and/or with HDPE as dispersed phases) were coated with a gold–palladium alloy. A JEOL 840 scanning electron microscope, operating at 10 kV, was used to examine the surfaces.

### 2.5. Image analysis

A semi-automatic image analyzer was used to measure

the diameters of the dispersed phase. The operation of this instrument has been described elsewhere [29]. SEM photomicrographs were analyzed for each sample to calculate the number average diameter,  $d_n$ , and volume average diameter,  $d_v$ . Since the microtome does not necessarily cut the dispersed phase at the equator and since it is necessary to correct for polydispersity, a correction factor [30] was applied to the diameters determined from SEM micrographs of microtomed surfaces. On average, 200–300 diameters were measured per sample. For the noncompatibilized blends, the uncertainty of the average diameter measurements by this method is about 10%, and for the compatibilized blends, about 5%.

### 3. Results and discussion

#### 3.1. General tendencies of the emulsification curve

Fig. 1(a) demonstrates a typical idealized emulsification

curve such has been studied in this laboratory for several polymer blend systems [4,5,23–25]. The emulsification curve is characterized by an initial significant drop in the size of the dispersed phase with the addition of copolymer followed by the obtention of an equilibrium value ( $d_{eq}$ ) at a critical concentration of copolymer ( $C_{crit}$ ). As mentioned earlier, 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 agent to achieve interfacial saturation, due to the higher total interfacial area. One of the most important features of the emulsification curve is that it can be used to estimate the interfacial area occupied by the interfacial modifier molecule at the interface ( $A$ ) or its reciprocal, the areal density ( $\Sigma$ ).

Knowing the equilibrium particle diameter and the critical concentration for emulsification, the interfacial

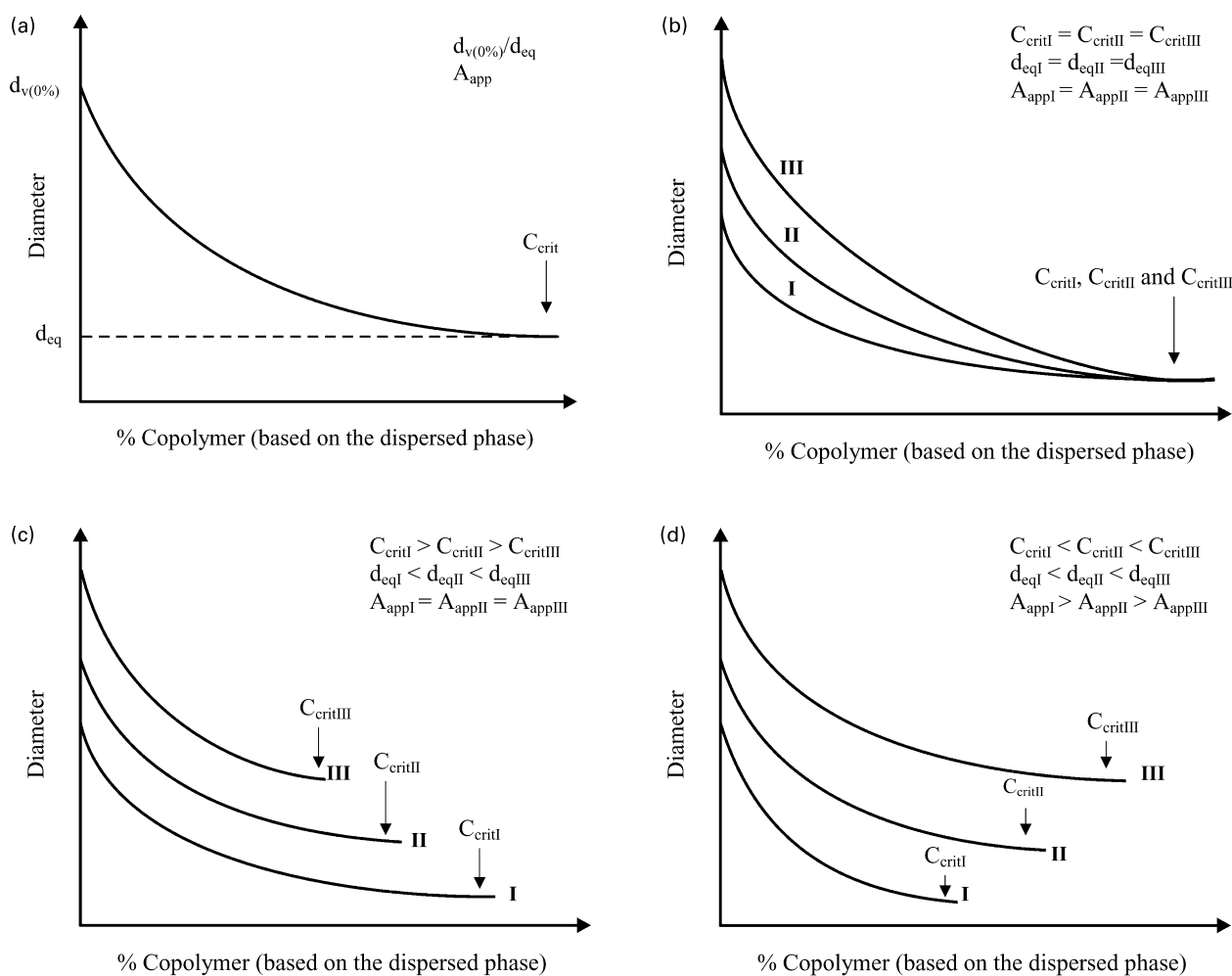


Fig. 1. General conceptual tendencies of emulsification curves. I, II and III represent dispersed phase concentrations where  $I < II < III$ . (a) General features of an emulsification curve; (b) family of emulsification curves expected for a system in which all the modifier migrates to the interface and the modifier entirely suppresses dynamic coalescence; (c) family of emulsification curves expected for the case where all the modifier migrates to the interface, but the modifier is ineffective at completely suppressing dynamic coalescence; and (d) family of emulsification curves expected for a system in which the modifier is not effectively driven to the interface due to micelle formation.

area occupied per molecule may be calculated using the following equation

$$A = \frac{6\varphi_d M}{d_{eq} N_A \varphi_c \rho_c} \quad (1)$$

where  $\varphi_d$  is the volume fraction of dispersed phase,  $N_A$  is Avogadro's number,  $M$  is the molecular weight of the copolymer,  $d_v$  is the volume average diameter of the dispersed phase,  $\varphi_c$  is the volume fraction of the compatibilizer, and  $\rho_c$  is the density of the compatibilizer. The best measure of the diameter is its surface average value, but the volume average diameter is also acceptable since it results in a similar value [5].

An important assumption must be made in the above calculation—one must assume that at the critical concentration, all the interfacial agent added to the system is located at the interface. For this reason, in this study we will refer to the interfacial area occupied per modifier molecule as an apparent area,  $A_{app}$ .

### 3.2. Idealized trends

Based on the above fundamental information, a number of idealized trends can be extrapolated for the emulsification curve. If one studies a family of emulsification curves based on different dispersed phase concentrations (e.g. 1, 5, and 20%) different behaviors related to the efficacy of the interfacial modifier would be expected. In Fig. 1(b)–(d) we show three basic tendencies for three different dispersed phase concentrations (I,II,III).

(i) Fig. 1(b) represents the family of emulsification curves expected for a system in which all the modifier migrates to the interface and the modifier entirely suppresses dynamic coalescence. In such a case,  $C_{crit}$  and  $d_{eq}$  are both independent of dispersed phase volume fraction. It follows then that the  $A_{app}$  is also

independent of volume fraction. In that case  $A_{app}$  represents the true interfacial area occupied by the interfacial modifier molecule.

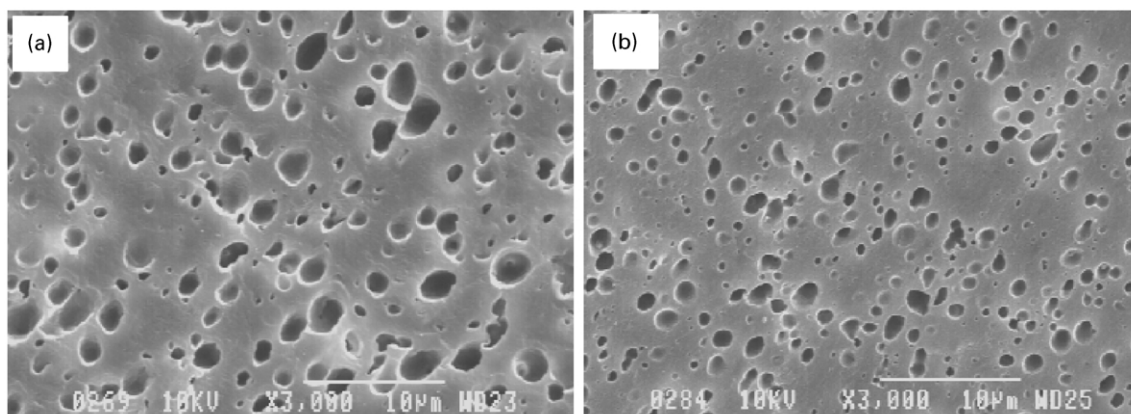
(ii) Fig. 1(c) represents the case where all the modifier migrates to the interface, but the modifier is ineffective at completely suppressing dynamic coalescence. In such a case, the  $d_{eq}$  will increase with dispersed phase volume fraction,  $C_{crit}$  will decrease with dispersed phase volume fraction and  $A_{app}$  will be independent of volume fraction. In this case as well,  $A_{app}$  represents a true interfacial area.

(iii) Fig. 1(d) demonstrates the expected trends for a system in which the modifier is not effectively driven to the interface due to micelle formation. In this case  $d_{eq}$  will increase with volume fraction of dispersed phase, since micelle formation is concentration dependent. Since the modifier is not migrating effectively to the interface  $C_{crit}$  will increase with volume fraction. These changes in  $d_{eq}$  and  $C_{crit}$  will result in a decrease of  $A_{app}$  with volume fraction. In this case  $A_{app}$  does not represent the true interfacial area occupied per modifier molecule since the system is only partially emulsified.

### 3.3. Family of emulsification curves for PS dispersed in HDPE

Microtomed surfaces, followed by minor phase dissolution, for 10%PS/90%HDPE blends in the absence of and with compatibilizer are shown in Fig. 2(a) and (b). It can be immediately seen that the presence of interfacial modifier in the blends results in a decrease in the diameters of the dispersed phase.

The effect of the interfacial modifier on the morphology of the HDPE/PS blends at various PS concentrations (1, 2, 5, 10, 20, and 30%) is shown in Fig. 3(a) and (b). Fig. 3(a) and (b) clearly indicate an increase in  $d_{eq}$  with dispersed phase volume fraction as well as a tendency for  $C_{crit}$  to increase.



Scale bar: ————— 10 μm

Fig. 2. SEM of 90%HDPE/10%PS blends without and with compatibilizer: (a) 0% of SEBS1; (b) 15% of SEBS1.



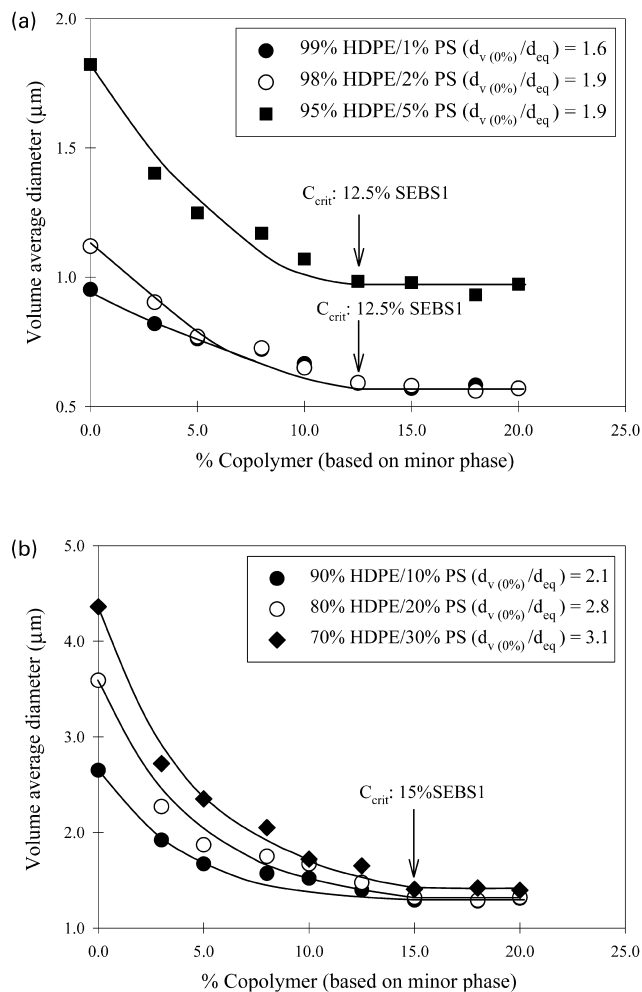


Fig. 3. A family of experimentally determined emulsification curves for the HDPE/PS blends at various dispersed phase concentrations. The copolymer interfacial modifier is SEBS1. (a) Emulsification curves for 99%HDPE/1%PS, 98%HDPE/2%PS and 95%HDPE/5%PS blends; (b) emulsification curves for 90%HDPE/10%PS, 80%HDPE/20%PS and 70%HDPE/30%PS blends.

The equilibrium volume average diameter as well as the  $A_{app}$  at the critical concentration is given in Table 2 for each minor phase concentration. From 1 to 30% dispersed phase, one observes an increase in the critical concentration from 12.5 to 15% and an increase in the  $d_{eq}$  from 0.58 to 1.41  $\mu\text{m}$ .

Fig. 4 shows the estimated  $A_{app}$  values at  $C_{crit}$  as a

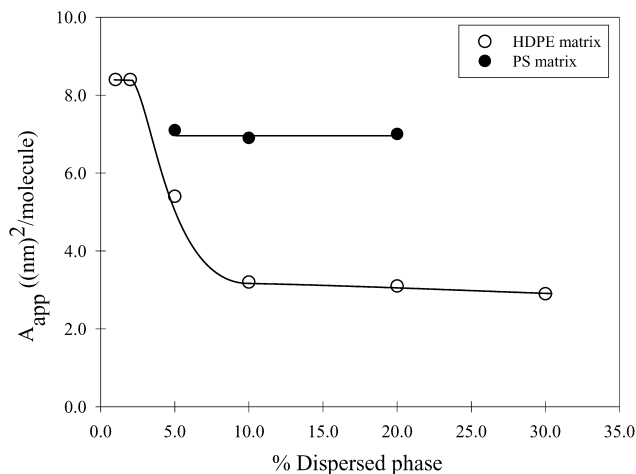


Fig. 4.  $A_{app}$  of SEBS1 copolymer vs. dispersed phase concentration for blends with both HDPE and PS as matrix.

function of dispersed phase volume fraction. There is a significant decrease in the apparent interfacial area occupied per molecule with increasing minor phase concentration. SEBS1 in 99%HDPE/1%PS and 98%HDPE/2%PS possesses the same  $A_{app}$  values ( $8.4 \text{ nm}^2$ ). A sharp decrease of  $A_{app}$  occurs at 95%HDPE/5%PS ( $5.4 \text{ nm}^2$ ), and after that this value stays more or less constant for 90%HDPE/10%PS ( $3.1 \text{ nm}^2$ ), 80%HDPE/20%PS ( $3.1 \text{ nm}^2$ ), 70%HDPE/30%PS ( $2.9 \text{ nm}^2$ ) and 50%HDPE/50%PS ( $2.7 \text{ nm}^2$ ). This phenomenon will be discussed in terms of interfacial coverage later. SEM observation and gravimetric analysis demonstrate that the sample of 70%HDPE/30%PS is partially co-continuous and 50%HDPE/50%PS blend is fully co-continuous. The  $A_{app}$  of 50%HDPE/50%PS was obtained using the surface area value obtained by the BET technique [21] and the  $A_{app}$  of the other samples were obtained by image analysis. To verify if the  $A_{app}$  obtained from the two different methods is consistent, the  $A_{app}$  of 70%HDPE/30%PS obtained by BET was compared with that of the same sample obtained by image analysis. The data from the two different methods are basically identical.

Based on the previous discussion, the above results indicate a system with an interfacial modifier that demonstrates significant micelle formation (Trend III behavior; Fig. 1(d)). Since the above study uses an SEBS triblock interfacial modifier with a 30%PS/70%EB

Table 2

Equilibrium volume average diameter ( $d_{eq}$ ), apparent interfacial area occupied per copolymer molecule ( $A_{app}$ ) and apparent areal density ( $\Sigma_{app}$ ) for the HDPE/PS blends compatibilized with SEBS1 at the critical concentration (HDPE as matrix)

Blends	$C_{crit}$ (%)	$d_{eq}$ ( $\mu\text{m}$ )	$d_{v(0\%)/d_{eq}}$	$A_{app}$ ( $\text{nm}^2/\text{molecule}$ )	$\Sigma_{app}$ ( $\text{molecule}/\text{nm}^2$ )
99%HDPE/1%PS	12.5	0.58	1.6	8.4	0.12
98%HDPE/2%PS	12.5	0.58	1.9	8.4	0.12
95%HDPE/5%PS	12.5	0.98	1.9	5.4	0.19
90%HDPE/10%PS	15.0	1.29	2.1	3.2	0.31
80%HDPE/20%PS	15.0	1.31	2.8	3.1	0.32
70%HDPE/30%PS	15.0	1.41	3.1	2.9	0.34

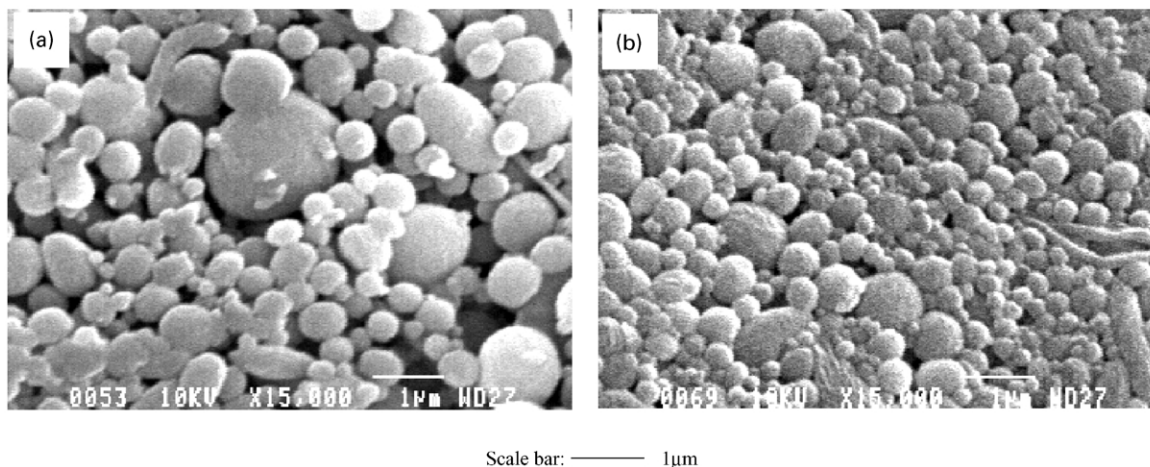


Fig. 5. SEM of 10%HDPE/90%PS blends without and with compatibilizer after matrix dissolution: (a) 0% of SEBS1; (b) 12.5% of SEBS1.

composition, it would be very useful to test the performance of that same modifier for the same blend system but with PS as the matrix.

#### 3.4. Emulsification curves for HDPE dispersed in PS

In Section 3.3 excellent visualization of the dispersed phase morphology on the SEM was made possible by pre-extracting the PS dispersed phase (Fig. 2(a) and (b)). Since it is not possible to dissolve HDPE without dissolving PS, in this part the dispersed phase size is estimated using a matrix dissolution approach as outlined in Section 2. The morphologies of the dispersed HDPE (from 10%HDPE/90%PS blend) without and with compatibilizer after matrix dissolution are shown in Fig. 5(a) and (b). A significant particle size reduction is observed by the addition of 12.5% SEBS1. Fig. 6 shows the emulsification curve of 90%PS/10%HDPE. The results show that the critical concentration for 90%PS/10%HDPE is 12.5% SEBS1. The equilibrium diameter of dispersed HDPE in the 90%PS/10%HDPE blend is  $0.71 \mu\text{m}$  at 12.5% SEBS1 with an  $A_{\text{app}}$  of  $6.9 \text{ nm}^2/\text{molecule}$ . For comparison purposes, the 90%HDPE/10%PS emulsification curve is also shown. It is clear that the SEBS1 modifier is much more effective at reducing the particle size when PS is the matrix. The reduction in particle size is 3.2 ( $d_{v(0\%)} / d_{\text{eq}}$ ) as compared to 2.1 ( $d_{v(0\%)} / d_{\text{eq}}$ ) for the HDPE matrix system. These results indicate quantitatively that the chemical composition of the block copolymer plays a critical role in determining micelle formation for these systems.

Fig. 4 also shows the  $A_{\text{app}}$  data of the SEBS1 copolymer for the system with PS as matrix at three different concentrations of dispersed phase. Note that it was not possible to reliably apply the matrix dissolution technique at 1 and 2% minor phase concentrations. A value of about  $7 \text{ nm}^2/\text{molecule}$  for 5, 10 and 20% dispersed HDPE phase is obtained. The  $A_{\text{app}}$  value is essentially independent of dispersed phase concentration (Table 3). The  $A_{\text{app}}$  data obtained from the PS matrix system is very close to those of

99%HDPE/1%PS and 98%HDPE/2%PS (about  $8.4 \text{ nm}^2/\text{molecule}$ ), especially when one considers that a different technique was used to examine the morphology. The close relationship between the  $A_{\text{app}}$  values at 1%PS/99%HDPE and 2%PS/98%HDPE with the concentration independent values for  $A_{\text{app}}$  with 5%HDPE/95%PS, 10%HDPE/90%PS and 20%HDPE/80%PS strongly suggests that no micelle formation occurs under those conditions and that essentially all the modifier is migrating to the interface. Micelle formation in such systems, which are highly effective at repulsing the interfacial modifier to the interface, would only be observed at values exceeding  $C_{\text{crit}}$ . In other words micelle formation would only be observed after interfacial saturation.

Fayt et al. [1] investigated an LDPE/PS blend system compatibilized by HPB-*b*-PIP-*b*-styrene block copolymer ( $M_n$ : 65 000–15 000–50 000) via TEM observation. They noted qualitatively that in their 80%LDPE/20%PS blend system, a part of HPB-*b*-PIP-*b*-PS block copolymer was

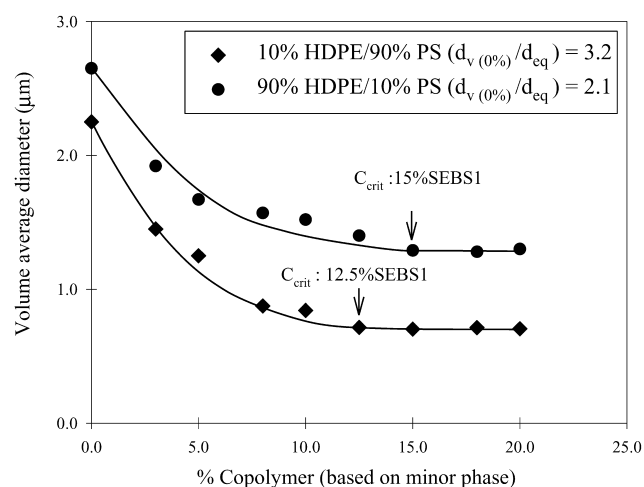


Fig. 6. Emulsification curves for 90%HDPE/10%PS and 90%PS/10%HDPE blends modified by SEBS1 triblock copolymer. The arrows indicate the critical concentration for interfacial saturation of the blend systems.

Table 3

Equilibrium volume average diameter ( $d_{eq}$ ), apparent interfacial area occupied per copolymer molecule ( $A_{app}$ ) and apparent areal density of copolymer ( $\Sigma_{app}$ ) for the HDPE/PS blends compatibilized with SEBS1 at the critical concentration (PS as matrix)

Blends	$C_{crit}$ (%)	$d_{eq}$ ( $\mu\text{m}$ )	$d_{v(0\%)/d_{eq}}$	$A_{app}$ ( $\text{nm}^2/\text{molecule}$ )	$\Sigma_{app}$ ( $\text{molecule}/\text{nm}^2$ )
95%PS/5%HDPE	12.5	0.68	2.2	7.1	0.14
90%PS/10%HDPE	12.5	0.70	3.2	6.9	0.14
80%PS/20%HDPE	12.5	0.69	4.2	7.0	0.14

dispersed in the LDPE phase but not in the PS phase. This study is consistent with their observation. The affinity between HDPE and SEBS1 is significant due to the 70% EB block in SEBS1. This behavior leads to difficulties in migrating the modifier to the interface.

### 3.5. Interfacial coverage

In Section 3.4 it was established that all the modifier migrates to the interface (for concentrations at or below  $C_{crit}$ ) for 1 and 2% PS in HDPE and for all the HDPE in PS blends studied. Based on this result it should then be possible to estimate interfacial coverage for these systems in the following way:

$$\% \text{Interfacial coverage} = (A_{appi\%}/A_{1\%}) \times 100 \quad (2)$$

where  $A_{appi\%}$  is the apparent interfacial area occupied per copolymer molecule at  $C_{crit}$  and a dispersed phase concentration of  $i\%$ ,  $A_{1\%}$  is the interfacial area occupied per copolymer molecule at  $C_{crit}$  for 1% dispersed phase.

Fig. 7 shows the interfacial coverage vs. %minor phase for the PS in HDPE blends compatibilized by SEBS1. The interfacial coverage for 99%HDPE/1%PS and 98%HDPE/2%PS is the same with a value of 100%. Then it decreases with increasing dispersed phase concentration, from 64% for the 95%HDPE/5%PS to 32% for the 50%HDPE/50%PS. If all the copolymer had migrated to the interface the interfacial area occupied per molecule would not change with the concentration of the minor phase, resulting in a saturated interface with constant interfacial coverage at a value of 100%. The relationship between the interfacial coverage and dispersed phase concentration can be categorized into three regions:

- Region I.** All modifier migrates to the interface. At 1 and 2% dispersed phase the amount of copolymer in the mixture is relatively low since the amount is based on the dispersed phase concentration. Under these conditions all the copolymer molecules find their way to the interface between the dispersed phase and matrix. The copolymer molecules do not form micelles at modifier concentration less than or equal to the critical concentration. Interfacial coverage is 100%.
- Region II.** Onset of micelle formation. With the addition of more minor phase the amount of the copolymer increases as well. The sharp decrease of the interfacial coverage indicates that only a portion of copolymer

migrates to the interface, while the rest is trapped in the matrix forming micelles. The interfacial coverage diminishes from 100 to 38% and this zone can be considered as the onset region of micelle formation.

- Region III.** Quasi equilibrium between micelle formation and partially saturated interface. At minor phase concentrations in excess of 10% a quasi equilibrium between micelle formation and partially saturated interface is established at the critical concentration of modifier. An almost constant interfacial coverage (about 30%) vs. %minor phase is obtained in this region.

### 3.6. Influence of the copolymer architecture and chemical composition on its migration to the interface

#### 3.6.1. Diblock copolymer vs. triblock copolymer

Direct comparisons of diblock and triblock copolymer efficacy were made on systems comprising 90%HDPE/10%PS and 80%HDPE/20%PS, modified by both SEBS1 (triblock) and SEB1 (diblock) interfacial agents. The emulsification curves for the two blend systems are shown in Fig. 8(a) and (b). The critical concentrations for the triblock copolymers have already been shown in Fig. 3(a) and (b) as well as in Table 2. For the diblock copolymer the  $C_{crit}$  is somewhat more difficult to determine

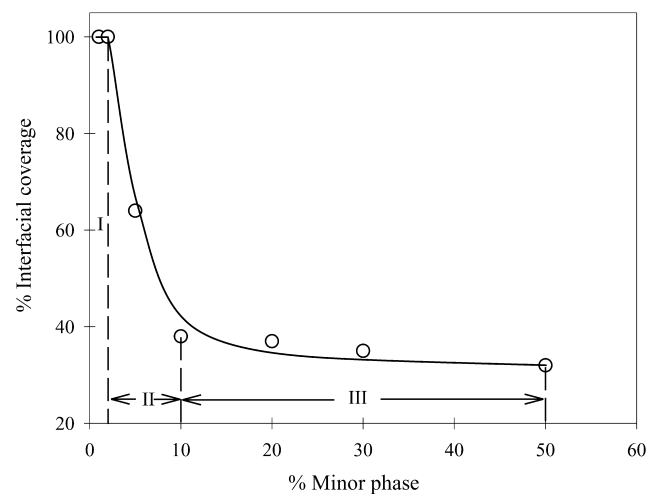


Fig. 7. Interfacial coverage at  $C_{crit}$  vs. the dispersed phase concentration for PS dispersed in HDPE with SEBS1 as the interfacial modifier. Three distinct regions are observed in this system. Region (I) all of the copolymer goes to the interface; Region (II) onset of micelle formation in the system; and Region (III) a quasi equilibrium between micelle formation and a partially saturated interface.



and hence is shown as a range in Fig. 8(a) and (b) and the midpoint value is used in the calculations for the interfacial area. The estimated  $d_{eq}$ ,  $d_{v(0\%)} / d_{eq}$  values, the midpoint critical concentration and the interfacial area occupied per molecule for the diblock curves are shown in Fig. 8(a) and (b) and reported in Table 4. It is clear from the  $d_{v(0\%)} / d_{eq}$  values that the diblock copolymer is less effective at reducing the particle size than the triblock. This is consistent with the previous investigation [9] on PS/EPR blends compatibilized by triblock and diblock copolymers.

The estimated apparent interfacial areas for the diblock copolymer at 10 and 20% PS dispersed phase are 4.2 and 3.5 nm<sup>2</sup>/molecule. The interfacial area for the diblock copolymer at 1% dispersed phase was found to be 6.0 nm<sup>2</sup>/molecule. At 1% dispersed phase, presumably in the absence of any micelle effects, the diblock demonstrates a lower interfacial area (6.0 nm<sup>2</sup>/molecule) than the corresponding triblock copolymer (8.4 nm<sup>2</sup>/molecule). This is reasonably expected since the diblock possesses one joint while the triblock possesses two joints and must

loop in and out of the interface. These results support previous observations by Cigana et al. [9]. However, the difference in interfacial area occupied per molecule between diblock and triblock copolymers in this study are less pronounced than in the previous one.

By treating the above apparent interfacial areas according to Eq. (2), the interfacial coverage for the diblock copolymer can also be reported in Fig. 9. The evolution of interfacial coverage with dispersed phase concentration can now be directly compared for both diblock and triblock copolymers. Although the diblock also demonstrates significant difficulties in migrating to the interface, it appears to be somewhat less susceptible to micelle formation than the triblock copolymer for the blends with HDPE as the matrix. If we recall the observation that the diblock copolymer was a less effective emulsifier overall than the triblock copolymer (Fig. 8(a) and (b)), this suggests that the poorer capacity of the diblock copolymer to reduce particle size is likely related to less suppression of dynamic coalescence. The triblock copolymer loops in and out of the interface as opposed to the diblock which possesses only one joint. These results support previous observations from this laboratory [9]. The above results raise a series of other questions. Is it the looping or the density of joints across the interface that affects dynamic coalescence? This could be studied by a variation in the molecular weight of the interfacial modifier. Matos and Favis [5] demonstrated that an equivalent  $d_{eq}$  was obtained for a series of SEBS modifiers of widely different molecular weights for an EPR dispersed in PS system. Those results coupled with these strongly indicate that it is the looping effect of the triblock more than the absolute number of interfacial joints that influence dynamic coalescence. Another possible explanation could be that the diblock is less effective at reducing interfacial tension than the triblock copolymer. This latter possibility is not very likely since Leibler [31] has shown theoretically that diblocks were slightly more effective than

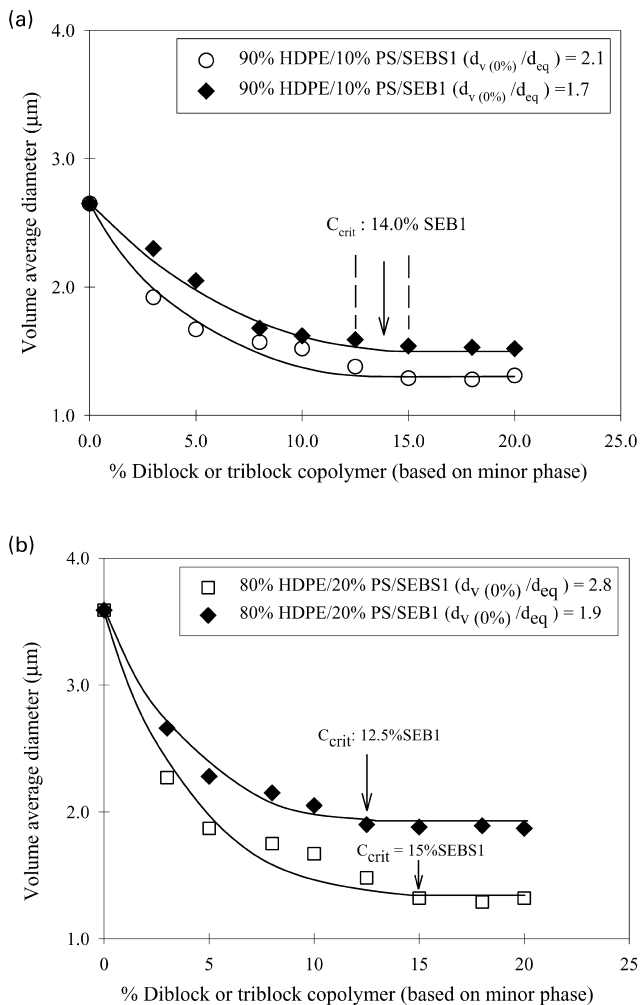


Fig. 8. The influence of the architecture of the copolymer (diblock vs. triblock) on the emulsification of (a) 90%HDPE/10%PS and (b) 80%HDPE/20%PS blend systems.

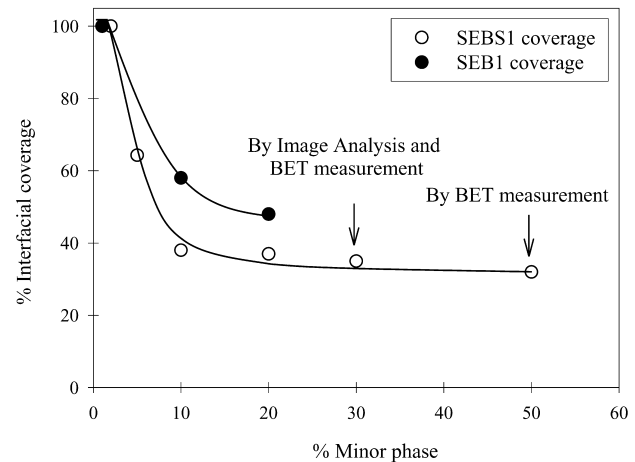


Fig. 9. Interfacial coverage vs. the dispersed phase concentration for blends compatibilized by diblock and triblock copolymer.

Table 4

Influence of the copolymer architecture and chemical composition on emulsification for the 90%HDPE/10%PS and 80%HDPE/20%PS blends

Blends	$C_{crit}$ (%)	$d_{eq}$ ( $\mu\text{m}$ )	$d_{v(0\%)} / d_{eq}$	$A_{app}$ ( $\text{nm}^2/\text{molecule}$ )	$\Sigma_{app}$ ( $\text{molecule}/\text{nm}^2$ )
90%HDPE/10%PS/SEBS1	15.0	1.29	2.1	3.2	0.31
90%HDPE/10%PS/SEB1	14.0	1.54	1.7	4.2	0.24
80%HDPE/20%PS/SEBS1	15.0	1.31	2.8	3.1	0.32
80%HDPE/20%PS/SEB1	12.5	1.88	1.9	3.5	0.29
90%HDPE/10%PS/SEBS2	15.0	0.71	3.8	10.0	0.1
90%HDPE/10%PS/SEB2	15.0	1.00	2.7	6.2	0.19

triblocks at reducing the interfacial tension in a ternary blend.

### 3.6.2. Effect of the chemical composition of the triblock copolymer

In order to investigate the effect of chemical composition of the triblock copolymer on compatibilization, blends of 90%HDPE/10%PS modified by SEBS1 and SEBS2, respectively, were prepared. Fig. 10 shows these data. An equilibrium dispersed phase size ( $d_{eq}$ ) of 1.29  $\mu\text{m}$  is obtained for 90%HDPE/10%PS/15%SEBS1, and 0.71  $\mu\text{m}$  for the 90%HDPE/10%PS/15%SEBS2 (Table 4). The  $d_{eq}$  obtained in the latter case is virtually identical to the 1 and 2% dispersed PS phase systems reported in Fig. 3(a). From the above results, it is demonstrated that triblock micelle formation can be virtually eliminated through the use of a triblock copolymer with a symmetrical 50:50 composition. It appears clear, in light of these results, that the principle driving force for micelle formation as demonstrated in Figs. 9 and 10 is the asymmetrical structure of the interfacial agent, and its enhanced affinity to the HDPE matrix.

### 3.6.3. Effect of the chemical composition of the diblock copolymer

Fig. 11 demonstrates the emulsification effect of 90%HDPE/10%PS modified by SEB1 (67 kg/mol and 30% styrene) and SEB2 (63 kg/mol and 53% styrene)

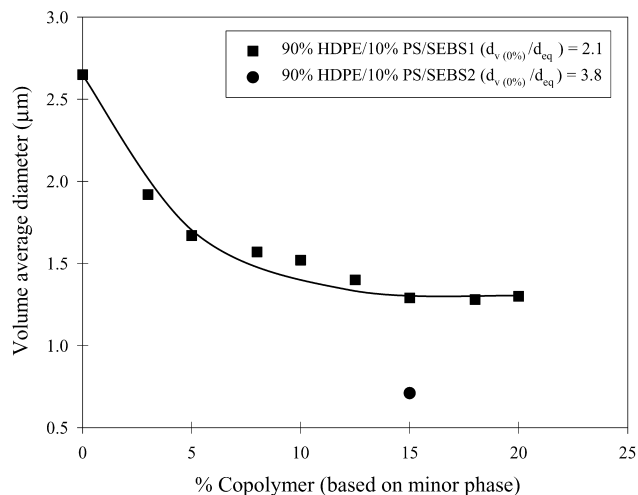


Fig. 10. The influence of the chemical composition of triblock copolymer on the emulsification of HDPE/PS blends.

diblock copolymers, respectively. At this dispersed phase composition SEB2 reduces the particle size more significantly than SEB1 ( $d_{v(0\%)} / d_{eq}$  is 2.7 vs. 1.7). The equilibrium diameter obtained for the blend compatibilized by SEB2 has a value of 1.0  $\mu\text{m}$  as compared to 1.54  $\mu\text{m}$  with SEB1 (Table 4). If we assume a similar  $C_{crit}$  for the system 90%HDPE/10%PS/SEB2 an  $A_{app}$  of 6.2  $\text{nm}^2/\text{molecule}$  is obtained as compared to an  $A_{app}$  of 3.5  $\text{nm}^2$  for SEB1. The above results indicate that the diblock with the balanced composition clearly emulsifies the blend more effectively than that with a lower styrene weight fraction.

Leibler [3] suggested that to form a thermodynamically stable droplet phase in a strongly incompatible blend system, a symmetrical copolymer should be used. Diblock copolymers with an equal block composition (symmetrical) would be more effective interfacial agents than asymmetrical copolymers. This is due to the fact that for such a symmetrical diblock copolymer, the spontaneous curvature is low and it would be subjected to a less severe entropic penalty at a plane interface than in a spherical micelle (the interface of a spherical particle with a diameter of a few tenths of a micrometer is essentially plane on a molecular scale); the asymmetrical diblock, on the other hand, would 'prefer' the spherical micelle configuration. Thus, according to Leibler, the more symmetrical a diblock copolymer, the more efficient it would be in emulsifying a polymer blend. Although this effect can play a part in determining micelle

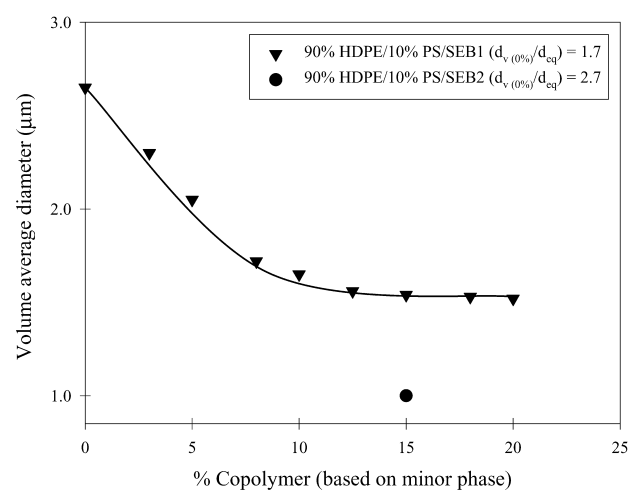


Fig. 11. The influence of the chemical composition of diblock copolymer on the emulsification of HDPE/PS blends.

formation this study clearly illustrates the dominant role of the affinity of the modifier for the matrix phase in micelle formation.

#### 4. Conclusions

In this study it is shown that a family of emulsification curves, prepared at a variety of dispersed phase concentrations, can be used as a powerful tool to estimate the efficacy of interfacial modifier migration to the interface in an immiscible polymer blend. Through an examination of the evolution of the equilibrium dispersed phase size after interfacial saturation, as well as a comparison of the apparent interfacial area occupied per modifier molecule ( $A_{app}$ ) at the different dispersed phase concentrations, it is possible to detect the onset of micelle formation. An approach to estimate the extent of interfacial coverage based on these data is also presented. This approach was applied to polyethylene/PS blends. When PS is dispersed in polyethylene it is shown that an asymmetric 70EB/30PS SEBS triblock copolymer demonstrates an onset of micelle formation at 5% of dispersed phase. Three regions are identified: (I) a region where all modifier migrates to the interface (1 and 2% dispersed phase); (II) an onset region of micelle formation (5–10% dispersed phase) and (III) a region of quasi-equilibrium between micelle formation and a partially saturated interface (>20% dispersed phase). When the reverse system of polyethylene dispersed in PS is studied, it is shown, using the same approach, that all the modifier migrates to the interface over a wide range of dispersed phase concentrations. This clearly underlines the dominant role of the affinity of the EB block in the asymmetric copolymer for HDPE in determining micelle formation. Use of an asymmetric diblock copolymer for the PS dispersed in HDPE blend also demonstrates significant micelle formation, although the phenomenon is less pronounced than the triblock case. Micelle formation in the PS dispersed in HDPE system can be virtually eliminated through the use of a symmetric (50:50) triblock or diblock copolymer.

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