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Interfacial modification of polymer blends—the emulsification curve: 1. Influence of molecular weight and chemical composition of the interfacial modifier

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The effect of several parameters such as molecular weight, chemical composition and architecture of the interfacial agent on the dispersed particle size is investigated in polystyrene/ethylene–propylene rubber blends. The study is based on the dependence of the dispersed phase size *versus* the concentration of interfacial modifier, the so-called emulsification curves. A critical concentration value of interfacial agent based on the volume of the minor phase was determined beyond which no further changes in particle size were observed. These results show that block copolymers also display an emulsification curve. The influence of the molecular weight (from 50×10^3 to 174×10^3 g mol^{-1}) of the saturated triblock poly(styrene-*block*-ethylene–butylene-*block*-styrene) interfacial modifier is demonstrated to have little effect on emulsification phenomena. The influence of the chemical composition of the interfacial modifier on the shape of the emulsification curve appears to be a critical consideration. The presence of double bonds in the copolymer modifier significantly diminishes its emulsification capability. It is interesting to note that, once the emulsification phenomenon has been significantly reduced due to the presence of double bonds, imposing a conformational restriction (star-shape architecture) has little effect on the emulsification curve.

(Keywords: interface; compatibilization; blends)

INTRODUCTION

The vast majority of polymers are mutually immiscible and demonstrate poor adhesion between the matrix and dispersed phase. One way to improve the interfacial interactions is by addition of a suitably chosen modifier to the blend, just as detergents promote the mixing of oil and water in classical oil–water emulsions. In the case of polymer blends, these interfacial agents are usually block or graft copolymers whose segments are often composed of the homopolymer phases[1–4]. The effectiveness of copolymers, in other words their capacity to emulsify the blend, is generally believed to depend on the molecular weight, block composition and molecular architecture. It is important to anchor these interfacial agents at the interface, and the segments should be long enough to have sufficient cohesive forces to anchor them firmly into the domains they penetrate[5]. Nevertheless, there are few detailed studies considering the influence of molecular parameters of the interfacial modifier on emulsification phenomena.

In classical oil–water emulsions stabilized by surfactants, the efficacy of the interfacial modifier for the interface is often characterized by the so-called emulsification curves, which essentially follow the evolution of dispersed phase size with modifier concentration[6]. The shape of the emulsification curve is highly dependent on surfactant type and on processing technique[7].

The emulsification curves have been studied for several polymer blend systems[8–10] and they display a key characteristic, an initial significant drop in the size of the dispersed phase with the addition of the copolymer followed by the obtention of an equilibrium value at higher concentrations of modifier.

For polymer blends, the modification of the interface serves to reduce the interfacial tension between the major components and results in a significant diminution in the dispersed phase particle size[11,12]. Taylor's theory[13,14] predicts a direct relationship between the interfacial tension and size of the dispersed phase. The shape of the dependence of interfacial tension as a function of copolymer concentration is similar to that of the emulsification curve.

This work deals with the influence of several parameters such as molecular weight, chemical composition and architecture of the interfacial modifier on the particle size and the emulsification curve.

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Table 1 Main characteristics for the pure blend components

Resin	M_w (g mol^{-1})	Density (g ml^{-1})	*MFI* (g/10 min)
PS	275 400	1.05	1.5
EPR	173 000	0.85	

Table 2 Main characteristics of the interfacial agents

Interfacial agent reference	PS (%)	Copol. $M_n \times 10^{-3}$	End-block $M_n \times 10^{-3}$	Mid-block $M_n \times 10^{-3}$	Specific gravity
SEBS-1 (triblock)	30.0	50	7.5	35	0.91
SEBS-2 (triblock)	28.6	70	10	50	0.91
SEBS-3 (triblock)	33.3	174	29	116	0.91
SBu-1 (triblock)	45.4	66	15	36	0.88
SBu-2 (star shape)	31.8	176	30[a]	14[b]	0.88
SBu-3 (triblock)	30.0	70	10.5	49	0.92

[a] Refers to the butadiene blocks
[b] Refers to the styrene blocks

EXPERIMENTAL

Materials

The blends investigated in this study are based on 90% volume fraction of polystyrene (PS) obtained from Dow Chemical (Styron D685) and 10% random copolymer of ethylene–propylene rubber (EPR) supplied by Exxon Chemical (Vistalon V-504). Some properties of these materials are shown in *Table 1*.

Two types of interfacial agents were chosen since they are well characterized in terms of molecular weight and structure. The first class of modifiers consists of three hydrogenated triblock copolymers of styrene and butadiene (rubber mid-block and styrene end-blocks) with different molecular weights, from Shell Development Co.: Kraton G1652 (SEBS-1), Kraton G1650 (SEBS-2) and Kraton G1651 (SEBS-3). After hydrogenation, the mid-block is essentially a random copolymer of ethylene (1,4-addition of butadiene) and butylene (1,2-addition of butadiene). The second class of modifiers consists of three unsaturated styrene–butadiene copolymers: two triblock copolymers of styrene–butadiene–styrene from Dexco Chem (SBu-1 and SBu-3), and one four-arm star-shaped copolymer of styrene–butadiene from Fina Corp. (SBu-2). The molecular weights of these materials are shown in *Table 2*. All the material molecular weights were measured by g.p.c. (ECP Enichem). The molecular-weight values of the styrene-*block*-ethylene–butylene-*block*-styrene (S-EB-S) copolymers were obtained from the supplier. For this copolymer series, the number- and volume-average molecular weight values are essentially the same.

The concentrations of interfacial modifiers used in the blends were 2.5, 5, 7.5, 10, 15, 20 and 30%. These concentrations are expressed as the volume of interfacial modifier per unit volume of dispersed phase.

Rheological properties

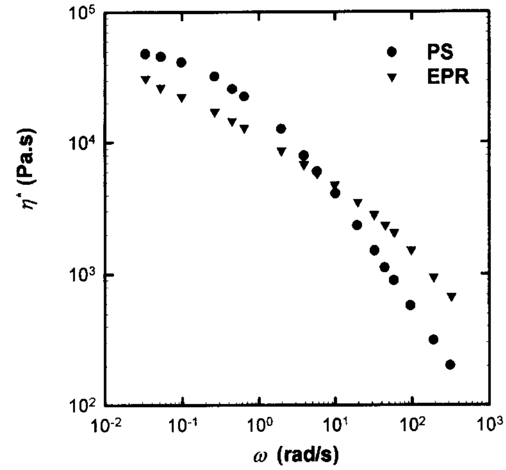

Figure 1 Complex viscosities of PS and EPR as a function of frequency at 200°C

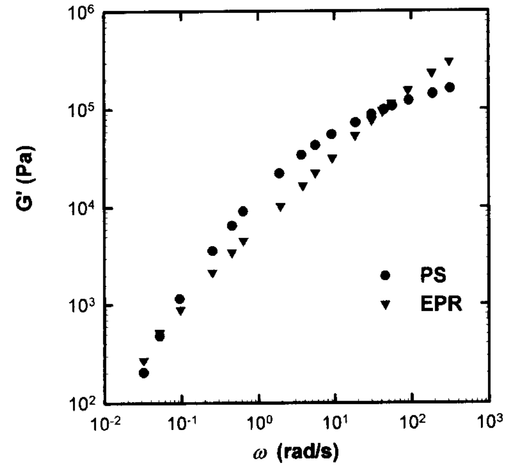

Figure 2 Storage modulus of PS and EPR as a function of frequency at 200°C

The complex viscosities and storage moduli of the PS and EPR are plotted as a function of frequency in *Figures 1* and *2* respectively. The measurements were made using a Bohlin CSM Constant Stress Rheometer equipped with 2.5 cm diameter parallel plates, at 200°C. The gap between plates was 1.5 mm. *Figure 3* shows the rheological behaviour of the 10% EPR/90% PS blends without interfacial agent and with 50% SEBS-1. It is evident that the addition of interfacial agent has little effect on the rheology of the system, even at this very high concentration of interfacial modifier.

Blend preparation

Blending of 24 g samples was performed using a Brabender Plasticorder. The mixing chamber temperature was 200°C, the roller blade speed was 50 r.p.m. and the time of blending was 7 min. After the mixing step, the melt was cooled in cold water.

All the components of each blend were dry blended before melt mixing. Throughout the text, the blend compositions are given in terms of volume fraction and the interfacial modifier compositions are given in terms of percentage based on the volume of the dispersed phase.

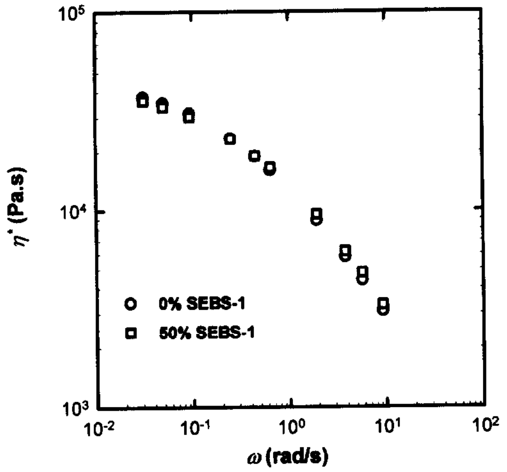

Figure 3 Effect of compatibilizer on complex viscosity of 10% EPR/90% PS blend at 200°C, with 0 and 50% SEBS-1 based on the dispersed phase

Scanning electron microscopy

Plane surfaces were prepared on each specimen using a Reichert Jung Supercut 2050 microtome equipped with a diamond knife. While cutting, the surface of the sample was held at approximately −100°C to reduce the degree of surface deformation.

The samples were gold/palladium-coated prior to electron microscopy. Micrographs were taken by a JEOL model 820 scanning electron microscope (SEM).

Image analysis

The semi-automatic image analyser used to measure the diameters of the dispersed phase has been described elsewhere[11]. For each sample, eight SEM photomicrographs were analysed, and averages then calculated for the number-average diameter d_n, the volume-average diameter d_v, the surface-average diameter d_s and polydispersity (d_v/d_n). A correction factor developed by Saltikov was applied to the diameters determined from SEM photomicrographs of microtomed surfaces[15,16]. This step was carried out to account for the fact that the observed plane does not necessarily cut through the particles at their equator, and also to correct for polydispersity effects. On average, 250–300 diameter measurements were taken per blend preparation. The uncertainty on the average diameter measurements by this method is better than ±10%.

RESULTS AND DISCUSSION

Dispersed phase dimensions

The emulsifying effect of the interfacial agents used in this work on the 10% EPR/90% PS blend is shown in *Figure 4*. The micrograph of a microtomed surface shown in *Figure 4a* demonstrates a two-phase morphology, indicating immiscibility of the components. The effect of the addition of interfacial modifier during the melt blending process in the Brabender mixing chamber can be seen as a significant reduction in the size of the dispersed rubber phase relative to that observed for the uncompatibilized blend. For example, the addition of 15% of the S-EB-S triblock copolymer (based on the volume of the dispersed phase) results in an average particle size reduction of three times (see *Table 3* and *Figure 4b*), whereas for the S-Bu-S triblock and star copolymers the reduction of the particle size is less than two with significantly more scatter in the results (*Figures 4c* and *4d*).

The particle size distributions of the systems can be inferred from *Table 3*. In general, the interfacial modification with S-EB-S triblock copolymer has produced a narrowing of the size distribution (d_v/d_n), which means that the compatibilization has rendered the morphology of the PS/EPR blend more homogeneous. These results can also be correlated to emulsion studies, where the addition of surfactant has been shown to narrow the particle size distribution until a certain concentration of emulsifier has been reached[7]. For larger quantities of modifier (higher than 30%), significant scatter in the diameter results was observed, which could be related to the preference of the interfacial agent for one of the homopolymer phases or to possible micelle formation. It should be noted that, for higher concentrations of the interfacial agent (higher than 30%), the image analysis for the determination of the average diameters was very difficult owing to the heterogeneity of the morphology and the severe plastic deformation of the particles observed during the cutting of the surfaces, despite the fact that microtoming was performed at very low temperatures.

Figure 5a shows the cumulative percentage dispersed particle size distribution for the 10% EPR/90% PS on a linear scale. The plot shows the cumulative percentage of particles with diameter less than or equal to a given diameter. A 'sigmoidal' shape of the curve is observed, which becomes slightly narrower when larger quantities of copolymer are added. The same data are plotted on a log-normal scale in *Figure 5b* and the slope gives an idea of the blend polydispersity. The steeper the slope, the narrower the size distribution. For the particular system 10% EPR/90% PS, the interfacial modification with 2.5% of SEBS-2 produces a narrowing of the size distribution. This effect illustrates that the compatibilization has rendered the morphology of the 10% EPR/90% PS blends more homogeneous. No significant difference occurs between 2.5 and 15% of copolymer SEBS-2. It can also be seen that the diameters measured follow a log-normal distribution.

Effect of interfacial modifier on phase size

A typical emulsification curve for the blend 10% EPR/90% PS compatibilized with S-EB-S triblock copolymer (SEBS-2) is shown in *Figure 6*. It is interesting to note that the shape of the curve is similar to that of classical emulsions. A rapid drop in particle size with concentration of interfacial modifier was observed up to a critical concentration of 15%, beyond which a quasi-equilibrium particle size is observed.

The emulsification curves (dependence of volume-average diameters on the interfacial modifier concentration) of the 10% EPR/90% PS compatibilized with five types of interfacial agents are shown in *Figures 7* and *8*. In all cases, the previously described characteristic shape of the curve can be observed. For the blends compatibilized with three types of S-EB-S triblock copolymers, it appears that approximately 15% of the interfacial modifier based on the minor phase produces a maximum reduction of the dispersed phase size (see also

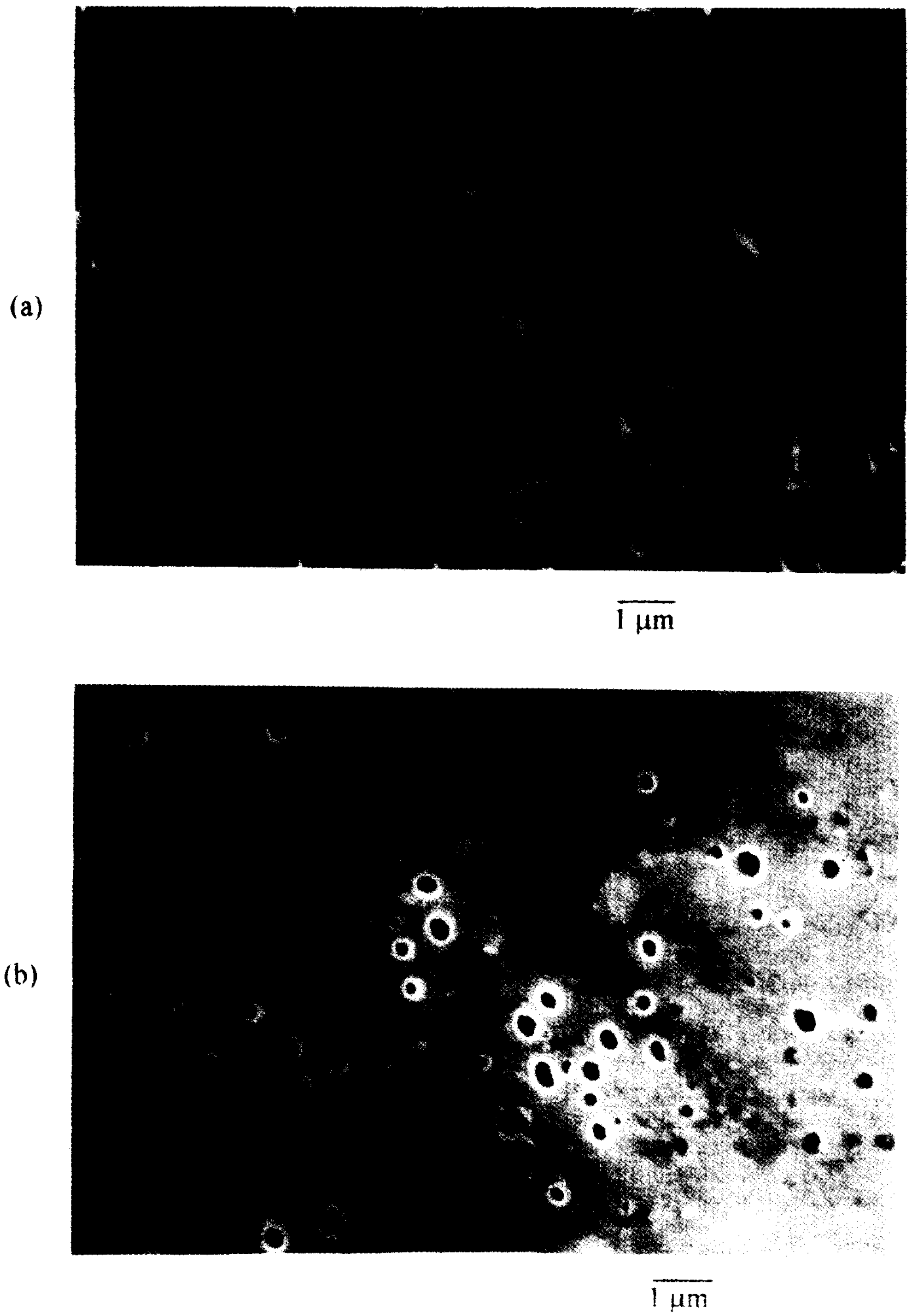

Figure 4 Micrographs of microtomed surfaces of 10% EPR/90% PS: (a) 0% of interfacial modifier; (b) 15% of hydrogenated S-EB-S (SEBS-1); (c) 15% of unsaturated S-Bu-S (SBu-1); and (d) 15% of unsaturated star-shape S-Bu (SBu-2)

Figure 4). Favis *et al.*[8,10] have already observed this general shape of the emulsification curve for polyolefin/polyamide systems. They have also shown a significant reduction in the dispersed phase size with 5% of modifier (based on the minor phase). The previous work considered *in situ* generated graft copolymers. It is interesting to note that a block copolymer also generates the typical emulsification curve. This typical behaviour can be explained based on Taylor's theory[13,14] derived for Newtonian systems in shear flow. The theory predicts a drop in the dispersed phase size with the interfacial tension owing to the balance of the surface tension forces, tending to keep a droplet in one piece, and the viscous forces, tending to burst it.

An equilibrium dispersed phase size (d_v) of $0.35 \pm 0.05\,\mu m$ was obtained for the 10% EPR/90% PS modified with S-EB-S triblock copolymer (SEBS-1, SEBS-2 and SEBS-3). This is evidence of the strong emulsifying effect of the S-EB-S type interfacial agents. By contrast, the equilibrium phase size achieved for the system modified with S-Bu-S triblock copolymer (SBu-1) and the S-Bu copolymer (SBu-2) was approximately $0.5–0.6\,\mu m$. The same behaviour of particle size as a function of copolymer concentration was

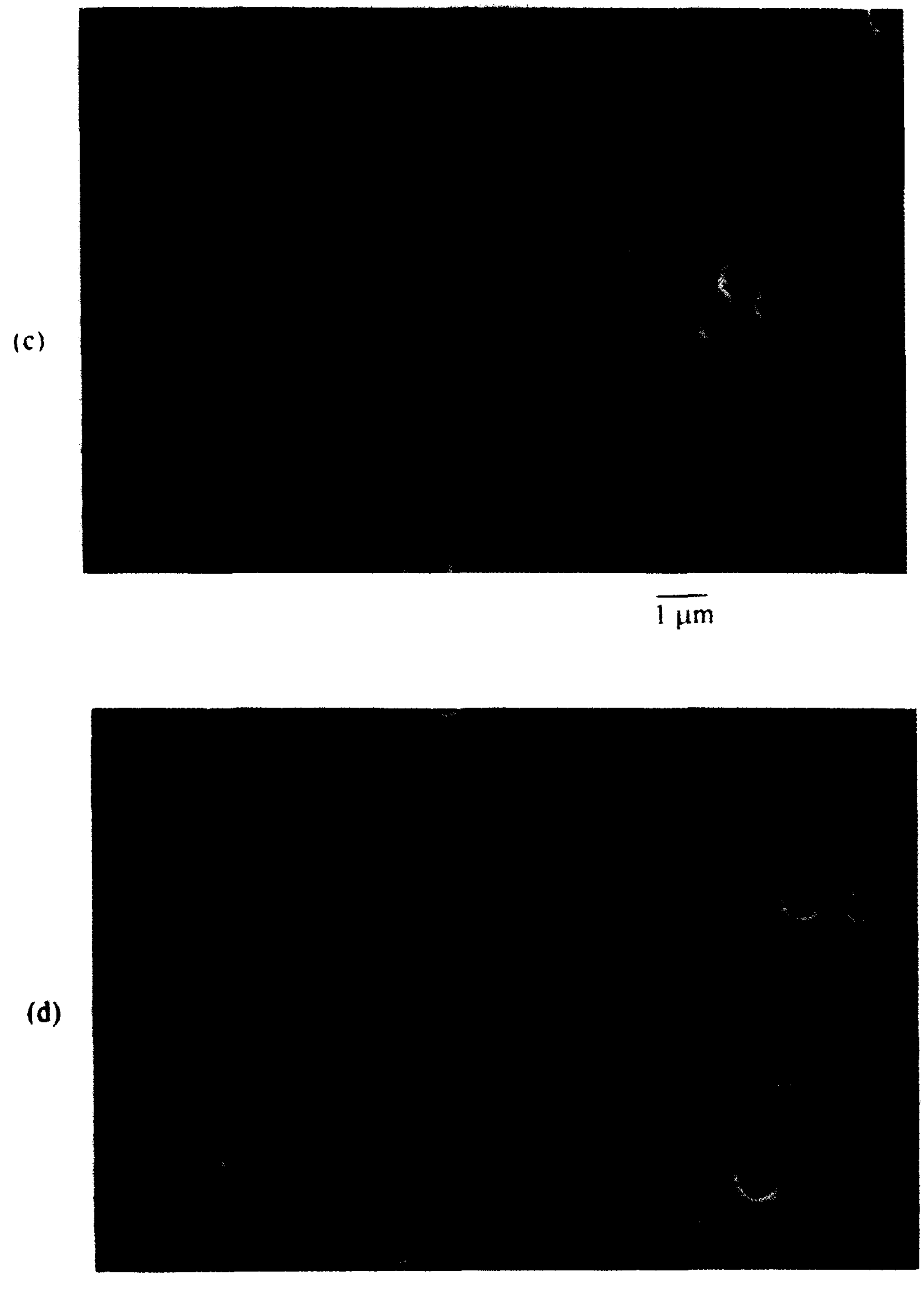

Figure 4 (continued)

obtained for the number- and surface-average diameter values.

Effect of molecular weight

In order to study the influence of molecular weight of the interfacial modifier on the dispersed particle size, three S-EB-S copolymers with different molecular weights were used (SEBS-1, SEBS-2 and SEBS-3). *Figure 7* illustrates the emulsification curves for the three copolymers. It can be seen that there is little effect of interfacial modifier molecular weight on the shape of the curve; for example, at 10% copolymer concentration the d_v values for the three systems are very similar. In all cases, it appears that approximately 15% of copolymer based on the minor phase is sufficient to produce a maximum reduction of the dispersed phase size. No further decrease in phase size is achieved by adding more copolymer, as seen from the plateau regions of the plots shown in these graphs.

These results suggest that the molecular-weight requirement of copolymers used as interfacial modifiers is not so critical in emulsification during melt blending. Teyssié *et al.*[17] studied the influence of molecular weight

Table 3 Diameter values[a] for the compatibilized and non-compatibilized blends

System analysed	Type of interfacial agent	Concentration of the interfacial agent (%) 0	2.5	5	7.5	10	15	20
PS/EPR		0.57						
		0.89						
		0.76						
PS/EPR/SEBS-1	Saturated	0.57	0.44	0.32		0.31	0.24	0.27
	triblock copolymer	0.89	0.54	0.40		0.37	0.30	0.34
	S-EB-S	0.76	0.50	0.37		0.35	0.28	0.31
PS/EPR/SEBS-2	Saturated	0.57	0.41	0.39	0.34	0.34	0.30	0.33
	triblock copolymer	0.89	0.53	0.51	0.44	0.42	0.32	0.35
	S-EB-S	0.76	0.48	0.46	0.40	0.39	0.31	0.34
PS/EPR/SEBS-3	Saturated	0.57	0.45	0.44		0.31	0.30	0.31
	triblock copolymer	0.89	0.58	0.59		0.40	0.34	0.37
	S-EB-S	0.76	0.52	0.54		0.37	0.32	0.34
PS/EPR/SBu-1	Unsaturated	0.57		0.42		0.55	0.27	0.37
	triblock copolymer	0.89		0.71		0.79	0.43	0.50
	S-Bu-S	0.76		0.60		0.70	0.37	0.45
PS/EPR/SBu-2	Unsaturated	0.57		0.40		0.54	0.33	
	star-shaped copolymer	0.89		0.70		0.68	0.52	
	$(S\text{-}Bu)_4$	0.76		0.58		0.63	0.45	

All the diameter values are in μm. Diameter values are listed downwards within each 'block' as
d_n
d_v
d_s

Table 4 Estimation of the area occupied per molecule of interfacial modifier

Type of interfacial agent	$M_n \times 10^{-3}$ ($g\,mol^{-1}$)	Area occupied per molecule (nm^2)
SEBS-1	50	13
SEBS-2	70	18
SEBS-3	174	45

of block copolymers for PS/PE blends in the melt state and they demonstrated that the molecular weight (the so-called block length rule) is not a limitation in the use of block copolymers as emulsifiers of polymer blends. That conclusion was supported indirectly via mechanical properties. In the present work, the study of the influence of several parameters such as molecular weight, chemical structure and molecular architecture on the emulsification process is based on direct observations and quantification of blend morphologies (emulsification curves).

An estimation of the interfacial area occupied per modifier molecule at the critical concentration can be made from the data of the emulsification curve for the PS/EPR/SEBS systems. It is assumed that the critical concentration represents the onset of interfacial saturation and also that all modifier goes to the interface. Then, calculating the interfacial area of the dispersed phase and the number of molecules of compatibilizer, the area occupied per molecule can be calculated. The estimation of the interfacial area occupied per molecule can be estimated here directly from the emulsification curve data (critical concentration) and using the following equations:

$$A = n \times 4\pi R^2 \tag{1}$$

where A is the total area occupied by the dispersed phase, R is the radius of the dispersed phase particle, and n is the number of particles of the minor phase, which can be estimated from equation (2):

$$n = \frac{\phi_d V_d}{\frac{4}{3}\pi R^3} \tag{2}$$

where ϕ_d is the volume fraction of the dispersed phase and V_d is the volume of the dispersed phase. Then, the number of molecules of interfacial agent can be estimated as follows:

$$N = mN_{Avo}/M_n \tag{3}$$

where m is the quantity (in grams) of interfacial agent used, N_{Avo} is the Avogadro number and M_n is the number-average molecular weight of the interfacial modifier. Dividing equations (1) and (3) one can determine the area occupied per molecule of interfacial agent. The values obtained are shown in *Table 4*. As expected, the higher the molecular weight, the higher the area values. In previous work, Fayt *et al.*[18] obtained an area value of 2.6 nm^2 for a low-density polyethylene dispersed in a polystyrene matrix compatibilized by a poly(hydrogenated butadiene-*b*-styrene) copolymer. This value was estimated by a qualitative examination of TEM photomicrographs suggesting a saturated interface. Favis[10] reported a value of 5 nm^2 for a polyamide/polyolefin/ionomer system containing an *in situ* generated graft copolymer, and in the present work a value of 13 nm^2 was obtained for the triblock copolymer SEBS-1. The area occupied per molecule should be considered as more reliable for the block copolymer system in this study since the *in situ* generated graft copolymer must react as well as migrate to the interface. Block copolymers need only to migrate to the interface. It is important to note that these values represent a minimum baseline since it is highly unlikely that all the interfacial modifier migrates to the interface.

Effect of modifier composition and architecture

The influence of two copolymers having the same architecture (triblock) and different chemical composition (S-EB-S and S-Bu-S) on the modifier efficacy was

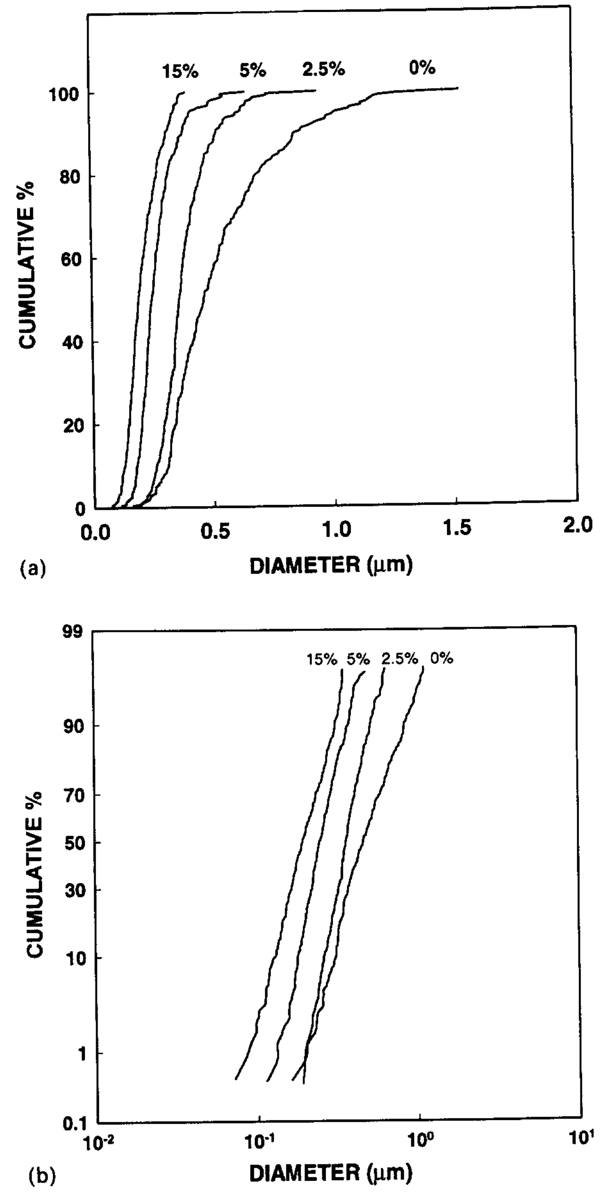

Figure 5 (a) Particle size as a cumulative distribution (linear scale) for the 10% EPR/90% PS system for 0, 2.5, 5 and 15% of SEBS-1. (b) Log-normal scale particle size distribution for the 10% EPR/90% PS system for 0, 2.5, 5 and 15% of SEBS-1

studied and the corresponding emulsification curves are illustrated in *Figure 8*. It can be seen in *Figure 8* that the S-EB-S saturated copolymer (SEBS-2) has more significantly diminished the particle size at low concentrations of interfacial modifier than the S-Bu-S unsaturated triblock copolymer (SBu-1). The stronger emulsifying capability of the S-EB-S type interfacial agent (SEBS-1), which does not contain unsaturated bonds, is evident, rather than the S-Bu-S copolymer (SBu-1), which contains double bonds. Evaluation of SBu-3 at two levels of modifier concentration (*Figure 9*) indicates somewhat poorer emulsification than SBu-1, which is at a more balanced composition. Even though copolymer SBu-1 has a somewhat more balanced composition than the SEBS series, a fact that is generally considered to improve emulsification phenomena, it can be seen in *Figure 8* that only a marginal emulsification is observed. The results of particle diameter reduction could be related to the higher

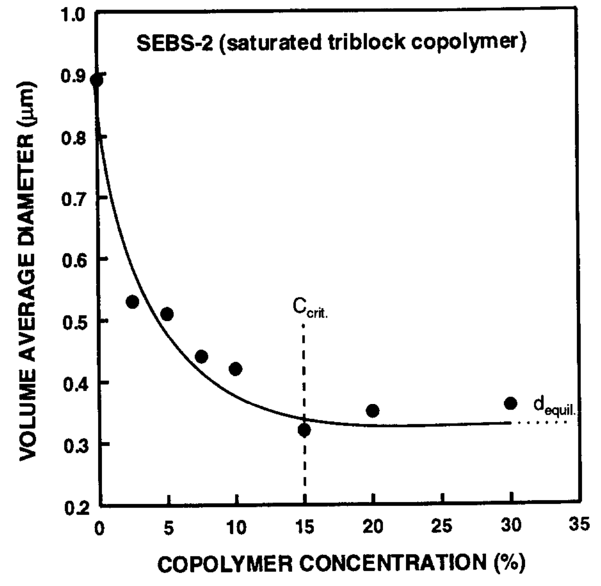

Figure 6 Emulsification curve of the 10% EPR/90% PS compatibilized by an S-EB-S hydrogenated triblock type copolymer. On average, 250–300 particle diameter measurements were taken per blend preparation

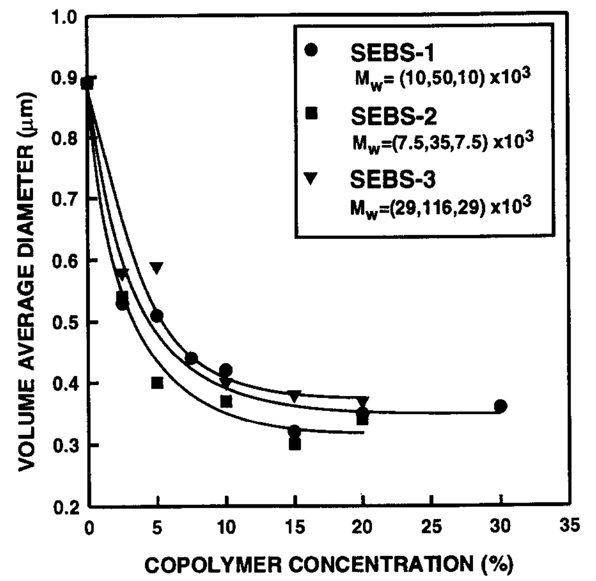

Figure 7 Influence of the molecular weight of the S-EB-S saturated triblock copolymer on the emulsification curve

affinity that the saturated ethylene–butylene middle block of the S-EB-S interfacial modifiers has to the ethylene–propylene rubber dispersed phase, than the unsaturated butadiene block of the S-Bu interfacial agents (SBu-1 and SBu-2). It is important to note that the emulsification curve is highly sensitive to changes in chemical composition.

The influence of molecular architecture for the unsaturated S-Bu type copolymers is shown in *Figure 9*. The same curve was plotted for both (triblock and star-shaped) copolymers owing to the similarity of the diameter values and the significant scatter in the results. The average spread in the data is around 30% for this type of copolymer because of the poor emulsifying activity of the S-Bu modifiers. It is important to note that

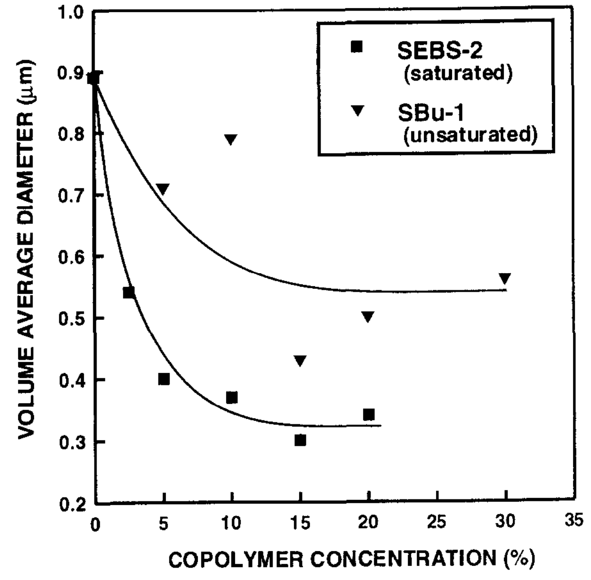

Figure 8 Influence of an unsaturated triblock copolymer (S-Bu-S) on the emulsification curve as compared to a hydrogenated S-EB-S

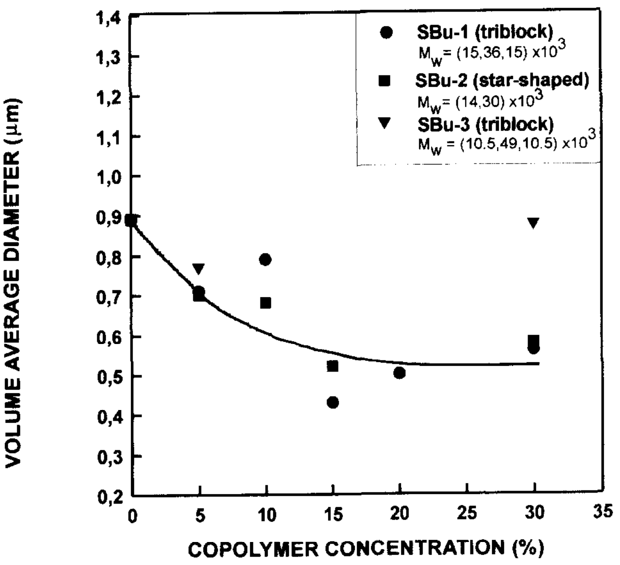

Figure 9 Influence of molecular architecture (triblock vs. star-shaped) on the emulsification curve for the S-Bu unsaturated copolymers. Composition of SBu-1 is 45% polystyrene; compositions of SBu-2 and SBu-3 are 32 and 30% polystyrene, respectively

this error value is not related to the efficacy of the morphology techniques used in this study (emulsification curves). Nevertheless, there appears to be a marginal emulsifying effect of the copolymers due to the reduction in particle size: an equilibrium diameter of approximately 0.5–0.6 μm is obtained, which is higher in comparison with the S-EB-S copolymers (0.3–0.4 μm) (*Figure 7*). Morphological observations also support the poor emulsifying activity of the star-shaped copolymer (*Figure 4c*). In the case of the star-shaped copolymer it would be expected that branching could restrict the opportunities for the backbone to penetrate its homopolymer phase and then to locate itself at the interface (entropic restriction). It is interesting to note that, once the emulsification phenomenon has been significantly reduced due to the chemical composition (unsaturated triblock copolymer), imposing a further conformational restriction by using an unsaturated star copolymer has little effect on the emulsification curve.

Critical concentration of modifier for interfacial saturation

Recently, Lomellini *et al.*[19] developed an expression to estimate the minimum amount of block copolymer needed to saturate the interface for the case of dispersed spherical particles. This expression does not depend on the molecular weight itself but only on the relative composition of the blocks. The theoretical base of this model is explained in a detailed manner in part 2 of this study[19]. In accordance with the authors, the amount of copolymer normalized per unit volume needed to saturate the interface was obtained by dividing the dispersed particle surface into pseudo-cubic elements. It is assumed that the interfacial modifier possesses a random-coil conformation at the interface and that the average projection of the end-to-end vector on any one of the three Cartesian axes of the cubic element on the surface is $R_{ee}/\sqrt{3}$. The theoretical critical concentration (C_{crit}) normalized to the whole blend was estimated as follows:

$$C_{crit} = \frac{1}{W_A} \frac{9kM_A}{R_{ee}^2 \rho R N_{Avo}} \qquad (4)$$

where A refers to the matrix-like part of the copolymer; M_A is the molecular weight of block A; W_A is the weight of type A blocks in the copolymer; R_{ee} is a statistical parameter that characterizes the A block copolymer chain size and is called the end-to-end distance; R is the dispersed particle radius; and k is a parameter that has to be determined from the experiments and is related to the number of A copolymer blocks occupying the unit mesh into which the surface of one dispersed particle has been divided. This factor is physically related to the extent of lateral chain entanglement. Equation (4) was applied to the particular system of 10% EPR/90% PS and it is estimated that a k value of about two styrene blocks per cubic element corresponds well to the experimental results ($C_{crit} = 15\%$). It is important to note that this critical concentration is proportional to the A molecular weight and inversely proportional to the end-to-end distance (R_{ee}), which is also proportional to the molecular weight. That means that the molecular weight does not affect the critical amount of copolymer needed for interfacial saturation. This point is supported by the experimental results mentioned before and is shown in *Figure 7*, where the critical concentration values for the three S-EB-S saturated triblock copolymers with different molecular weights are essentially equivalent. A critical concentration of approximately 15% was obtained for all the SEBS type interfacial agents.

CONCLUSIONS

It has been shown that an emulsification curve exists for the 10% EPR/90% PS system stabilized by block copolymers and that it can provide significant information concerning the efficacy of an interfacial agent for a particular multiphase system. The emulsifying ability of the interfacial agents tested caused a reduction in the dispersed particle size and polydispersities, but the

S-EB-S saturated triblock copolymers were found to be better emulsifiers for 10% EPR/90% PS blends than the unsaturated S-Bu-S. For the three hydrogenated triblock copolymers (S-EB-S) having molecular weights from 50×10^3 to $174 \times 10^3\,\mathrm{g\,mol^{-1}}$, little influence of this parameter on the emulsification phenomenon has been observed. The chemical composition of the modifier, however, plays a more important role on the EPR dispersed particle size than the molecular weight. The presence of double bonds in the copolymer modifier affects significantly its emulsification capability. By imposing both double bonds and a further conformational change (star-type architecture) it is interesting to note that the emulsification curve remains essentially the same. A critical concentration for interfacial saturation of around 15% based on the volume of the minor phase was obtained for the three S-EB-S type copolymers, from which an equilibrium surface particle diameter of 0.31 μm (resulting from the average of the values in the equilibrium zone of the emulsification curve) was achieved. Encouraging results have been obtained from the quantitative comparison between a model of interfacial saturation and the experimental data.

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