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Morphologies and interfacial tensions of immiscible polypropylene/polystyrene blends modified with triblock copolymers

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Abstract

The morphology and the response to small amplitude oscillatory shear (SAOS) of polypropylene/polystyrene (PP/PS 90/10) blends compatibilized with styrene–butadiene–styrene (SBS) or styrene–ethylene/butylene–styrene (SEBS) triblock copolymer were studied in this work. The possibility of inferring the interfacial tension between PP and PS as a function of amount of triblock copolymer added to the blend using the morphological and rheological measurements was investigated. The concentration of compatibilizers ranged from 0 to 25% relative to the weight of the dispersed phase (PS). The addition of compatibilizers resulted in a reduction of the size of the dispersed phase particles following an emulsion curve. SBS was shown to form a third phase when added, at high concentrations, to the blend. The addition of compatibilizers to the PS phase resulted in a reduction of interfacial tension following an emulsion curve. It was shown that for both compatibilizers the concentration at which the interfacial tension essentially levels off is smaller than the concentration at which the average radius of the dispersed phase essentially levels off. The morphological, viscosity and interfacial tension results showed that SEBS is a better compatibilizer for the PP/PS blend than is SBS. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Immiscible blends; Interfacial tension; Rheology

1. Introduction

Polymer blends have gained an increasing popularity in the field of polymer science and industry during the last 30 years. The growth in the use of polymer blends is mainly due to their ability to combine the properties of their phases in a unique product [1]. The final properties of polymer blends are directly related to the quality of their morphology, which in turn depends on the rheological properties of the phases of the blend, on the composition of the blend, on the processing conditions of the blend, and on the compatibility between the polymers forming the blend [2]. When working with polymer blends, it is important to obtain at least partial compatibility between the phases of the product. However, most of polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases and poor mechanical properties. The compatibility between the phases of a blend can be improved by the addition of compatibilizers [3,4] which results in a finer and more stable morphology, better adhesion between the phases of the blends and consequently better properties of the final product [5]. The efficiency of the compatibilization can be evaluated using the emulsion curve introduced by Favis [6], which correlates the size of the dispersed phase particles (in the case of a dispersion of droplets type morphology) to the concentration of compatibilizer added to the blend. It has been shown that this improvement of the morphological characteristics, from coarse to fine particles, is related to a decrease of interfacial tension between the phases forming the blend [7–10]. However, studies correlating the emulsion curves to the decrease of interfacial tension are still scarce due to the experimental difficulties encountered in the determination of interfacial tension between two molten polymers.

Among the various methods to measure interfacial tension between two liquids, only a few are suitable for polymers because of their high viscosity. In general, the equilibrium methods are most commonly used. These methods involve the evaluation of a profile of either sessile, spinning, or pendant drop (a good review of the static methods can be found in Ref. [11]); dynamic methods based on the breaking thread and imbedded fiber were also used [12–15]. During the last 10 years, a large effort has been conducted to increase the understanding of the relationship between viscoelastic properties and the morphology of polymer blends. Some theoretical models have been developed to study the linear viscoelastic behavior of polymer blends under flow [16–29]. Those models relate the

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Table 1
Materials used in this work

Polymers	$\bar{M}_n \leq$ (g/mol)	$\bar{M}_w/\bar{M}_n$	Melt index (g/10 min)	Viscosity (η_0) at 200°C (10^4 Pa s)	Structure	Supplier
PP	75,200	4.65	1.5	4.64	Homopolymer	Polibrasil
PS	91,200	2.5	2.2	3.39	Homopolymer	Estireno do Brasil
Kraton D 1102 CS	120,000	1.04	6.0	6.41	Linear S-B-S bound styrene 29.5% mass	Shell Chemical
Kraton G 1652	71,600	1.03	–	14.3	Linear S-E/B-S bound styrene 30% mass	Shell Chemical

dynamic response of polymer blends to their morphology, composition and interfacial tension between the phases of the blend. Using those models, it is possible to infer interfacial tension from the dynamic behavior of the blend once the morphology of the blend is characterized.

In this work, an experimental study of the influence of addition of SBS and SEBS triblock copolymers on the morphology and on the dynamic behavior of PP/PS immiscible blend was carried out. Initially, experiments using a pendant drop apparatus were performed in order to evaluate interfacial tension between the phases of the blend. It was not possible to use that method to evaluate the influence of addition of compatibilizer on interfacial tension and another procedure was needed. The possibility of inferring the interfacial tension between PP and PS as a function of amount of triblock copolymer added to the blend, using the morphological and rheological measurements was studied.

2. Experimental

2.1. Material

Commercial polypropylene (PP) from Polibrasil S.A., and polystyrene (PS) from Estireno do Brasil were used in this work. Linear triblock copolymers styrene–butadiene–styrene (SBS) and styrene–butadiene–styrene with hydrogenated polybutadiene (PBD) midblock (SEBS) from Shell Chemical were used as compatibilizers. The characteristics of the materials used in this work are shown in Table 1.

Blends of PP/PS were prepared in a 9/1 (PP/PS 90/10) weight concentration. The effect of the addition of a compatibilizer on the rheological behavior and morphology was studied. Concentrations of compatibilizers (either SBS or SEBS), ranging from 0 to 25 wt% with respect to the minor phase PS were used. The blends were prepared in two steps in a Werner–Pfleiderer twin screw extruder, model ZSK-30, with six zones of temperature, which varied from 190 to 220°C, along the barrel of the extruder. Both the non-modified and compatibilized blends were prepared in two steps. The copolymer SBS or SEBS was first mixed with the minor phase (polystyrene) and then blended with the matrix (polypropylene). In the case of the non-modified blends the minor phase was processed twice in order to undergo the same thermomechanical history.

2.2. Rheological measurements

Discs of 25 mm in diameter and 1 mm in thickness were obtained by compression molding for all blends and pure polymers. They were compressed during 25 min under an isostatic pressure of 18 MPa at 200°C.

Rheological characterization of the samples was carried out using a controlled shear rheometer (model SR-5000 from Rheometric Scientific®) under dry nitrogen atmosphere. A parallel plate configuration was used with a gap of 0.6 mm and plate diameter of 25 mm. Strain and stress sweeps were performed for all blends and pure polymers to define the region of linear viscoelasticity. Dynamic frequency sweeps were performed for all blends and pure polymers. The stress was varied from 10 to 500 Pa and the strain from 3 to 6%. The frequency range used was 0.01–500 rad/s. Creep tests were also performed to evaluate the zero shear stress viscosity of the blend and different phases. All rheological experiments were performed at a temperature of 200°C.

2.3. Morphological characterization

The morphology of rheological samples, compatibilized or not, was observed by Scanning Electron Microscopy (SEM) using a Cambridge, model Stereoscan 240 microscope. The samples were fractured in liquid nitrogen and then covered with gold using a Balzers sputter coater, model SCD-050. To improve the contrast in the non-modified PP/PS (90/10) blend, the minor phase (polystyrene) was extracted using ethyl acetate at room temperature, under continuous stirring for four hours. Thereafter, the samples were dried under vacuum at temperature of 60°C during 24 h.

The morphology was quantified using an appropriate software. The average diameter and volume fraction of the minor phase was calculated after analysis of the SEM photomicrographs. About 500 particles were considered to calculate these parameters. For the calculation of the average size of the minor phase Saltikov's [30] correction was used. This correction takes into account the polidispersity of the samples and the fact that the fracture in the sample does not always occur at the maximum diameter of the droplets of the dispersed phase.

The morphology of PP/PS (90/10) blend compatibilized

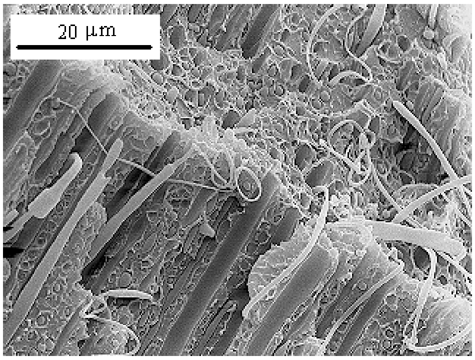
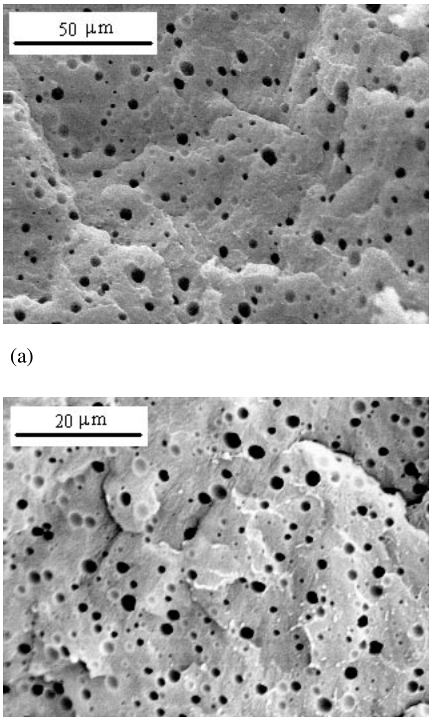


Fig. 1. Morphology of extruded PP/PS (90/10) blend.

with 25 wt% of SBS or 25 wt% SEBS in respect to the dispersed phase was studied by Transmission Electron Microscopy (TEM). The main objective was to observe if the copolymer was located at the interface between PP and PS. Prior to the microscope examination the samples compatibilized with SBS or SEBS were stained following the procedures reported in Kato [31] and Kakugo and Satatoshi [32], respectively: the samples compatibilized with SBS were immersed in an aqueous solution of 0.7% of OsO_4 during 7 h at 65°C; the samples compatibilized with SEBS were first immersed in 1,7 octadiene during 24 h at room temperature and dried during 5 min, then stained with OsO_4 following the same procedure as for the samples compatibilized with SBS. Then the samples were sliced using a microtome at low temperature (−70°C).



(a)

(b)

Fig. 2. Morphology of compatibilized PP/PS blend after compression molding. (a) PP/PS/SBS (90/10/0.05). (b) PP/PS/SEBS (90/10/0.05).

3. Results and discussions

3.1. Morphology

Fig. 1 shows the morphology of PP/PS (90/10) blend after extrusion in the longitudinal direction. It can be seen that the blend shows a fibrilar morphology. Such morphology was observed for all the blends, compatibilized or not, after extrusion. In order to evaluate the interfacial tension between the phases of the blend using rheological measurements it is necessary to have a dispersion of droplets in a continuous matrix type of morphology [16,20–23,24]. Therefore, we evaluated the time necessary for the fibers to breakup into spheres during compressing molding.

The time required for the breakup of PS fibers can be roughly estimated knowing the viscosity of both phases (PP and PS) and the interfacial tension between both phases using Tomokita's equation for Newtonian fluids [33], given by:

$$t_b = \frac{\eta_m R_n}{\Omega_{max} \gamma} \ln(1.39 \gamma R_n^2 / kT) \qquad (1)$$

where t_b is the breakup time, R_n the number average radius of the fiber, γ the interfacial tension between the phases of the blend, k the Boltzman constant, T the temperature in K, η_m the viscosity of the matrix, and Ω_{max} is a parameter dependent on the viscosity ratio.

The number average radius of PS fibers, R_n, was evaluated by SEM and had a value of about 0.5 μm. Using a value of interfacial tension between PP and PS at 200°C of 6.46 mN/m [34], a zero shear viscosity of PP matrix of 4.64×10^4 Pa s, and a Ω_{max} of 0.08 [35], the breakup time of PS fibers at 200°C was found to occur at about $t_b =$ 10 min. When compatibilizer is added to the blend, the time for breakup is expected to increase because the interfacial tension decreases. However, the radius of the fiber is also expected to decrease, reducing t_b. If we consider that the addition of a compatibilizer could reduce the value of interfacial tension in half, and does not affect the value of the radius of the fiber, t_b is found to be equal to 19 min. Since the addition of compatibilizer results in a decrease of the radius of the fiber in the case of compatibilized blends, t_b is expected to be even less than 19 min. Therefore, a compression time for all rheological samples of 25 min was used in order to ensure fiber breakup.

Fig. 2a and b shows the morphology of the PP/PS (90/10) blend compatibilized with 5 wt%, relative to the dispersed phase, of SBS and SEBS, respectively, after compression molding. A droplet dispersion morphology type can be observed. This type of morphology was observed for all the blends after heat compressing molding. It can be seen that the average radius of the dispersed phase for the blend

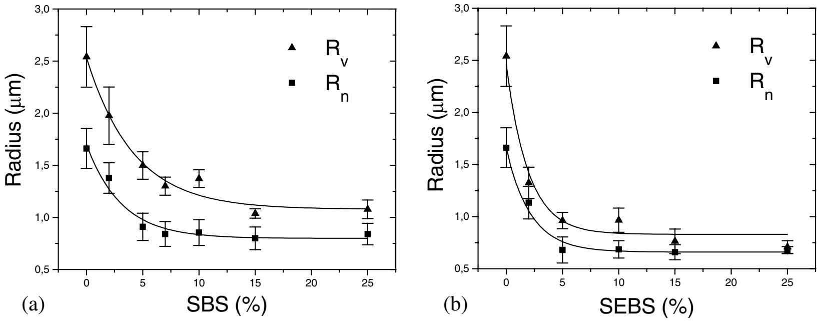


Fig. 3. Emulsion curve for compatibilized PP/PS (90/10) blends. (a) PP/PS (90/10) compatibilized with SBS. (b) PP/PS (90/10) compatibilized with SEBS.

compatibilized with SEBS is smaller than the average radius of the dispersed phase for the blend compatibilized with SBS (0.6 μm compared to 0.9 μm). Note the difference of scale for the two photomicrographs presented here.

Fig. 3a and b shows the number and volume average radii of the dispersed phase as functions of the concentration of SBS and SEBS added to the blend, respectively. The number and volume average radii are defined as:

$$R_\mathrm{n} = \frac{\sum_i n_i R_i}{\sum_i n_i} \tag{2}$$

$$R_\mathrm{v} = \frac{\sum_i (R_i \phi_i)}{\sum_i \phi_i} \tag{3}$$

where R_i is the radius of each droplet, n_i the number of droplets with a radius of R_i, and ϕ_i the volume fraction of each droplet.

It can be seen that the average radii of the dispersed phase (both number and volume average) decrease when either compatibilizer is added to the dispersed phase following an emulsion curve [6]. The following exponential equation provides a good estimate of the dependency of the average radius on the copolymer concentration.

$$\frac{(R_\mathrm{nc} - R_\infty)}{(R_0 - R_\infty)} = \exp(-n_1 c) \tag{4}$$

where R_nc is the number average radius for a concentration c of compatibilizer, R_0 is the number average radius for a blend without compatibilizer, R_∞ is a constant, and n_1 is a constant that determines the efficiency of the compatibilizer as an emulsifier.

The results presented in Fig. 3a and b indicate that $R_\mathrm{nc} - R_\infty$ decreases exponentially with increasing concentration of compatibilizer. In order to compare the efficiency of both compatibilizers, we picked up a compatibilizer concentration $c_{R0.05}$, at which $(R_\mathrm{nc} - R_\infty)/(R_0 - R_\infty) = 0.05$. For concentrations higher than $c_{R0.05}$, the decrease of the value of R_nc can be considered negligible. Table 2 presents the constants R_∞ and n_1 for Eq. (4), as well as the concentration $c_{R0.05}$. It can be seen that n_1 is 50% larger for SEBS than for SBS, R_∞ is 18% smaller for SEBS than for SBS, and that $c_{R0.05}$ is 9.4% for SBS and 6.2% for SEBS. All these results indicate a higher efficiency of SEBS than SBS as an emulsifier for PP/PS blend. At $c_{R0.05}$ the number average radius is reduced by a factor of 2 and 2.3 when SBS and SEBS are added to the blend, respectively.

Table 2
Fitting parameters of Eq. (4)

Compatibilizer	R_∞ (μm)	n_1	$c_{R0.05}$
SBS	0.80	0.32	9.4%
SEBS	0.66	0.48	6.2%

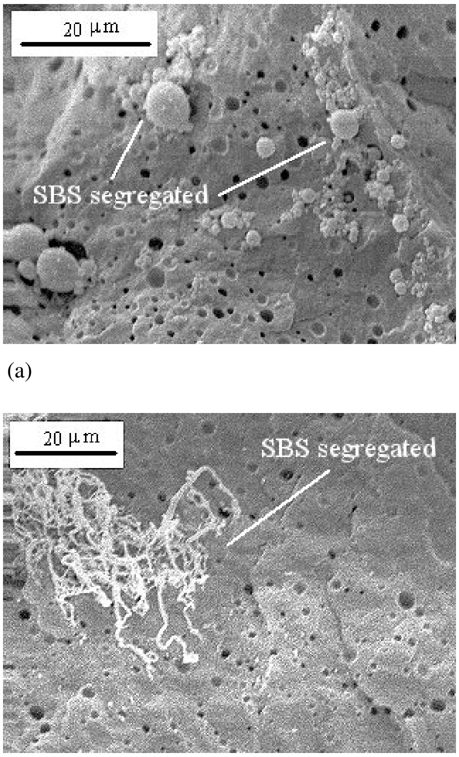


Fig. 4. Segregation of SBS for PP/PS/SBS (90/10/0.15) blend. (a) Segregation of SBS as dispersed droplets. (b) Segregation of SBS as fibers.

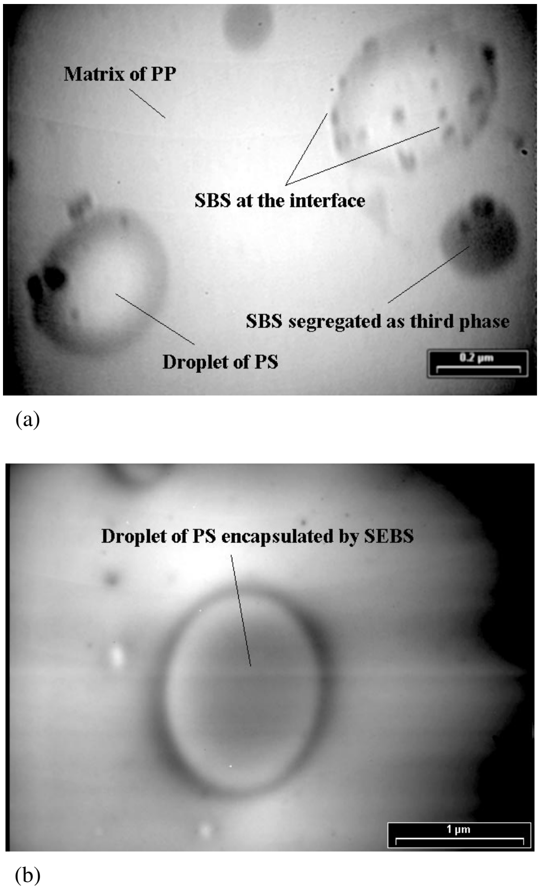


Fig. 5. Transmission electron micrographs of compatibilized PP/PS (90/10) blend. (a) PP/PS/SBS (90/10/0.25) blend. (b) PP/PS/SEBS (90/10/0.25) blend.

Fig. 3a and b also shows that the difference between R_v and R_n is much smaller for SEBS than for SBS. This indicates that the morphology of blends compatibilized with SEBS is more uniform than the morphology of blends compatibilized with SBS.

The better efficiency of SEBS as an emulsifier can be the result of a better interaction between ethylene/butylene block (E/B) of SEBS and the polypropylene of PP/PS blend than between the butadiene of SBS and PP of PP/PS blends. Similar results have been obtained by Lepers et al. [36].

Fig. 4a shows the morphology of PP/PS blends to which SBS was added in a concentration of 15 wt% relative to the dispersed phase. The PS was extracted using ethyl acetate. It can be seen from Fig. 4a that SBS segregates and forms droplets of a third dispersed phase. The SBS segregation was also seen in a fibrilar form. Fig. 4b shows the segregation of SBS as a third phase in a form of fiber. For all concentrations of SBS above 15 wt% these two kinds of SBS segregation were observed. No segregation of SEBS was observed for any concentration added to the PS phase.

Fig. 5a and b shows the morphology of PP/PS compatibilized blends with 25 wt% of SBS and 25 wt% of SEBS, respectively. The micrographs were obtained by transmission electron microscopy (TEM) after staining the samples. It can be seen from Fig. 5a that SBS (small black points) is located at the interface of the PP/PS blend, but quite irregularly. Also, it can be seen that SBS segregates as a third phase, corroborating the morphological observations obtained by SEM. This segregation phenomenon is probably due to the weak interaction between the compatibilizer and the phases of the blend. In the case of SEBS, the photomicrograph presented in Fig. 5b seems to indicate that SEBS encapsulates the droplets of PS. Similar behavior has been observed by Wilkinson et al. [37] who studied the morphology of PP/PA6/SEBS blends.

3.2. Rheological properties

Fig. 6a and b shows the storage (G') and loss (G'') moduli of the PP/PS (90/10) blend and of the pure phases at a temperature of 200°C, respectively. It can be seen that for low frequencies (0.01–1 rad/s) the storage moduli of the PP/PS (90/10) blend are greater than those of the pure phases. That type of behavior has already been reported by many researchers [18–29] for different polymer blends. The increase of elasticity for low frequencies can be attributed to a relaxation process of the dispersed droplets of the minor phase when slightly deformed [21]. The increase of elasticity for lower frequencies has also been observed for all the compatibilized blends with SBS or SEBS studied in this work. The increase of elasticity can be used to evaluate

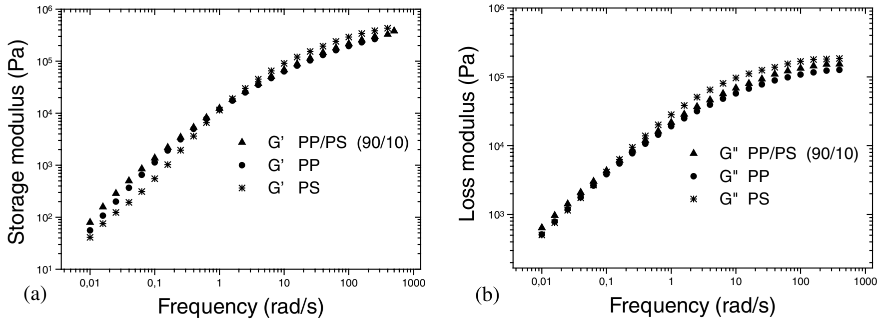


Fig. 6. Dynamic moduli of PP/Ps (90/10) blend and of pure phases at 200°C. (a) Storage modulus. (b) Loss modulus.

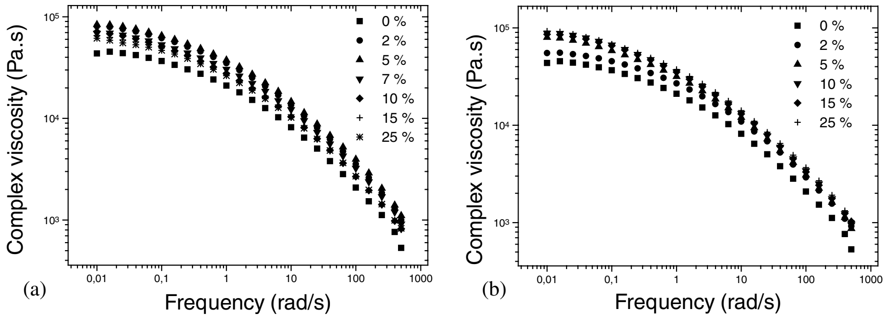


Fig. 7. Complex viscosity of compatibilized PP/PS (90/10) blend at 200°C. (a) PP/PS (90/10) blend compatibilized with SBS. (b) PP/PS (90/10) blend compatibilized with SEBS.

the interfacial tension between the phases of the blend using emulsion models [18–28]. This will be shown later in the paper.

Fig. 7a and b shows the complex viscosity, at a temperature of 200°C, of the PP/PS (90/10) blends compatibilized with SBS and SEBS, respectively. In the case of SEBS, it can be seen that with increasing compatibilizer concentration the complex viscosity increases and levels off for a concentration of about 10 wt%. In the case of SBS, it can be seen that with increasing compatibilizer concentration the complex viscosity first increases (up to concentration of 5 wt%), and then decreases. This phenomenon is more pronounced for lower frequencies. The same effect was obviously observed for the zero shear stress viscosity as can be seen in Fig. 8. The same type of phenomenon has already been observed by other researchers for other polymer pairs [38]. The increase of viscosity is probably due to a compatibilizing effect of copolymer. When SEBS is added to the blend (for concentration up to 10 wt%), it gives better adhesion between PS and PP. When the concentration of SEBS is above 10 wt%, the interface is already saturated with SEBS and no further increase of viscosity is observed. When SBS is added to the blend (for concentrations up to 5 wt%), similar behavior as the one observed with SEBS involving an increase of viscosity can be seen. When the concentration of SBS is above 15 wt%, it was mentioned above that it segregates in a third phase. This behavior could explain the decrease of the viscosity of the blend.

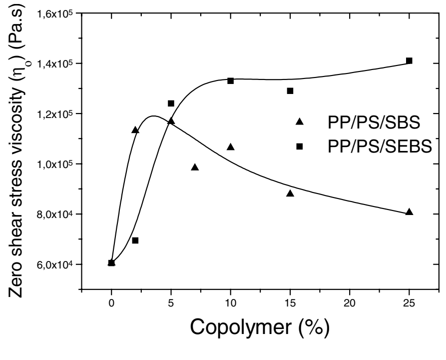


Fig. 8. Zero shear stress viscosity of PP/PS (90/10) blend compatibilized with SBS or SEBS at 200°C.

The zero shear stress viscosities of the non-modified and compatibilized blends were compared to values obtained using the log additivity rule introduced by Irving [39], given by:

$$\log(\eta_0) = \sum_i x_i \log(\eta_{0i}) \qquad (5)$$

where: η_0 is the zero shear stress viscosity of the blend, x_i the weight fraction of the phase i, and η_{0i} the zero shear stress viscosity of the phase i.

The results of this analysis are presented in Tables 3 and 4. It can be seen that for each concentration of the compatibilizer, the blend shows a positive deviation behavior. This positive deviation behavior is characteristic of compatibilization [40]. It can be seen that the positive behavior is larger when SEBS is added than when SBS is added to the blend showing that SEBS is a better compatibilizer than SBS for PP/PS.

3.3. Interfacial tension analysis

In a first approach, it was tried to evaluate the interfacial tension between the phases of the blend using the pendant drop method following the procedure reported in Demarquette and Kamal [41]. It was not possible to evaluate the interfacial tension between the phases of the compatibilized blends. The pendant drop of PS, to which SEBS was added, in a matrix of PP did not form a typical drop shape.

It has been shown that it is possible to infer interfacial tension between polymers forming an inhomogeneous polymer blend using small amplitude oscillatory shear [18–28]. The analysis of Gramespacher and Meissner [24] to evaluate interfacial tension from rheological measurements was used for the blends studied here. In their work, Gramespacher and Meissner developed a constitutive equation for an emulsion based on the work of Choi and Schowalter [17] and on a linear mixing rule, which considers the complex shear modulus of a blend as a combination of the contribution of the shear moduli of the viscoelastic phases plus the contribution of the interface. These researchers obtained the following equations for the complex, storage and loss

Table 3
Zero shear stress viscosity of PP/PS (90/10) blend compatibilized with SBS

SBS %	η_0 blend (10^4 Pa s)	η_0 PP (matrix) (10^4 Pa s)	η_0 PS/SBS (10^4 Pa s)	log(η_0) blend	log(η_0) Eq. (5)
0	6.05	4.64 ± 0.25	3.39 ± 0.20	4.78	4.65
2	11.31	4.64 ± 0.25	3.06 ± 0.03	5.05	4.65
5	11.68	4.64 ± 0.25	3.58 ± 0.17	5.07	4.66
7	9.83	4.64 ± 0.25	3.75 ± 0.13	4.99	4.66
10	10.64	4.64 ± 0.25	2.56 ± 0.13	5.03	4.64
15	8.79	4.64 ± 0.25	2.13 ± 0.12	4.94	4.63
25	8.06	4.64 ± 0.25	2.64 ± 0.06	4.91	4.64

shear moduli of the blend:

$$G^*(\omega) = \phi G_{\mathrm{d}}^*(\omega) + (1-\phi)G_{\mathrm{m}}^*(\omega) + G_{\mathrm{interface}}^*(\omega) \tag{6}$$

$$G'(\omega) = \phi G'_{\mathrm{d}}(\omega) + (1-\phi)G'_{\mathrm{m}}(\omega) + \frac{\eta}{\tau_1}\left(1-\frac{\tau_2}{\tau_1}\right) \times \left(\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2}\right) \tag{7}$$

$$G''(\omega) = \phi G''_{\mathrm{d}}(\omega) + (1-\phi)G''_{\mathrm{m}}(\omega) + \frac{\eta}{\tau_1}\left(1-\frac{\tau_2}{\tau_1}\right) \times \left(\frac{\omega\tau_1}{1+\omega^2\tau_1^2}\right) \tag{8}$$

with

$$\eta = \eta_{\mathrm{m}}\left(1 + \phi\frac{(5K+2)}{2(K+1)} + \phi^2\frac{5(5K+2)^2}{8(K+1)^2}\right) \tag{9}$$

$$\tau_1 = \frac{(19K+16)(2K+3)}{40(K+1)}\frac{\eta_{\mathrm{m}}R}{\gamma}\left(1+\phi\frac{5(19K+16)}{4(K+1)(2K+3)}\right) \tag{10}$$

$$\tau_2 = \frac{(19K+16)(2K+3)}{40(K+1)}\frac{\eta_{\mathrm{m}}R}{\gamma}\left(1+\phi\frac{3(19K+16)}{4(K+1)(2K+3)}\right) \tag{11}$$

where G^* is the complex modulus of the blend, G_{d}^* the complex modulus of the dispersed phase, G_{m}^* the complex modulus of the matrix, $G_{\mathrm{interface}}^*$ the complex modulus of the interface, G'', G''_{d} are the blend and dispersed phase loss moduli, respectively, G', G'_{m} are the blend and matrix storage moduli, respectively, ω the frequency of oscillation, η, η_{m}, η_{d} are the blend, matrix and dispersed phase Newtonian viscosities, respectively, $K = \eta_{\mathrm{d}}/\eta_{\mathrm{m}}$ is the viscosity ratio, γ the interfacial tension between the phases of the blend, R the radius of the monodisperse spheres and ϕ the volume fraction of the dispersed phase.

The term τ_1 corresponds to the relaxation time in the discrete relaxation spectrum of the blend due to the relaxation of the interface between the phases of the blend. The blend relaxation spectrum is a combination of the relaxation spectra of the different phases of the blend and an additional relaxation time (τ_1), from which the interfacial tension between the phases forming the blend can be inferred using Eq. (10).

Fig. 9 shows the weighted relaxation spectrum of PP/PS (90/10) blend and of PP and PS pure phases at a temperature of 200°C. The relaxation spectrum can be calculated by several methods [42–45], in this work the relaxation spectrum was calculated using a nonlinear regression method from the storage modulus raw data. The mathematical method is available in the stress rheometer SR-5000 software package from Rheometrics. In Fig. 9, it is perfectly possible to identify three relaxation times. Two are related to the phases of the blend (PP and PS), since they are of the same order of magnitude as the ones of the pure phases. The remaining peak was associated with the contribution of the interface, being $\tau_1 = 35$ s. In order to verify if this relaxation time could really be associated with the relaxation of the interface, we compared its value to the one predicted by Palierne's emulsion model [16]. In his work, Palierne derived an equation to predict the longest relaxation time due to the relaxation of the interface, for an emulsion of Newtonian uniform size droplets immersed in a

Table 4
Zero shear stress viscosity of PP/PS blend compatibilized with SEBS

SEBS%	η_o blend (10^4 Pa s)	η_0 PP (matrix) (10^4 Pa s)	η_0 PS/SEBS (10^4 Pa s)	log(η_0) blend	log(η_0) Eq. (5)
0	6.05	4.64 ± 0.25	3.39 ± 0.20	4.78	4.65
2	6.95	4.64 ± 0.25	3.09 ± 0.20	4.84	4.65
5	12.4	4.64 ± 0.25	3.48 ± 0.15	5.09	4.66
10	13.33	4.64 ± 0.25	4.36 ± 0.06	5.13	4.67
15	12.85	4.64 ± 0.25	4.20 ± 0.10	5.11	4.67
25	14.06	4.64 ± 0.25	4.13 ± 0.09	5.15	4.68

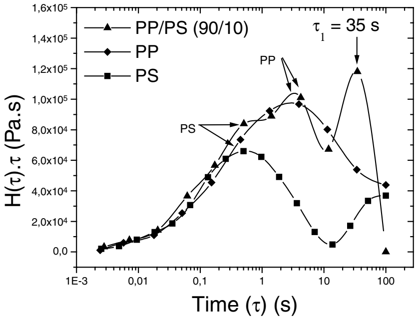


Fig. 9. Weighted relaxation spectrum of PP/Ps (90/10) blend and of the pure phases at 200°C.

Newtonian matrix. The hypothesis of considering Newtonian liquids can be done here because the experiments were performed in the linear viscoelastic regime [20–23,27]. Also, for polymer blends with narrow distribution of droplets size, good agreement between Palierne model [16] and rheological experimental data can be achieved when the individual radii of the droplets are replaced by the volume average radius (R_v) [20–23,27]. Thus, an estimation of the longest relaxation time due to interfacial tension is given by:

$$\tau_1 = \frac{R_v \eta_m}{4\gamma} \frac{(19K + 16)(2K + 3 - 2\phi(K - 1))}{10(K + 1) - 2\phi(5K + 2)} \tag{12}$$

where R_v is the volume average radius of droplets; $K = \eta_d/\eta_m$ where η_d and η_m are the Newtonian viscosity of the dispersed phase and the matrix, respectively; ϕ is the volume fraction of the dispersed phase and γ is the interfacial tension.

As it was possible to infer interfacial tension between PP and PS using the pendant drop method [34], we used Eq. (12) to estimate the interface relaxation time. The calculated value was $\tau_1 = 37.4$ s, which corroborates with the value obtained from the relaxation spectrum shown above. Thus, using Eq. (10) and the values reported in Table 5, it was therefore possible to calculate the interfacial tension between PP and PS at a temperature of 200°C. The interfacial tension between PP and PS was found to be equal to 6.25 ± 0.87 mN/m, corroborating the value obtained with the pendant drop method reported elsewhere [34].

Fig. 10a and b shows the weighted relaxation spectrum for the compatibilized blends with SBS and SEBS, respectively. The spectrum is plotted only for few concentrations of compatibilizer for the sake of clarity of the figures. It can be seen that the relaxation spectrum of each blend shows an additional relaxation time except for the relaxation spectrum of the PP/PS (90/10) blend compatibilized with 25 wt% of SBS. In order to find the value of τ_1 for the compatibilized blends the same procedure as the one used for the non-modified blends was used. In Fig. 10a and b it is possible to identify several peaks: some for which $\tau < 0.5$ s and some for which $\tau > 0.5$ s. Knowing that relaxation times for polymer blends range from some seconds to hundreds of seconds [22], and that interface relaxation occurs only at low frequencies, we could never associate small relaxation times ($\tau < 0.5$ s) to the relaxation of the interface between PP and PS. For $\tau > 0.5$ s only three peaks can be observed. The peaks associated with the relaxation of the pure phases (PP and PS) can be identified easily by comparison with the relaxation spectrum of the pure phases, the third was associated with the relaxation of the interface.

Table 5
Parameters for interfacial tension calculation

Parameter	PP/PS (90/10) blend
Viscosity of the matrix of PP (η_m)	$(4.64 \pm 0.25) \times 10^4$ Pa s
Viscosity of the dispersed phase of PS (η_d)	$(3.39 \pm 0.20) \times 10^4$ Pa s
Viscosity ratio $K = \eta_d/\eta_m$	0.73
Volume fraction of the dispersed phase of PS (ϕ)	0.095 ± 0.013
Number average radius of the dispersed phase spheres of PS (R_n)	1.66 ± 0.19 μm

Also, it was observed that the determination of the relaxation time of the interface through weighted relaxation spectrum for the PP/PS (90/10) blend, compatibilized or not, was well reproducible experimentally, and the location of its maximum statistically significant.

Tables 6 and 7 show the value of the additional relaxation time for the compatibilized blends with SBS and SEBS, respectively. It can be seen from Fig. 10a and b and the values presented in Tables 6 and 7 that the relaxation time associated with the relaxation of the interface is shifted to higher values when a compatibilizer is added to the blend. This can be explained if we recall that the relaxation of the interface is due to a balance between two forces [46,47]: a shearing force, proportional to $\eta\dot{\gamma}$ (where η is the viscosity and the $\dot{\gamma}$ is the shear rate) that tends to deform the droplets of the dispersed phase and a cohesive force, proportional to the ratio γ/d (where γ is the interfacial tension between the two polymers and d is the diameter of the drop) that contributes to the retraction of the dispersed phase into a spherical shape. When SBS or SEBS is added to polystyrene, it would be expected that the interfacial tension between PP and PS decreases, which is indeed the case. The force proportional to the interfacial tension then decreases and the relaxation time of the dispersed phase is longer.

The emulsion model of Gramespacher and Meissner [24] was not originally derived for being used with compatibilized blends. However, due to the low concentrations of compatibilizers (maximum of 2.5 wt% with respect to the whole blend weight) used to modify the PP/PS (90/10) blend, we assumed that the emulsion model could be used to evaluate interfacial tension. The contribution of the dispersed phase was then considered as a sum of the contribution of the dispersed phase of PS and the contribution of the compatibilizer (SBS or SEBS). Such an assumption has already been used by other researchers [26]. Equation (10) was used to evaluate the interfacial tension between PS

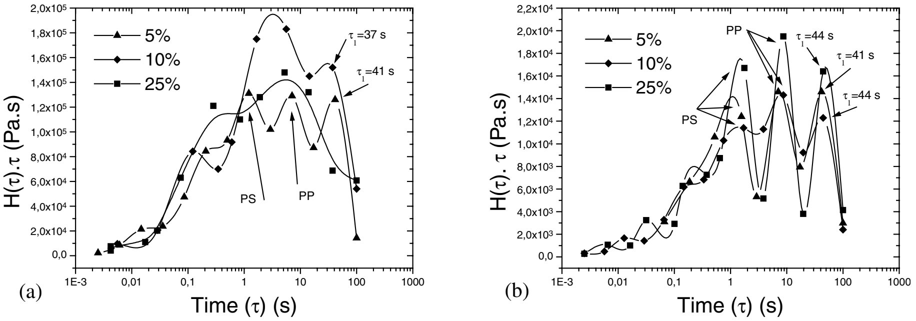


Fig. 10. Weighted relaxation spectrum of compatibilized pp/ps blends at 200°C. (a) PP/Ps blends compatibilized with sbs. (b) PP/PS blends compatibilized with SEBS.

modified with SBS or SEBS, and PP. The parameters used in the calculations and the interfacial tensions found by the analyses are reported in Tables 6 and 7. It was not possible to visualize an additional relaxation time for the PP/PS blends with the PS modified with SBS at concentrations higher than 15 wt%. Probably, due to the SBS segregated as third phase, which should present an independent rheological behavior masking the relaxation of the interface. Therefore, the interfacial tension between PS (to which more than 15 wt% of SBS was added) and PP was not calculated using Gramespacher and Meissner analysis [24]. In addition, application of Gramespacher and Meissner emulsion model [24], for interfacial tension calculation, would not be appropriate for the case where a third phase is observed. The results presented in Tables 6 and 7 suggest that adding a block copolymer reduces the interfacial tension by 2 or 3 fold. However, the variation in τ_1 is of the order of 25% or so. A close examination of Eq. (10) indicates that interfacial tension is a stronger function of the independently measured values of the dispersed phase particles radius rather than of τ_1 obtained from the rheological data. In compatibilized systems the main effect in reducing particle size is now known to be the decrease of droplet coalescence (due to steric stabilization) [48] rather than the case of droplet breakup owing to reduced interfacial tension. Therefore, if one uses Gramespacher and Meissner [24] theory to evaluate the interfacial tension for compatibilized system, one could be led to an erroneously calculation in terms of reduction of the interfacial tension. Therefore, the values of interfacial tension reported in Tables 6 and 7 should be considered as estimated. More experiments, for blends for which the effect of coalescence can be neglected are being performed and will be subject of a next communication.

Table 6
Relaxation times of the interface for the compatibilized blends with SBS

SBS	η_o (PS/SBS) (10^4 Pa.s)	τ_1 (s)	R_n (μm)	γ (mN/m)
0	3.39 ± 0.20	35	1.66 ± 0.19	6.25 ± 0.87
2	3.05 ± 0.03	41	1.38 ± 0.15	4.25 ± 0.53
5	3.75 ± 0.17	41	0.91 ± 0.13	3.00 ± 0.49
7	3.58 ± 0.13	43	0.84 ± 0.12	2.61 ± 0.42
10	2.56 ± 0.13	37	0.85 ± 0.12	2.86 ± 0.46
15	2.13 ± 0.12	not observed	0.80 ± 0.11	–
25	2.64 ± 0.06	not observed	0.84 ± 0.10	–

Fig. 11 shows the interfacial tension between the modified PS and PP at a temperature of 200°C as a function of the compatibilizer concentration added to PS (although as mentioned above the absolute values of interfacial tension could be slightly different). It can be seen that for both types of compatibilizers, interfacial tension decreases when the concentration of compatibilizer added increases, following a typical behavior of an emulsion curve.

A similar expression as the one used for the radius of the dispersed phase can be used to estimate the dependency of interfacial tension on the copolymer concentration:

$$\frac{(\gamma_c - \gamma_\infty)}{(\gamma_0 - \gamma_\infty)} = \exp(-n_2 c) \tag{13}$$

where γ_c is the interfacial tension for a concentration c of compatibilizer, γ_0 is the interfacial tension between PP and PS without compatibilizer, γ_∞ is a constant, and n_2 is a constant that determines the efficiency of the compatibilizer to decrease the interfacial tension.

In order to compare the efficiency of both compatibilizers, we picked up a compatibilizer concentration $c_{\gamma 0.05}$, at which $(\gamma_c - \gamma_\infty)/(\gamma_0 - \gamma_\infty) = 0.05$. For concentrations above $c_{\gamma 0.05}$ the decrease of the value of γ_c can be considered negligible. Table 8 presents the constants γ_∞ and n_2 for Eq. (13), as well the concentration $c_{\gamma 0.05}$. It can be seen that n_2 is 51% larger for SEBS than for SBS, that γ_∞ is 15% smaller for SEBS than for SBS, and that $c_{\gamma 0.05}$ is 7% for SBS and 4.6% for SEBS. At $c_{\gamma 0.05}$ the interfacial tension is reduced by a factor of 2.2 and 2.6 when SBS and SEBS are added to the blend, respectively. Therefore, SEBS is more efficient in decreasing the interfacial tension between PS and PP than is SBS when added to PS.

Chen and White [49] measured the interfacial tension for a polyethylene/polystyrene polymer pair non-modified and compatibilized with 5 wt% of SEBS (based on the PS weight) and observed a decrease of interfacial tension from 5.8 to 1.1 mN/m. Similar results have been obtained by Mekhilef et al. [50] with similar systems. The decrease of

Table 7
Relaxation times of the interface for the compatibilized blends with SEBS

SEBS	η_o (PS/SEBS) (10^4 Pa s)	τ_1 (s)	R_n (μm)	γ (mN/m)
0	3.39 ± 0.20	35	1.66 ± 0.19	6.25 ± 0.87
2	3.09 ± 0.20	41	1.13 ± 0.16	3.51 ± 0.56
5	3.48 ± 0.15	41	0.68 ± 0.13	2.22 ± 0.44
10	4.35 ± 0.06	44	0.69 ± 0.08	2.26 ± 0.32
15	4.20 ± 0.10	44	0.66 ± 0.07	2.16 ± 0.29
25	4.13 ± 0.09	44	0.68 ± 0.03	2.28 ± 0.20

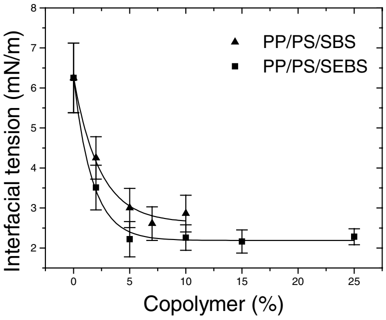


Fig. 11. Interfacial tension between modified PS (to which SBS or SEBS was added) and PP at 200°C.

interfacial tension between PP and PS when SEBS is added to the blend shown here is not as greater as in the case of Mekhilef et al. [50], most probably because SEBS is a better compatibilizer for the PE/PS system than for the PP/PS system.

3.4. Comparison of morphology and interfacial tension emulsion curve

Table 8
Fitting parameters of Eq. (13)

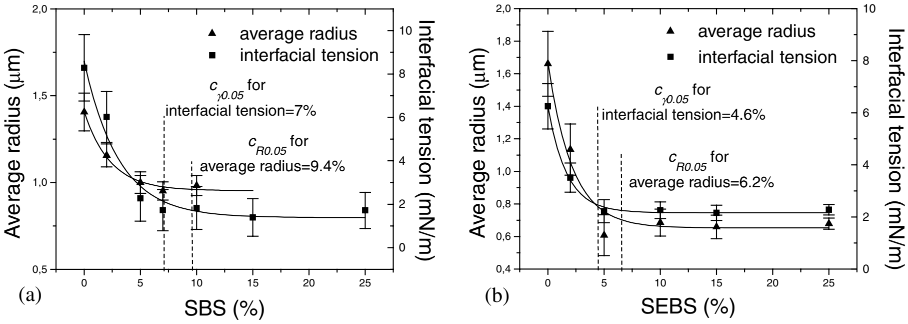
Compatibilizer	γ_∞ (mN/m)	n_2	$c_{\gamma 0.05}$ (%)
SBS	2.62	0.43	7
SEBS	2.24	0.65	4.6

Fig. 12a and b shows the superposition of morphology and interfacial tension emulsion curves for the compatibilized PP/PS blends with SBS and SEBS, respectively. Table 9 reports the values of $c_{R0.05}$ and $c_{\gamma 0.05}$ as well the factor of reduction for dispersed phase size and interfacial tension for these concentrations. It can be seen that for both compatibilizers $c_{\gamma 0.05}$ is lower than $c_{R0.05}$. This phenomenon has already been observed by other researchers [26,50]. In particular, Mekhilef et al. [50] studied the influence of the addition of SEBS on the morphology of PS/PE 90/10 blend and on the interfacial tension between PE and PS. They showed that the average radius and interfacial tension levels off when 10 and 5 wt% of SEBS, respectively, were added to the dispersed phase weight. The decrease of the average radius when a compatibilizer is added to the blend can be attributed to two reasons: a decrease of interfacial tension and also a decrease of coalescence of the dispersed phase [51]. In the case of the blends studied in this work the decrease of the average radius occurs for higher concentrations of compatibilizers than the decrease of interfacial tension. This is probably due to the fact that the PP/PS blend studied here had a composition of 90/10. At this composition, there is still a certain coalescence when the interfacial tension reaches its minimum. More experiments are being conducted with PP/PS blends of different compositions to understand the exact role of interfacial tension and coalescence in controlling the decrease of average radius of dispersed phase. It should also be kept in mind that the interfacial tension between modified PS and PP was evaluated using Gramespacher and Meissner's emulsion model [24], although it was not derived for this specific case.

4. Summary and concluding remarks

In this work, the morphology and dynamic behavior of PP/PS blend compatibilized with SBS or SEBS were studied. The blends were obtained using a twin screw extruder. After compression molding all the blends, non-modified and compatibilized, showed a dispersion of droplets of minor phase in a matrix type of morphology.

Addition of compatibilizer to the dispersed phase of the blend was found to reduce the size of the dispersed phase particles following a typical emulsion curve behavior. It was



(a) (b)

Fig. 12. Superposition of emulsion curves for modified PP/PS (90/10) blend. (a) PP/PS (90/10) blends compatibilized with SBS. 12b: PP/PS (90/10) blends compatibilized with SEBS.

Table 9
Parameters of emulsion curves

	Average radius		Interfacial tension	
Compatibilizer	SBS	SEBS	SBS	SEBS
Concentration	$c_{R0.05} = 9.4\%$	$c_{R0.05} = 6.2\%$	$c_{\gamma 0.05} = 7\%$	$c_{\gamma 0.05} = 4.6\%$
Factor of reduction	2	2.3	2.2	2.6

found that SEBS was more efficient than SBS as an emulsifier for the PP/PS blend. The morphological observations showed that SBS forms a third phase when added to the blend and that SEBS is located at the interface.

Addition of SBS resulted in an increase of the complex viscosity at a temperature of 200°C for concentrations up to 5 wt%. For higher concentrations of SBS the complex viscosity was shown to decrease. Addition of SEBS resulted in an increase of the complex viscosity for concentrations up to 10 wt%. For higher concentrations of SEBS the complex viscosity was shown to level off. The increase of viscosity was attributed to the compatibilizing effect of SEBS and SBS. The decrease of viscosity for concentrations of SBS higher than 15 wt% was attributed to the segregation of some of the SBS as a third phase.

The weighted relaxation spectra of all blends were studied. They were found to be a combination of the weighted relaxation spectra of the pure phases of the blend and an additional relaxation time associated with the interface. The interfacial tension for the polymer pairs studied here was calculated using this additional relaxation time following the analysis of Gramespacher and Meissner [24]. The value of the interfacial tension for PP/PS polymer pairs at a temperature of 200°C corroborated the value of the interfacial tension obtained directly by the pendant drop method (6.25 ± 0.87 mN/m) using rheological data, and (6.46 ± 0.25 mN/m) using the pendant drop method [34]). It was found that the relaxation time associated with the interface increased when the concentration of compatibilizer increased. The increase of this relaxation time was of the order of 25%. Using the analysis of Gramespacher and Meissner it was found that the addition of compatibilizer reduces interfacial tension by 2 or 3 fold. Most likely, this calculated reduction is erroneously large due to the fact that the theory does not take into account the decrease of coalescence in the case of compatibilized blends.

Addition of SEBS or SBS to the PS was found to reduce the interfacial tension following a typical behavior of an emulsion curve. Further addition of compatibilizer did not result in further decrease of interfacial tension. It was found that SEBS was more efficient in decreasing the interfacial tension between PS and PP than was SBS.

The morphology and interfacial tension emulsion curves were compared. It was shown that for both compatibilizers the concentration at which the interfacial tension levels off is smaller than the concentration at which the average radius of dispersed phase levels off. This is probably due to the fact for a compatibilized PP/PS (90/10) blend there is still a residual coalescence when interfacial tension is reduced to its minimum. More experiments need to be conducted to understand the exact role of interfacial tension and coalescence in controlling the decrease of average radius of the dispersed phase particles.

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