

Interfacial Tension, Morphology and Linear Viscoelasticity Behavior of PP/PS Blends

Paulo H. P. Macaúbas and Nicole R. Demarquette

Abstract: Blends of polypropylene and polystyrene compatibilized with styrene-butadiene-styrene (SBS) or styrene-ethylene/butylene-styrene (SEBS) copolymers were studied. The morphology of these blends was studied by Scanning Electron Microscopy. Emulsion curves relating the average radius of the dispersed phase to the concentration of compatibilizer added to the blend were obtained. The rheological behavior of the blends was studied by small amplitude oscillatory shear, and correlated to the morphological observations. The interfacial tension between the components of the blends was evaluated from the rheological data. In addition, the applicability of time-temperature superposition (TTS) method for PP/PS blend was studied.

Keywords: *Polymer blend, rheology, morphology, interfacial tension.*

Introduction

Due to the ability to combine the properties of their components in a unique product, polymer blends are being used for the development of new materials in a large number of industrial areas^[1]. One important feature of polymer blends is the compatibility of their components, because it controls the morphology, which is directly related to the final properties of these materials. However, most of polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases, and poor mechanical properties. Through the addition of block copolymers, it is possible to improve the compatibility between the components of the blends^[2]. The improvement of the compatibility can be evaluated through the measurement of interfacial tension^[3].

Unfortunately, research in the field of interfacial tension has been limited because of experimental difficulties encountered in its determination. Recently, many efforts have been done to understand better the relationship that exists between viscoelastic properties and morphology of polymer blends. Many theoretical models have been developed to study the rheological behavior of polymer blends under flow^[4,5]. These models relate the dynamic response of polymer blends to their morphology, composition and interfacial tension between the components. Therefore, using these models, it is possible to infer interfacial tension from the dynamic behavior of the blend once the morphology of the blends is known.

In this work, an experimental study of the influence of addition of SBS and SEBS triblock copolymers on morphology and dynamic behavior

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of PP/PS (90/10) immiscible blend was carried out. The interfacial tension between PP and PS as a function of amount of triblock copolymer added to the blend was evaluated.

Emulsion Models

It has been shown that it is possible to infer interfacial tension between polymers forming a polymer blend using small amplitude oscillatory shear [6]. Making the assumption that small strain does not alter the morphology of polymer blends and that interfacial tension is independent of local area variation, Graebling et al.^[6], using Palierne's emulsion model^[4], obtained a constitutive equation that predicts the complex shear modulus ($G^*(\omega)$) of a blend, as a function of its blend morphology, the interfacial tension between the components of the blend and the complex shear modulus of the individual phases. The equation obtained by Graebling et al.^[6] is:

$$G^* = G_m^* \frac{40\left(\frac{\gamma}{R_v}\right)[G_m^* + G_d^*] + [2G_d^* + 3G_m^*][16G_m^* + 19G_d^*] + 3\phi\left[4\left(\frac{\gamma}{R_v}\right)[2G_m^* + 5G_d^*] + [G_d^* - G_m^*][16G_m^* + 19G_d^*]\right]}{40\left(\frac{\gamma}{R_v}\right)[G_m^* + G_d^*] + [2G_d^* + 3G_m^*][16G_m^* + 19G_d^*] - 2\phi\left[4\left(\frac{\gamma}{R_v}\right)[2G_m^* + 5G_d^*] + [G_d^* - G_m^*][16G_m^* + 19G_d^*]\right]} \quad (1)$$

where: G^* , G_m^* , G_d^* are the complex shear moduli of the blend, matrix, and disperse minor phase, respectively; γ is the interfacial tension between the components of the blend; f is the volume fraction of minor phase, and R_v is the volume-average radius, given by:

$$R_v = \frac{\sum_i (R_i \phi_i)}{\sum_i \phi_i} \quad (2)$$

where: R_i is the radius of droplets, ϕ_i is the volume fraction of droplets.

Using equation (2) in the expression of the complex shear modulus of the blend, is only valid if R_v/R_n is smaller than 2, with R_n defined as:

$$R_n = \frac{\sum_i R_i}{\sum_i n_i} \quad (3)$$

where: R_i is the radius of each droplet, n_i is the number of droplets with a radius of R_i .

In the case when R_v/R_n is higher than 2, each radius and volume fraction must be taken into

account individually, which provides a much more complex expression for $G^*(\omega)$ ^[6]. The model described above can be used to infer interfacial tension if a secondary plateau is observed in the storage modulus curve. This secondary plateau occurs because of the relaxation of the droplets of the dispersed phase. Using the model described above, Graebling et al.^[6], determined the interfacial tension for a polystyrene/polyethylmetacrylate (PS/PEMA) blend, at 180°C. They showed that there exists a good agreement between the dynamic behavior of polydimethylsiloxane/polyethylene-diol (PDMS/POE-DO) and polystyrene/polymethylmetacrylate (PS/PMMA) blends and the theoretical prediction with their model. However, they could not infer interfacial tension for these blends because no secondary plateau was observed in the storage modulus ($G'(\omega)$) of the blend as function of frequency.

In another work, Gramespacher and Meissner^[7], used the Choi and Schowalter's model^[5], develo-

ped for a mixture of two Newtonian fluids, to predict the dynamic behavior of a blend. They obtained the following equations for the storage and loss moduli of a blend:

$$G'(\omega) = \phi G_d'(\omega) + (1-\phi)G_m'(\omega) + \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1}\right) \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \quad (4)$$

$$G''(\omega) = \phi G_d''(\omega) + (1-\phi)G_m''(\omega) + \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1}\right) \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \quad (5)$$

with:

$$\eta = \eta_m \left(1 + \phi \frac{(5K+2)}{2(K+1)} + \phi^2 \frac{5(5K+2)^2}{8(K+1)^2}\right) \quad (6)$$

and:

$$\tau_2 = \tau_0 \left(1 + \phi \frac{3(19K+16)}{4(K+1)(2K+3)}\right) \quad (7)$$

$$\tau_1 = \tau_0 \left(1 + \phi \frac{5(19K+16)}{4(K+1)(2K+3)}\right) \quad (8)$$

$$\tau_0 = \frac{\eta_m R (19K + 16)(2K + 3)}{\gamma 40(K + 1)} \quad (9)$$

where: η , η_m , η_d are the blend, matrix, disperse phase Newtonian viscosity, respectively. $K = \eta_d/\eta_m$, γ is the interfacial tension, R is the average radius of disperse phase, ϕ is the volume fraction of disperse phase.

The term τ_1 corresponds to an extra relaxation time in the discrete relaxation spectrum of the blend due to the relaxation of the interface between the components of the blend. The blend relaxation spectrum is a combination of the relaxation spectra of the different phases of the blend and an additional peak, τ_1 , from which the interfacial tension between the components of the blends can be inferred. Gramespacher and Meissner^[7] used this method to measure the interfacial tension of a polystyrene/poly-methylmetacrylate (PS/PMMA) blend, at 170°C. Their result was in good agreement with the interfacial tension determined from recovery after melt elongation for this same blend.

Time-Temperature Superposition for Polymer Blends

Time-temperature superposition (TTS) is a very well known procedure applied either to determine the temperature dependence of the rheological behavior of a homopolymer or to expand the time or frequency regime at given temperature at which the material behavior is studied. Theoretical principles of time-temperature superposition have already been extensively developed and can be found elsewhere^[8].

In the case of polymer blends, the different components will in general display a different temperature dependent rheological behavior, so that TTS will not hold for polymer blends. Surprisingly, for several polymer blends, TTS is reported to hold^[9]. In principle, immiscible blends will not obey TTS due to different rheological contributions of their components. However, some features may affect the decision whether or not TTS holds for an immiscible polymer blend. First, the simplest reason may be the proximity between values of activation energies or WLF parameters of the components of the blend. Second, the experimental accuracy of rheological measurements

Table 1. Polymers

Homopolymers	PP	PS
Molecular Weight	5.105 (g/mol)	2,28.105 (g/mol)
Melt Index	1,5 (g/10 min)	2,2 (g/10 min)

Table 2. Compatibilizers

Compatibilizers	Structure
Kraton D (1102 – CS)	linear S-B-S
Kraton G (G – 1652)	linear S-E/B-S

can be taken account, since in many cases the criterion to define it TTS holds or not is the visual inspection of experimental results. Third, when the rheological contribution of one of the components is small. This is the case for either small volume fractions or low viscosity of one of the components. In this work, the applicability of TTS for a PP/PS immiscible blend was studied.

Experimental

Materials

In this work, commercial polypropylene (PP) from “Polibrasil”, and polystyrene (PS) from “Estireno do Brasil”, were used. As compatibilizers, Kraton D (SBS) and Kraton G (SEBS) triblock copolymers from Shell Chemical were used. The characteristics of the polymers and compatibilizers are described in Tables 1 and 2, respectively.

Blending and Sample Preparation

All blends, compatibilized or not, were obtained with a Werner & Pfeiderer, model ZSK-30, twin screw extruder. The pure blend PP/PS (90/10) was prepared in one step, and the compatibilized blends were prepared in two steps. The compatibilizers SBS and SEBS were first added to minor phase (polystyrene), and then blended with the matrix. The concentration of SBS and SEBS used ranged from 2 to 25 %, in respect to minor phase. Samples for rheological tests were obtained by compression molding. Discs of 25 mm diameter,

and 1mm thickness, were molded at 200°C, under a pressure of 18 MPa, during 25 minutes.

Rheological Measurements

Small amplitude oscillatory shear experiments were carried out using a Rheometric Scientific SR-5000 rheometer. A parallel plate configuration was used with a gap of 0.6 mm. Stress controlled sweep was carried out for all blends, compatibilized or not, under nitrogen atmosphere, and a range of oscillation from 0.01 to 500 rad/s was scanned. These experiments were carried out under temperatures ranging from 190 to 240°C. All measurements were carried out in the linear viscoelastic region of the polymers. Creep tests were performed to determine the zero-shear viscosity of the individual phases.

Morphology and Image Analysis

A Cambridge scanning electron microscope, model Stereoscan 240, was used to characterize the morphology of all blends, compatibilized or not. The rheometry samples were fractured in liquid nitrogen to allow investigation of the morphology, and then covered with gold in a Balzers sputter coater, model SCD-050. The morphology of all blends, compatibilized or not, was quantified by means of analysis of digitalized images, using an appropriate software. The average size and volume fraction of minor phase were calculated after analysis of many images. About 500 particles were considered to calculate these parameters. For the calculation of the average size of the minor phase the Saltikov^[10] correction was used. This correction accounts for the polydispersity of the samples and for the fact that the fracture in the sample does not always occur in the maximum diameter of droplets.

Results and Discussion

Morphology and Interfacial Tension

All the samples for rheological measurements, compatibilized or not, showed a morphology of dispersion of droplets in a continuous matrix. Figure 1 shows the average radius of the disperse phase as a function of SBS and SEBS concentration added

to the PP/PS (90/10) blend. It can be seen that the average radius of the disperse phase decreases when compatibilizer is added to the blend, following an emulsion curve^[11]. It can also be seen that the efficiency, as an emulsifier, is greater for SEBS than SBS. This 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 blend.

Figure 2 shows a comparison between the storage moduli of PP/PS (90/10) blend, and the matrix phase (PP) when submitted to oscillatory shear, at 200°C. It can be seen that the blend shows an increase of elasticity at low frequencies. This fact was reported by many authors^[6-8], and is related to the relaxation of droplets that form the disperse phase in a continuous matrix, when sheared. However, no secondary plateau can be distinguished in the storage modulus ($G'(w)$) curve for the PP/PS (90/10) blend at 200°C. This plateau is necessary to interfacial tension calculation when using Graebing et al.^[6] analysis. The value of plateau modulus (G_p), and relaxation time (λ_p), at which it occurs can be predicted using equation (1) if both polymers are considered to be Newtonian^[6]:

$$\lambda_p = \left(\frac{R_v \eta_m}{4\gamma}\right) \frac{(19K+16)(2K+3-2\phi(K-1))}{10(K+1)-2\phi(5K+2)} \quad (10)$$

$$G_p = 20 \left(\frac{\gamma}{R_v}\right) \phi \frac{1}{(2K+3-2\phi(K-1))^2} \quad (11)$$

where: η_m , η_d are the matrix, disperse phase Newtonian viscosities, respectively. $K = \eta_d/\eta_m$, γ is the interfacial tension, R_v is the volume-average

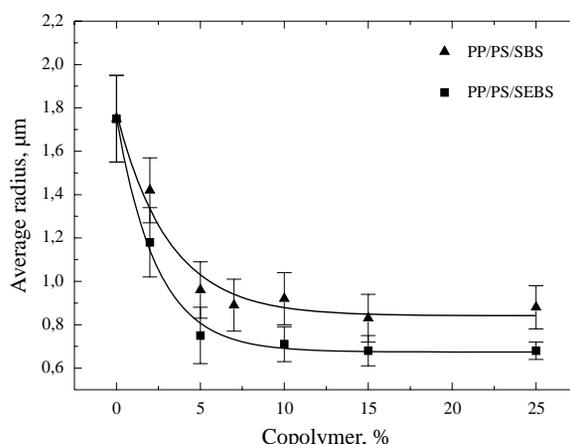


Figure 1. Emulsion curves for compatibilized PP/PS blends.

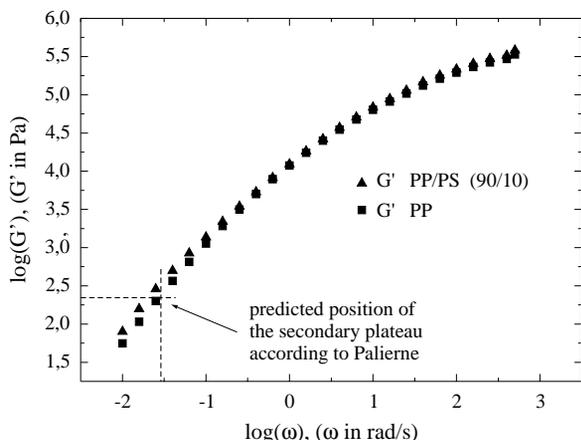


Figure 2. Storage modulus for PP/PS blend and pure phases at 200°C.

radius of disperse phase, ϕ is the volume fraction of disperse phase.

The secondary plateau can be seen only if the droplets relaxation process can be well distinguished from the relaxation process of the components of the blend^[6], i.e., when the storage modulus curve of the blend is well above of the matrix curve. The values at which the secondary plateau should occur are $G_p = 230$ Pa and $\lambda_p = 36.8$ s. The point at which the plateau should occur is shown with dashed lines in Figure 2. It can be seen that the difference between storage modulus curve of the blend and of the matrix is not large enough to allow the occurrence of the secondary plateau. Therefore, it is not possible to infer the interfacial tension for PP/PS (90/10) blend using Graebing et al. analysis^[6]. Using the same experimental data of PP/PS (90/10) blend, the interfacial tension between PP and PS was calculated using the weighted relaxation spectrum of the blend, following Gramespacher and Meissner analysis^[7].

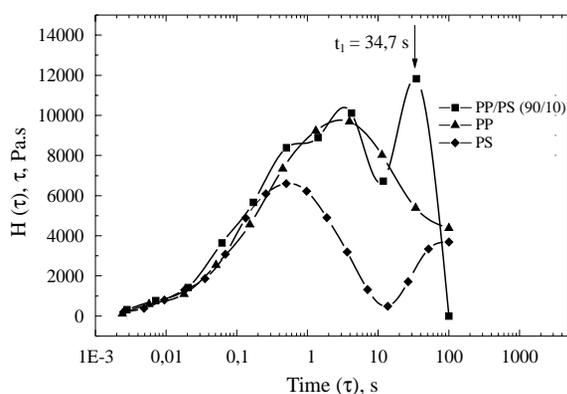


Figure 3. Weighted relaxation spectrum for PP/PS blend and pure phases at 200°C

Figure 3 shows the weighted relaxation spectra of pure phases and PP/PS (90/10) blend, at 200°C. All relaxation spectra were calculated from experimental storage modulus data ($G'(\omega)$), using a nonlinear spectrum calculation method, available in SR-5000 rheometer software. Three relaxation peaks can be observed in Figure 3, two relative to the individual phases of the blend and a third relative to the relaxation of the interface between the components of the blend, which is indicated, with an arrow. The relaxation time associated to the interface of PP/PS (90/10) blend, at 200°C, was found to be $\tau_1 = 34.7$ s. The zero-shear stress viscosities for matrix and disperse phase, at 200°C, obtained from creep tests, were $\eta_m = 46,368$ Pa.s and $\eta_d = 33,846$ Pa.s, respectively. The average radius of disperse phase was found $R = 1,66$ mm. Thus, using equation (8), the interfacial tension between PP and PS was found to be $\gamma = 6.25$ mN/m, at 200°C. This result shows good agreement to the one obtained with pendent drop method for the same blend, which is $\gamma = 6.86$ mN/m, at 200°C^[12].

The influence of addition of SBS and SEBS triblock copolymers on the interfacial tension between PP and PS was studied. The interfacial tension was calculated using Gramespacher and Meissner analysis^[7]. Figure 4 shows the interfacial tension between PP and PS as a function of amount of SBS and SEBS added to PS. It can be seen that the interfacial tension between PP and PS decreases as a function of increasing concentration of SBS and SEBS, following an emulsion curve. It can be seen that the decrease of interfacial tension in the case of SEBS is larger than in the case of SBS, corroborating with morphology results.

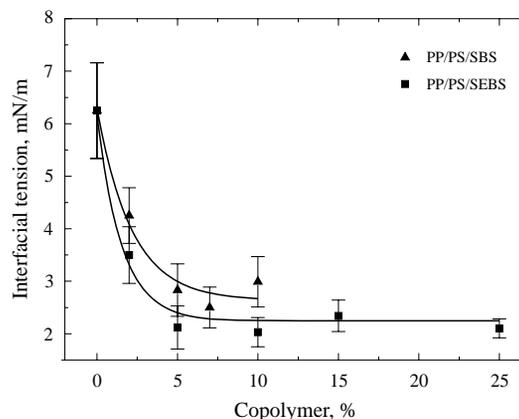


Figure 4. Emulsion curve for interfacial tension between PP and PS at 200°C

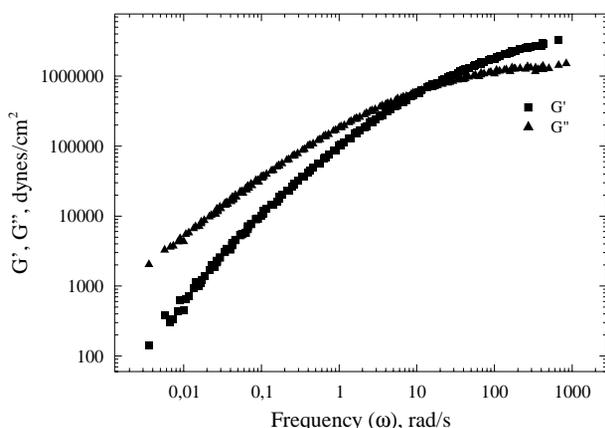


Figure 5. TTS for PP/PS (90/10) blend at 200°C

Time-Temperature Superposition

The applicability of TTS for PP/PS (90/10) blend was studied. The temperature of rheological measurements ranged from 190 to 240°C. All rheological curves obtained were shifted to a temperature of reference of 200°C. Figure 5 shows the master curve for dynamic moduli of PP/PS (90/10) blend at a temperature of 200°C. It can be seen that, in principle, TTS for this blend works. Figure 6 shows the horizontal (a_T) and vertical (b_T) shift factors as function of temperature for PP/PS (90/10) blend.

However, an accurate analysis of this result, following Gurr and Palmer method^[9], indicates that TTS for PP/PS (90/10) blend fails. Gurr and Palmer method^[9] is based on the analysis of the behavior of the phase angle delta ($\delta = \text{atan}(G''/G')$) versus the absolute value of the complex modulus of the blend (G^*). This way, the effect of shifting along the frequency axis is eliminated, and when TTS

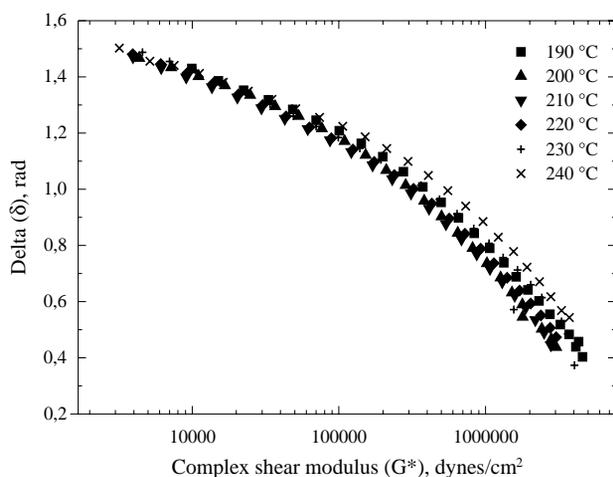


Figure 7. Phase delta as function of complex modulus for PP/PS (90/10) blend at 200°C.

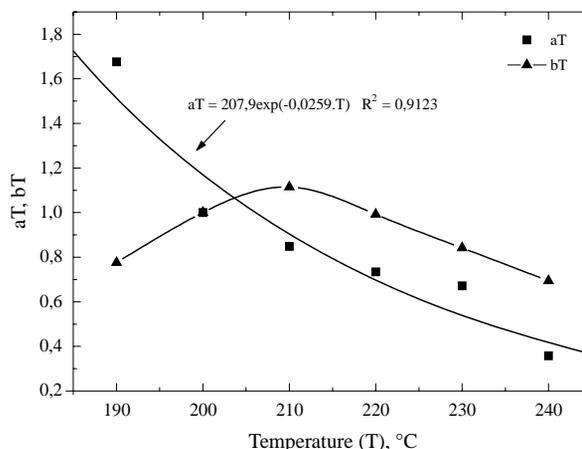


Figure 6. Horizontal and Vertical shift factors.

holds temperature independent curves are obtained. Figure 7 shows the behavior of phase angle delta (δ) as function of complex modulus (G^*). Significant deviations of phase angle delta (δ) for various temperatures indicate TTS fail for PP/PS (90/10) blend. The TTS fail can be result of different relaxation mechanisms for polystyrene and polypropylene domains, since these polymers are immiscible and should give separated rheological response to oscillatory flow applied.

Conclusions

In this work, the morphology and dynamic behavior of the PP/PS (90/10) blend compatibilized with SBS and SEBS was studied. It was shown that it was not possible to infer interfacial tension between PP and PS using Graebing et al. analysis^[6], because the secondary plateau in the storage modulus curve of the blend was not observed. The interfacial tension between PP and PS was determined using the weighted relaxation spectrum of the blend, following Gramespacher and Meissner analysis^[7]. The value of interfacial tension found using this method was in good agreement with the value found using the pendent drop method. The influence of the addition of SBS and SEBS to the morphology of PP/PS blend and on interfacial tension between PP and PS was studied. Emulsion curves for morphology and interfacial tension were obtained. Time-temperature superposition (TTS) does not hold for PP/PS (90/10) blend. It was observed deviations on phase delta which indicate different relaxation processes for the components of the blend.

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