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ORIGINAL CONTRIBUTION

Rheological behavior of poly(methyl methacrylate)/polystyrene (PMMA/PS) blends with the addition of PMMA-*ran*-PS

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Abstract In this work, the dynamic behavior of poly(methyl methacrylate)/polystyrene blend to which P($S_{0.5}$-*ran*-$MMA_{0.5}$) was added was studied. Several blend (ranging from 5 to 20 wt% of dispersed phase) and copolymer (up to 20 wt% with respect to dispersed phase) concentrations were studied. The rheological behavior of the blends was compared to Bousmina's (Rheol Acta 38:73–83, 1999) and Palierne's (Rheol Acta 29:204–214, 1990) generalized models. The relaxation spectra of the blends were also inferred, and the results were analyzed in light of the analysis of Jacobs et al. [J Rheol 43:1495–1509, 1999]. The relaxation spectra of the blends with smaller dispersed phase (below 10 wt%) and larger copolymer concentrations (above 0.4 wt%) showed the presence of four relaxation times, two corresponding to the blend phases, τ_F, corresponding to the relaxation of the shape of the dispersed phase of the blend and τ_β that can be attributed to the relaxation of Marangoni stresses tangential to the interface between the dispersed phase and matrix. The experimental values of τ_F and τ_β were used to infer the interfacial tension (Γ) and the interfacial complex shear modulus (β) for the different blends, Γ decreased with increasing copolymer concentration. β decreased with increasing blend dispersed phase concentration and decreasing copolymer concentration. The predictions of Palierne's generalized model were found to corroborate the experimental data once the values of Γ and β, found analyzing the relaxation spectra, were used in the calculations. Bousmina's model was found to corroborate the data only for larger dispersed phase concentration.

Keywords Interfacial tension · Linear viscoelasticity · Polymer blends · Rheology

Introduction

Immiscible polymers are often mixed together to obtain polymer blends that are used extensively in different industrial applications such as automobile, aeronautic and packaging due to the synergic properties that these materials present (Utracki 1995, 1998). These properties depend strongly on the blends morphology, which can be controlled through compatibilization. In turns, compatibilization can be achieved physically (through the addition of a copolymer having block miscible with both components of the blends) or modifying chemically one of the components of the blend to enhance a chemical reaction at the interface between the two polymers forming the blend. The compatibilization results in a reduction in the size of the dispersed phase delay of coalescence of the dispersed phase, decrease in interfacial tension (Utracki 1995) between the components of the blends and arise in interfacial elasticity due to an interfacial gradient induced by a variation of concentration of compatibilizer at the drop surface due to flow, besides (Riemann et al. 1996, 1997; Jacobs et al. 1999; Van Puyvelde et al. 2001; Van Hemelrijck et al. 2004, 2005) an improvement of properties.

The study of linear viscoelastic behavior of a blend can be a very important tool to evaluate the interfacial tension (Carreau et al. 1997) or quantify the morphology of polymer blends or its evolution (Van Hemelrijck et al. 2004, 2005). In particular, emulsion models to relate the

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rheological behavior of blends to their morphology and interfacial tension have been developed (Palierne 1990, 1991; Gramespacher and Meissner 1992; Lee and Park 1994; Riemann et al. 1996, 1997; Jacobs et al. 1999; Bousmina 1999), and for the last 15 years, a continuous effort has been applied to improve the understanding of the relationship between the viscoelastic properties of polymer blends, their morphology and interfacial tension between the components of the blends. However, if the linear viscoelastic behavior of noncompatibilized blends is well understood, there are still very few studies that tackle the rheological behavior of compatibilized blends (Iza et al. 2001; Velankar et al. 2004; Van Hemelrijck et al. 2004, 2005; Macaúbas et al. 2005; Wang and Velankar 2006).

When submitted to small amplitude oscillatory shear, immiscible binary blends show a higher elasticity in the low frequency range than the individual components of the blends. The higher value of elasticity of the blends can result in the presence of a secondary plateau in the curve of the storage modulus vs frequency for low frequencies. That phenomenon, which can be associated to a relaxation time, τ_F, is due to the relaxation of the shape of the blend dispersed phase when sheared (Graebling et al. 1993). In the case of compatibilized blends, there are several experimental studies that present the experimental evidence of an additional relaxation associated to a relaxation time, τ_β. That relaxation time, which has been observed for blends compatibilized through the addition of block copolymers (Riemann et al. 1996, 1997; Jacobs et al. 1999; Velankar et al. 2001; Shi et al. 2002; Van Hemelrijck et al. 2004, 2005) or through chemical modification of (Asthana and Jayaraman 1999; Moan et al. 2000) one of the polymers of the blends, can be attributed to the relaxation of Marangoni stresses tangential to the interface between the dispersed and matrix phase (Riemann et al. 1996, 1997; Moan et al. 2000; Velankar et al. 2001, 2004; Van Hemelrijck et al. 2004, 2005). These Marangoni stresses are induced by the presence of a gradient of compatibilizer concentration at the interface, which induces a gradient of interfacial tension (Van Puyvelde et al. 2001; Velankar et al. 2004; Van Hemelrijck et al. 2004, 2005). The presence of that additional relaxation time may not be observed experimentally because this terminal relaxation occurs at low frequencies, at the limit of resolution of the transducers of most rheometers (Riemann et al. 1997). Also, it may be superposed to the relaxation of the shape of the dispersed phase if the concentration of compatibilizer is too high (Moan et al. 2000; Velankar et al. 2004) for example.

Several constitutive equations have been proposed to model the linear viscoelastic behavior of polymer blends (Palierne 1990, 1991; Gramespacher and Meissner 1992; Lee and Park 1994; Jacobs et al. 1999; Bousmina 1999). Palierne (1990) was the first who considered non-diluted viscoelastic suspensions. He developed a constitutive equation that predicts the complex shear modulus $G^*(\omega)$ of the blend as a function of the complex moduli of the pure phases $G_d^*(\omega)$ and $G_m^*(\omega)$, the volume fraction of the dispersed phase (Φ), a quantification of the morphology, the equilibrium interfacial tension (Γ) between the components of the blends and two frequency dependent moduli; $\beta_d^*(\omega)$: the surface dilatation modulus, which can be attributed to the nonuniformity of the interface, due to the presence of a compatibilizer for example and $\beta_s^*(\omega)$ the surface shear modulus, which can be associated with the resistance to the shear deformation. Γ, $\beta_d^*(\omega)$, $\beta_s^*(\omega)$ characterize the interfacial stress at the interface. Both $\beta_d^*(\omega)$, $\beta_s^*(\omega)$ can be set equal to zero in the case of noncompatibilized blends.

According to Palierne (1990), the complex modulus of a blend can be written as

$$G^*(\omega) = G_m^*(\omega)\left[\frac{1 + 3/2\sum\limits_i \frac{\Phi_i E_i}{D_i}}{1 - \sum \frac{\Phi_i E_i}{D_i}}\right] \tag{1}$$

where

$$\begin{aligned} E_i = {} & 2\left(G_d^*(\omega) - G_m^*(\omega)\right)\left(19G_d^*(\omega) + 16G_m^*(\omega)\right) \\ & + \frac{48\beta_d^*(\omega)\Gamma}{R_i^2} + \frac{32\beta_s^*(\omega)\left(\Gamma + \beta_d^*(\omega)\right)}{R_i^2} \\ & + \frac{8\Gamma}{R_i}\left(5G_d^*(\omega) + 2G_m^*(\omega)\right) \\ & + \frac{2\beta_d^*(\omega)}{R_i}\left(23G_d^*(\omega) - 16G_m^*(\omega)\right) \\ & + \frac{4\beta_s^*(\omega)}{R_i}\left(13G_d^*(\omega) + 8G_m^*(\omega)\right) \end{aligned} \tag{2}$$

and

$$\begin{aligned} D_i = {} & \left(2G_d^*(\omega) + 3G_m^*(\omega)\right)\left(19G_d^*(\omega) + 16G_m^*(\omega)\right) + \frac{48\beta_d^*(\omega)\Gamma}{R_i^2} + \frac{32\beta_s^*(\omega)\left(\Gamma + \beta_d^*\right)}{R_i^2} + \frac{40\Gamma}{R_i}\left(G_d^*(\omega) + G_m^*(\omega)\right) \\ & + \frac{2\beta_d^*(\omega)}{R_i}\left(23G_d^*(\omega) + 32G_m^*(\omega)\right) + \frac{4\beta_s^*(\omega)}{R_i}\left(13G_d^*(\omega) + 12G_m^*(\omega)\right) \end{aligned} \tag{3}$$

where ***i*** refers to the ***i***th particle fraction, i.e., $R_{\boldsymbol{i}}$ is the radius of the ***i***th particle fraction, $G^*(\omega)$, $G_m^*(\omega)$ and $G_d^*(\omega)$ are the complex shear moduli of the blend, matrix and dispersed phase, $\beta_d^*(\omega)$: the surface dilatation modulus, $\beta_s^*(\omega)$ the surface shear modulus and Γ is the interfacial tension.

When both $\beta_d^*(\omega)$ and $\beta_s^*(\omega)$ are set equal to zero (in the case of noncompatibilized blends) and considering the morphology uniform ($R_\mathrm{v}/R_\mathrm{n}$<2.3), i.e. substituting the sum in Eq. (1) by R_v with:

$$R_v = \frac{\sum_i (R_i \Phi_i)}{\sum_i \Phi_i} \tag{4}$$

where R_i is the radius of each droplet and Φ_i the volume fraction of each droplet.

Equation (1) reduces to the simplified version of Palierne's model given by:

$$G^* = G_m^* \frac{40\left(\frac{\Gamma}{R_\mathrm{v}}\right)\left[G_\mathrm{m}^* + G_\mathrm{d}^*\right] + \left[2G_\mathrm{d}^* + 3G_\mathrm{m}^*\right]\left[16G_\mathrm{m}^* + 19G_\mathrm{d}^*\right] + 3\Phi\left[4\left(\frac{\Gamma}{R_\mathrm{v}}\right)\left[2G_\mathrm{m}^* + 5G_\mathrm{d}^*\right] + \left[G_\mathrm{d}^* - G_\mathrm{m}^*\right]\left[16G_\mathrm{m}^* + 19G_\mathrm{d}^*\right]\right]}{40\left(\frac{\Gamma}{R_\mathrm{vi}}\right)\left[G_\mathrm{m}^* + G_\mathrm{d}^*\right] + \left[2G_\mathrm{d}^* + 3G_\mathrm{m}^*\right]\left[16G_\mathrm{m}^* + 19G_\mathrm{d}^*\right] - 2\Phi\left[4\left(\frac{\Gamma}{R_\mathrm{v}}\right)\left[2G_\mathrm{m}^* + 5G_\mathrm{d}^*\right] + \left[G_\mathrm{d}^* - G_\mathrm{m}^*\right]\left[16G_\mathrm{m}^* + 19G_\mathrm{d}^*\right]\right]} \tag{5}$$

in order to simplify the Eq. (5) the (ω) have been omitted in equation, where G*, G_m^* and G_d^* are the complex shear moduli of the blend, matrix and dispersed phase, respectively; Γ is the interfacial tension between the components of the blend; Φ is the volume fraction of dispersed phase and R_v is the volume average radius, defined by Eq. (4).

The simplified version of Palierne's model has been used extensively to infer interfacial tension between molten polymers or quantify the morphology of a noncompatibilized polymer blend from the analysis of its dynamic behavior (Xing et al. 2000; Demarquette 2003). Rheological data of blends are normally fit to Eq. (5). If the morphology is quantified, the best fit of Eq. (5) to the data leads to the value of interfacial tension.

Due to the complexity of the fitting procedure of the generalized Palierne model and lack of, up to recent years, physical signification of the complex functions $\beta_d^*(\omega)$ and $\beta_s^*(\omega)$, Palierne's model has seldom been used to evaluate the influence of addition of compatibilizer on interfacial tension between polymers.

Bousmina (1999) developed another constitutive equation to predict the rheological behavior of polymer blends submitted to small amplitude oscillatory shear. The principal difference between Palierne's and Bousmina's models relies in a different treatment of the interface. Bousmina considered the blend as a three-region system: spherical droplets surrounded by matrix shells dispersed in a homogeneous matrix. Because of this assumption, Bousmina's model is more adequate than Palierne's model for fluids with internal structures such as liquid crystalline polymer, but is quantitatively similar. According to Bousmina (1999), the complex shear modulus $G^*(\omega)$ is given by:

$$G^*(\omega) = G_\mathrm{m}^*(\omega)\frac{2\left(G_\mathrm{d}^*(\omega) + \frac{\Gamma}{R_\mathrm{v}}\right) + 3G_\mathrm{m}^*(\omega) + 3\Phi\left(G_\mathrm{d}^*(\omega) + \frac{\Gamma}{R_\mathrm{v}} - G_\mathrm{m}^*(\omega)\right)}{2\left(G_\mathrm{d}^*(\omega) + \frac{\Gamma}{R_\mathrm{v}}\right) + 3G_\mathrm{m}^*(\omega) - 2\Phi\left(G_\mathrm{d}^*(\omega) + \frac{\Gamma}{R_\mathrm{v}} - G_\mathrm{m}^*(\omega)\right)} \tag{6}$$

where $G^*(\omega)$, $G_m^*(\omega)$ and $G_d^*(\omega)$ are the complex shear moduli of the blend, matrix and dispersed phase, respectively; Γ is the interfacial tension between the components of the blend; Φ is the volume fraction of dispersed phase, and R_v is the volume average radius, given by Eq. (4).

As pointed out by the study of Riemann et al. (1996, 1997), the relaxation phenomena can sometimes be easier visualized through the analysis of the relaxation spectrum of the blend. Starting from a slightly modified (to take into account a continuous distribution of morphology) version of the model of Palierne, Jacobs et al. (1999) derived expressions for the relaxation times τ_F and τ_β corresponding to the relaxations observed in the rheological behavior of compatibilized blends. To do so, they assumed that both polymers behave as Newtonian fluids, what can be done because the shape relaxation and terminal relaxation occur at low frequencies. They also assumed that $\beta_d^*(\omega)$ and $\beta_s^*(\omega)$ are purely elastic and can, therefore, be set equal to a constant independent of frequency called in their paper β_{10} and β_{20} and that only one of the two parameters β_{10} or β_{20} should be set different from zero, as their role can be easily exchanged. Recently, Wang and Velankar (2006) rewrote the expressions of τ_F and τ_β of Jacobs et al. (1999) in a slightly different algebraic form for all physical quantities to remain finite when $\beta/\Gamma=0$. They also pointed out a typographical error in the original work of Jacobs et al. (1999), which does not affect the expressions for τ_F and τ_β given below:

$$\tau_F = \frac{\tau_{12}}{2}\left[1-\left(1-4\frac{\tau_{11}}{\tau_{12}}\right)^{0.5}\right] \tag{7}$$

$$\tau_\beta = \frac{\tau_{12}}{2}\left[1+\left(1-4\frac{\tau_{11}}{\tau_{12}}\right)^{0.5}\right] \tag{8}$$

With

$$\tau_{11} = \frac{R_v\eta_m}{4\Gamma}\frac{(19K+16)[2K+3-2\Phi(K-1)]}{10(K+1)+\frac{\beta_{20}}{\Gamma}(13K+12)-2\Phi\left((5K+2)+\frac{\beta_{20}}{2\Gamma}(13K+8)\right)} \tag{9}$$

$$\tau_{12} = \frac{R_v\eta_m}{8\beta_{20}}\frac{10(K+1)+\frac{\beta_{20}}{\Gamma}(13K+12)-2\Phi\left((5K+2)+\frac{\beta_{20}}{2\Gamma}(13K+8)\right)}{(1-\Phi)} \tag{10}$$

where R_v is volume average radius defined by Eq. (4), η_m is the viscosity of the matrix, Φ is volume fraction of dispersed phase, K is viscosity ratio and Γ is interfacial tension.

In this work, the rheological behavior of poly(methyl methacrylate)/polystyrene (PMMA/PS) blends of different compositions to which a random copolymer P($S_{0.5}$-*ran*-$MMA_{0.5}$) was added in different concentrations was studied. The behavior was compared to the models of Palierne (1990) and Bousmina (1999). The relaxation spectra of the blends were inferred and analyzed using the equations of Jacobs et al. (1999). To our knowledge, no study has addressed, up to date, if the presence of a random copolymer could arise interfacial elasticity. Also, no systematic experimental study on the influence of blend composition on the rheological behavior of compatibilized blends has been reported.

Experimental

Materials

Commercial poly(methyl methacrylate; PMMA) from Companhia Química Metacril and polystyrene (PS) from InNova S.A were used in this work. The poly(styrene$_{0.5}$-*ran*-methyl methacrylate$_{0.5}$) random copolymer was synthesized via free radical technique and added to the PMMA/PS blends. The properties of the polymers and random copolymer are listed in Table 1. In this text, the random copolymer will not be called compatibilizer. Although, the addition of this copolymer has consequences similar to the ones that result from the addition of a compatibilizer, some doubts can be raised on the efficiency of a random copolymer as a compatibilizer (Lee et al. 1997).

Experimental procedures

Blends of PMMA/PS were prepared in different weight concentrations (95/05, 90/10, 85/15 and 80/20). Concentrations of P(S-*ran*-MMA) ranging from 0 to 20 wt% with respect to the dispersed phase PS were used for all PMMA/PS blend compositions. These concentrations correspond to a maximum of 4-wt% concentration with respect to the whole blend in the case of 80/20 blend. In the rest of the text, the random copolymer concentration will be given with respect to the whole blend.

Table 1 Materials used in this work

Polymer/ copolymer	M_w	M_n	M_w/M_n	Viscosity (η_0; Pa s) at 200 °C	% Sty	% MMA
PMMA	65,000	31,000	2.1	24,000	0	100
PS	198,000	87,000	2.2	3,200	100	0
P(S-*ran*-MMA)	207,000	66,500	3.1	–	50	50

The blends were prepared by melt blending in a Haake PolyLab 900/Rheomix 600 p batch mixer at a temperature of 200 °C using a rotor speed of 50 rpm. All blends were prepared in two steps. Before blending, the copolymer was mixed with the minor phase (PS) for 5 min and then mixed to the matrix (PMMA) for 7 min. In the case of the non-modified blends, the minor phase was processed twice to have undergone the same thermo-mechanical history.

Samples for rheological and morphological analysis were obtained by compression molding. Discs of 25-mm diameter and 1-mm thickness were molded at a temperature of 200 °C, under isostatic pressure of 18 MPa for 10 min.

The blend morphologies were characterized by scanning electron microscopy (SEM) using a Philips model XL 30 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 PMMA/PS blend, the minor phase (polystyrene) was extracted using cyclohexane at room temperature, under continuous stirring for 6 h. The morphology was quantified using appropriate software (KS300). The average diameter and volume fraction of the minor phase was calculated after analysis of the SEM photomicrographs. About 2,000 particles were considered to calculate these parameters. For the calculation of the average size of the minor phase, Saltikov's (Underwood 1970) correction was used. This correction takes into account the polydispersity of the morphology of the samples, and the fact that the fracture in the samples does not always occur at the maximum diameter of the droplets of the dispersed phase.

The rheological measurements of PMMA/PS blends were performed using a controlled stress rheometer (model SR-5000 from Rheometric Scientific®) under dry nitrogen atmosphere. A parallel-plate configuration was used with a gap size of 0.9 mm and plate diameter of 25 mm. Stress sweep tests were performed for all blends and pure polymers to define the linear viscoelasticity region. Dynamic frequency sweep tests were performed for all blends and pure polymers at a temperature of 200 °C. The stress varied from 100 to 600 Pa. The measurements were performed in one sequence decreasing the frequency from 300 to 0.01 Hz. The zero-shear viscosity of the individual phases necessary to calculate the interfacial tension was determined using the curve of complex viscosity (Pa s) vs frequency (rad/s) obtained from dynamic frequency sweeps tests. Time sweep tests were performed to check the thermal stability of the samples.

Results and discussion

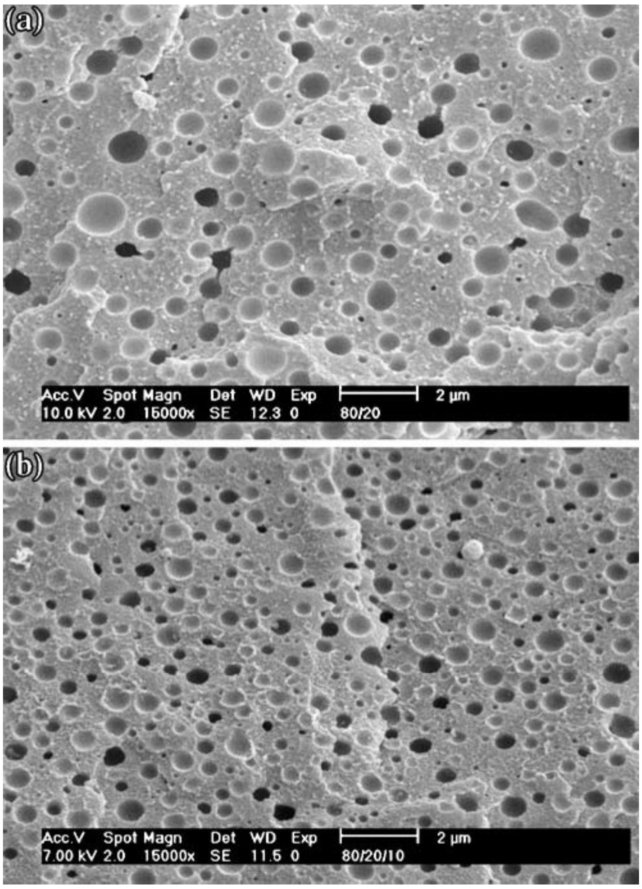

Fig. 1 Morphology of PMMA/PS (80/20) blends: **a** 0% copolymer; **b** 2% copolymer

Figure 1 shows typical morphologies that were obtained in this work. Figure 1(a) shows the morphology of PMMA/PS (80/20) blend and Fig. 1b of the same blend with 2-wt% random copolymer. For all the blends studied, a droplet dispersion type morphology was obtained. Also, for all blend compositions it was observed that the addition of copolymer resulted in a reduction in the size of the dispersed phase. None of the micrographs revealed the presence of a third phase of random copolymer dispersed in the matrix phase.

Table 2 shows the quantification of the morphology for the different blends studied here. It can be seen that the diameter of the dispersed phase decreases when the concentration of the random copolymer added to the blend increases indicating that the random copolymer behaves as a compatibilizer. It can also be seen from Table 2 that the ratio R_v/R_n is less than 2.3 for all the blends except for one of the 85/15 blends. Therefore, Eq. (5) can be used to analyze quantitatively the rheological data.

Figure 2a and b show the rheological dynamic moduli of PMMA/PS blend as a function of blend concentration. The blends present, at lower frequencies, an increase in elasticity that can be attributed to the relaxation of the shape of the dispersed phase when sheared. The magnitude of this elasticity increases when the concentration of the blends

Table 2 Quantitative analysis of the morphology and zero-shear viscosity of dispersed phase

Composition	Wt% of P (S-*ran*-MMA) (with respect to the whole blend)	R_v (μm)	R_n (μm)	R_v/R_n	η_0 (10^4 Pa s)
80/20	0	0.51	0.24	2.1	2.46
	0.4	0.45	0.19	2.3	2.56
	0.8	0.42	0.19	2.2	2.76
	1.6	0.38	0.16	2.3	2.94
	2	0.38	0.16	2.3	3.18
	4	0.37	0.17	2.1	3.24
85/15	0	0.309	0.14	2.2	2.29
	1.2	0.195	0.078	2.5	2.48
	1.5	0.183	0.073	2.3	2.56
90/10	0	0.125	0.069	1.8	2.24
	0.2	0.083	0.043	1.9	2.25
	0.4	0.060	0.031	1.9	2.28
	0.8	0.050	0.027	1.8	2.31
	1.0	0.047	0.026	1.8	2.44
	2.0	0.044	0.023	1.9	2.48
95/05	0	0.067	0.035	1.9	2.17
	0.4	0.035	0.016	2.2	2.20
	0.5	0.034	0.014	2.3	2.20

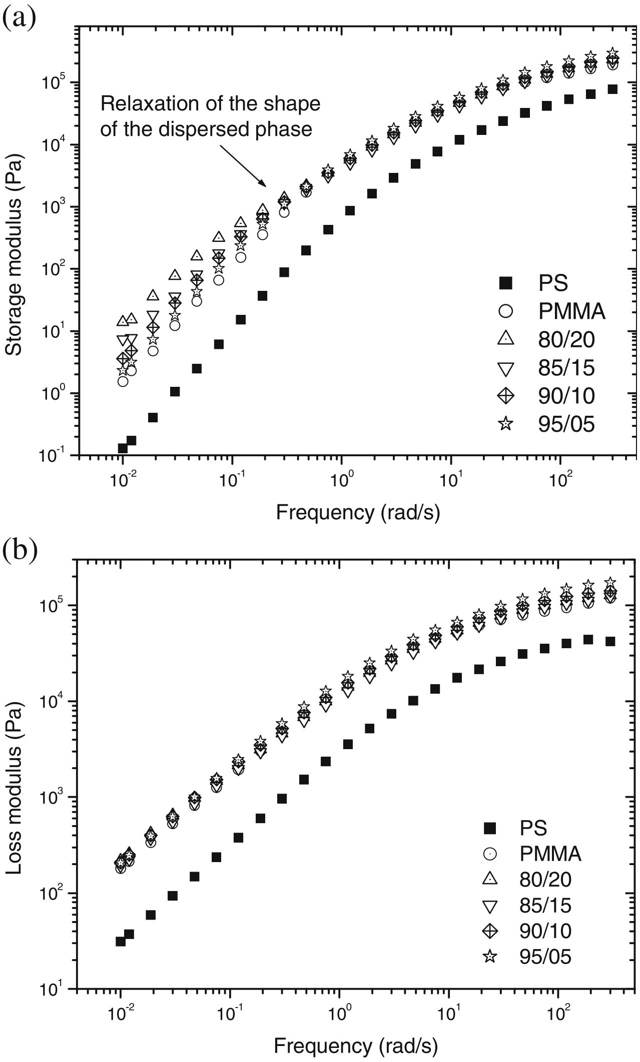

Fig. 2 Rheological dynamic moduli of PMMA/PS blends at a temperature of 200 °C: **a** storage moduli; **b** loss moduli

increases, as the size of the diameter of the dispersed phase increases. As the concentration of the dispersed phase increases, the relaxation phenomenon becomes more pronounced, and a secondary plateau can be observed. Similar behavior has been observed by Souza and Demarquette (2002) and Calvão et al. (2005).

Figure 3 shows the rheological dynamic moduli as well as the complex viscosity of PMMA/PS blends to which the random copolymer has been added (only the curves corresponding to the addition of 0.8 and 2 wt% of copolymer are shown for the sake of clarity of the figures). In this case, the blend composition is 80/20. It can be seen that the zero-shear viscosities of the blends increase with increasing concentration of copolymer added to the blend (see Fig. 3a). These values are reported in Table 2. It can also be seen that, at lower frequencies, a second relaxation phenomenon seems to appear, as the storage modulus is larger than the one of the pure blend at small frequencies. The behavior shown in Fig. 3 for the 80/20 blends was observed for all blend compositions. Similar behavior has been shown by Farhländer et al. (2001) who studied PS compounds containing rigid cross-linked particles of PMMA with a varying amount of covalently grafted carboxylic acid-terminated PS at their surface.

Figure 3 shows that the relaxation phenomena are difficult to visualize in the storage modulus curves. The second relaxation phenomenon may occur at frequencies lower than the ones covered by the rheological experiments. Therefore, to visualize better the relaxation phenomena, the relaxation spectra of the different blends studied in this work were calculated using the rheological data. The relaxation spectra were calculated using the Honerkamp and Weese method (Honerkamp and Weese 1993). In Fig. 4, the results are reported for the different blend compositions used in this work. The results are reported only for two concentrations of random copolymer for the sake of clarity of the figures. It can be clearly seen that the 80/20 and 85/15 composition blends present only two relaxation times, one corresponding to the superposition of relaxation of two phases of the blend and a second one that could correspond to the relaxation of the shape of the dispersed phase or to the superposition of τ_F and τ_β. In the case of 90/10 and 95/05 blends, three relaxation times can be observed, one corresponding to the superposition of the relaxations of the two phases of the blend, one corresponding to the relaxation of the shape of the

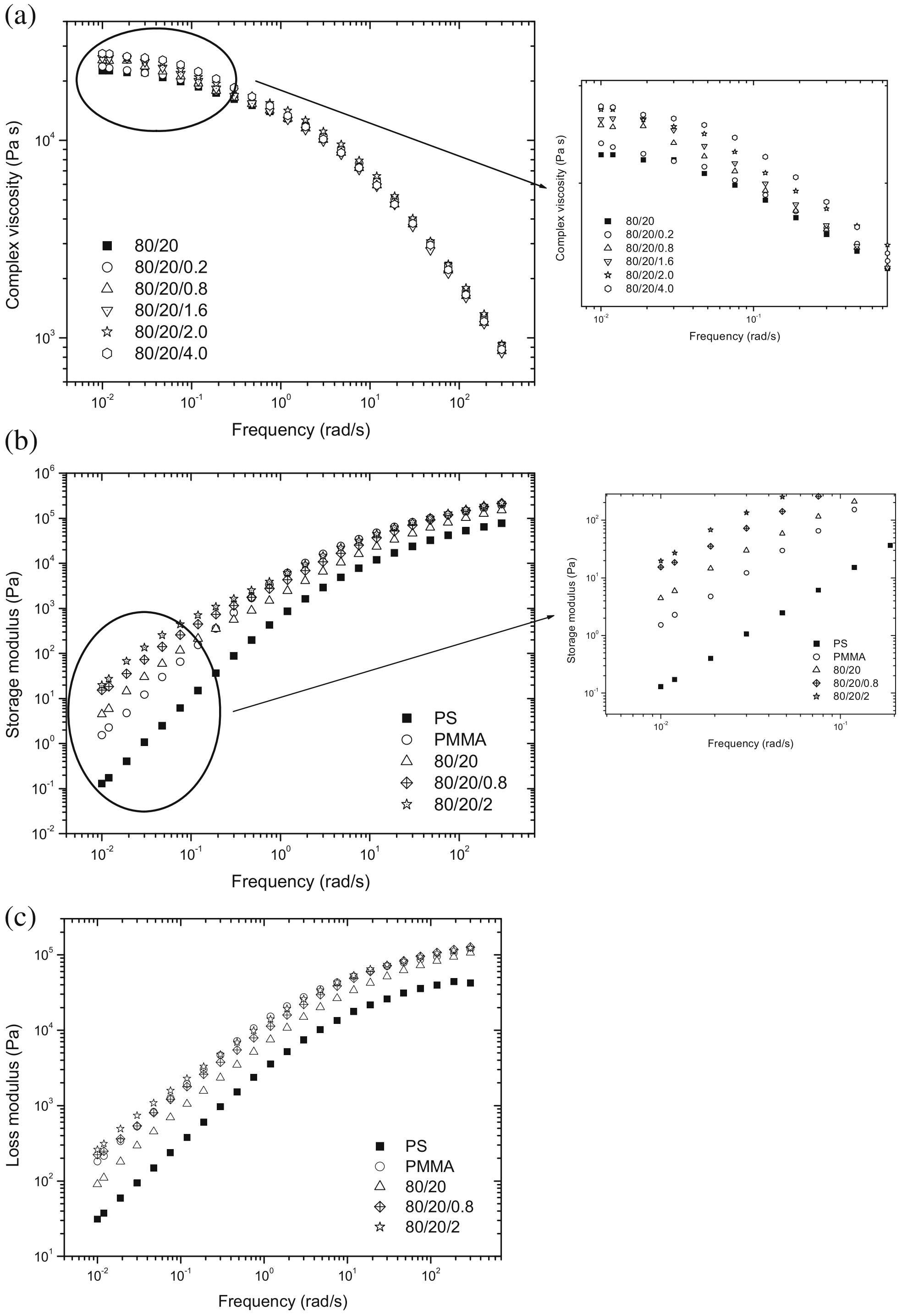

Fig. 3 Rheological behavior of PMMA/PS blends with 0.8 and 2% random copolymer at a temperature of 200 °C: **a** complex viscosity; **b** storage moduli; **c** loss moduli

dispersed phase and one that could correspond to τ_β. The third relaxation time cannot be attributed to the contribution of one of the isolated phases, as it did not appear in any of the relaxation spectra of the isolated phases (PS, PMMA or PS together with 10% of random copolymer—see the relaxation spectrum of PS to which P(S-ran-MMA) was added; Fig. 4a), indicating that this phenomenon originates from the presence of copolymer at the interface between PMMA and PS.

Table 3 presents the values of the relaxation times obtained for the different blends studied in this work. To see if the relaxation times observed correspond to τ_F and to τ_β, Eqs. (7) and (8) were used to estimate possible values for τ_F and τ_β. In these estimations, the dispersed phase

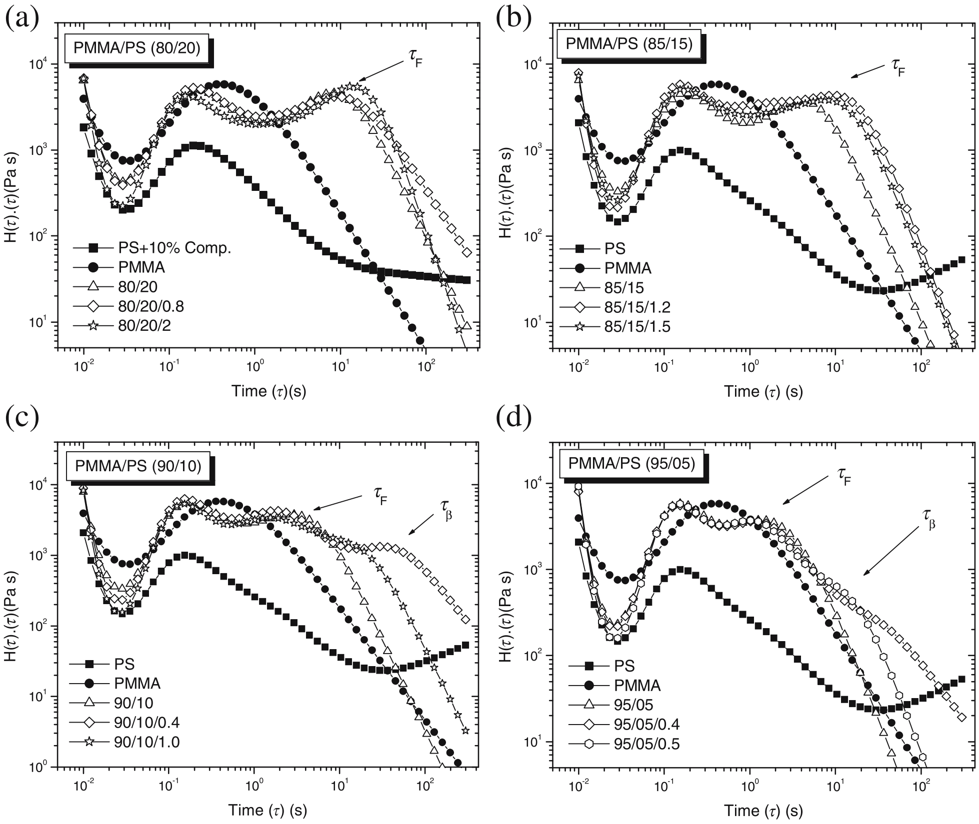

Fig. 4 Relaxation time spectra of PMMA/PS blends of different compositions with the addition of random copolymer: **a** (80/20) blends; **b** (85/15) blends; **c** (90/10) blends; **d** (95/05) blends

radius was taken from Table 1, the zero-shear viscosity of the individual phases and the blends was determined from rheological curves, the interfacial tension was taken as the one that corresponded to the best fit of the experimental values of G' (storage modulus) vs ω (frequency) with Bousmina's model (see below) and β_{20} ranged from 0.18 to 0.31 mN/m as shown in Table 3. The chosen values of β_{20} were based on the results of Jacobs et al. (1999) who also studied PMMA/PS polymer blends to which a block copolymer has been added. The estimated values of τ_F and τ_β are reported in Table 3. Assuming a relative error for the determination of R_v of 10%, for τ_F and τ_β of 15% and for the zero-shear viscosity of 3%, it can be seen that the values of the second (third if we consider that the first relaxation time corresponds to the relaxation of both PS and PMMA) and third (fourth if we consider that the first relaxation time corresponds to the relaxation of both PS and PMMA) relaxation times can be attributed to the shape relaxation of the drops and relaxation induced by the presence of the copolymer.

It can be seen that, for a fixed amount of copolymer, τ_F increases when the concentration of the blend, Φ, increases: when Φ increases, the overall value of the average radius of the dispersed phase increases and τ_F increases (see Eq. 7). For a fixed blend concentration, τ_F increases with increasing concentration of random copolymer for 80/20 and 85/15 blend concentrations and stays constant within experimental error for the two other blend concentrations. This behavior can be understood, as τ_F is proportional to R_v/Γ.

The results presented in Table 3 also show that for a fixed amount of random copolymer, τ_β, increases when the blend concentration increases. Although this result can be predicted by Eq. (8), it has never been shown experimentally to our knowledge. This trend could explain why a fourth relaxation time is not visualized in the relaxation spectrum of the 85/15 and 80/20 blends. The results presented in Table 3 also show that for a fixed blend concentration, τ_β, decreases with increasing amount of random copolymer. Similar behavior has been observed by other authors (Riemann 1996, 1997; Van Hemelrijck et al. 2004, 2005; Velankar et al. 2004) when adding a block copolymer to the blend. The results observed here corroborate the scaling law, suggested by Van Hemelrijck et al. (2004).

The values of τ_F and τ_β were used to estimate the values of interfacial tension Γ and of β using the equations developed by Jacobs et al. (1999). The values are reported in Table 4 and will be discussed further in the manuscript.

The rheological data of the blends, without the addition of copolymer, were fit to the simplified version of Palierne and Bousmina models to obtain the interfacial tension between PMMA and PS. It was observed that fitting the experimental data of storage modulus $[G'(\omega)]$ over the complete experimental frequency range yielded to results

Table 3 Relaxation times of the blends studied in this study

	C	τ_F E (s)	τ_β_2E (s)	Γ (mN/m)	β (mN/m)	τ_F T (s)	τ_β T (s)
80/20	0	8.63	–	1.4	–	–	–
	0.4	9.48	*		–	–	–
	0.8	10.68	*		–	–	–
	1.6	13.75	*		–	–	–
	2	14.68	*		–	–	–
	4	14.94	*		–	–	–
85/15	0	5.44	–	1.4	–	–	–
	1.2	10.06	*		–	–	–
	1.5	9.76	*		–	–	–
90/10	0	2.96	–	1.4	–	–	–
	0.2	2.20	*	1.1	0.18	2.57	17.24
	0.4	2.10	38.1	0.97	0.22	2.09	10.52
	0.8	1.93	25.5	0.85	0.36	1.97	8.87
	1.0	1.88	13.2	0.83	0.31	1.82	6.17
	2.0	1.80	7.5	0.83	0.31	1.71	5.78
95/05	0	1.24	–	1.4	–	–	–
	0.4	1.23	20.11	1.1	0.36	1.30	6.13
	0.5	1.17	9.43	0.97	0.31	1.22	4.36

C: wt% of P(S-*ran*-MMA)(with respect to the whole blend); τ_F_E and τ_β_E: experimental values of τ_F and τ_β; τ_F_T and τ_β_T: values of τ_F and τ_β found using Eqs. (7) and (8) and the values of Γ (interfacial tension) and β reported in the fifth and sixth column. The values of Γ correspond to the one found fitting the experimental data to Bousmina's model and β were taken from the literature. Both Γ and β do not correspond to the ones found using Jacob's et al. (1999) analysis.

*not observed

that differed from a fit over a limited frequency range located around the position of the shape relaxation time. Similar behavior has already been observed by others researchers (Vinckier et al. 1996; Souza and Demarquette 2002). In this work, the values of interfacial tension reported correspond to the ones that were obtained from a fitting over a limited frequency range located around the position of the shape relaxation time, as this type of fit has more physical meaning. Similar fitting procedures were adopted for all the subsequent analyses. A good fit was obtained only for 80/20 composition. For lower dispersed phase concentration, it was not possible to obtain a good agreement between the experimental data and Palierne's or Bousmina's emulsion models most likely because no well-defined secondary plateau could be observed in the storage modulus curve. Similar behavior was observed by Souza and Demarquette (2002). Figure 5 shows the comparison between the predictions of the simplified version of Palierne and Bousmina's models and the rheological data for the blends without copolymer (Fig. 5a, Palierne; Fig. 5b, Bousmina). It can be seen that a good fit was obtained between the models and the rheological data. The values of interfacial tension found fitting the simplified version of Palierne's and Bousmina's models as well as the ones using Choi and Schowalter (1975) analysis are reported in Table 4.

The rheological data of the blends to which the copolymer was added were also fit to Bousmina and the

Table 4 Interfacial tensions and interfacial stress moduli for the blends studied in this work

Blend composition	Wt% of P (S-*ran*-MMA) (with respect to the whole blend)	Relaxation spectrum analysis Jacob's et al. (1999) or Choi and Schowalter (1975) analysis		Palierne's analysis** (1990)	Bousmina's analysis (1999)
		Γ (mN/m)	β (mN/m)	Γ (mN/m)	Γ (mN/m)
80/20	0	2.4	–	1.6	1.4
	0.4	*	*		1.1
	0.8	*	*		0.97
	1.6	*	*		0.85
	2	*	*		0.83
	4	*	*		0.83
85/15	0	2.0	–	2.0	2.3
	1.2	*	*		***
	1.5	*	*		***
90/10	0	1.37	–	1.7	1.8
	0.2	*	*		***
	0.4	1.01	0.0581		***
	0.8	0.913	0.0729		***
	1.0	0.866	0.1351		***
	2.0	0.816	0.2316		***
95/05	0	1.56	–		***
	0.4	1.19	0.1202		***
	0.5	1.08	0.1956		***

*It was not possible to infer Γ and β because the relaxation spectra did not present four relaxation times.

**Only the simplified version of Palierne's model was fit to the data (see text) and, therefore, only the blends without compatibilizers could be analyzed.

***A good fit of Bousmina's model to the experimental data was not obtained.

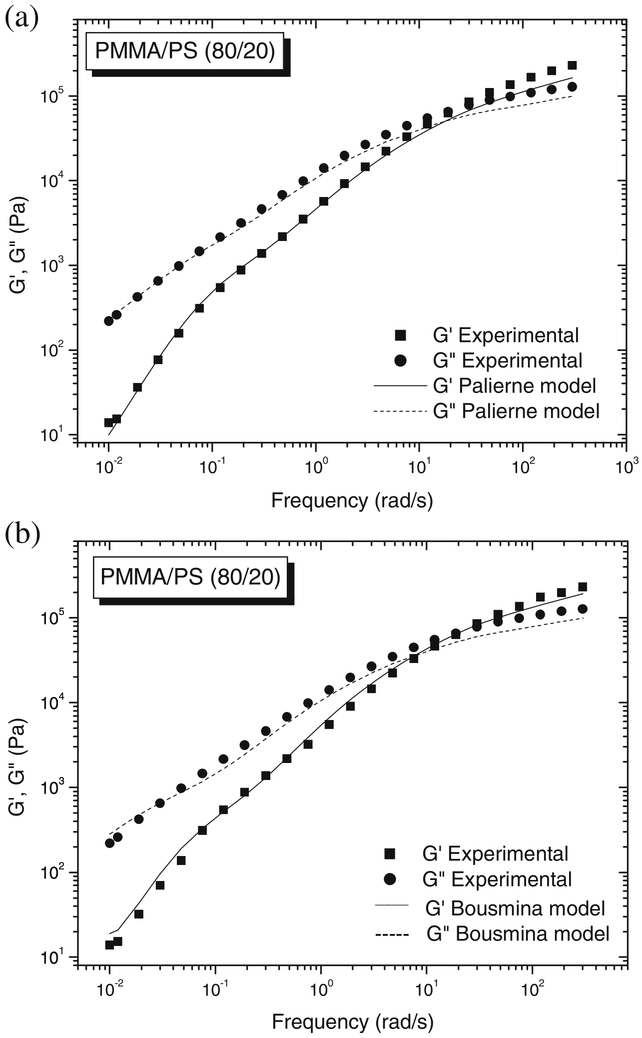

Fig. 5 Rheological behavior of PMMA/PS (80/20) blends at a temperature of 200 °C. **a** Comparison to the prediction of the simplified version of Palierne's model; **b** comparison to the prediction of Bousmina's model

simplified version of Palierne's model. Figure 6a and b show the comparison of the experimental data for 80/20/1.6 and 80/20/2 blends, respectively, to Bousmina's model. Figure 7 shows a typical result of a fit of experimental data to the simplified version of Palierne's model. In this case, it is shown that the behavior of 80/20 blend to which 2 wt% of copolymer has been added. It can be seen from Fig. 6a and b that a good fit between the experimental data and Bousmina's model was obtained. Although Bousmina's model was worked out for compatibilized free blends, it corroborated the experimental data. This can be understood because Bousmina's model considers the flow circulation inside and outside the droplet. The presence of a compatibilizer affects this circulation, which is, therefore, taken into account by the model. The values of interfacial tension obtained by this fit are reported in Table 4. The good fit between Bousmina's model and the experimental data was observed only for the 80/20 blend concentration. We could not find an explanation for this fact. Possibly, the model overestimates the intensity of the relaxations. It can be seen from Fig. 7 that the simplified version of Palierne's model does not corroborate the experimental behavior of the blend for any value of Γ tested.

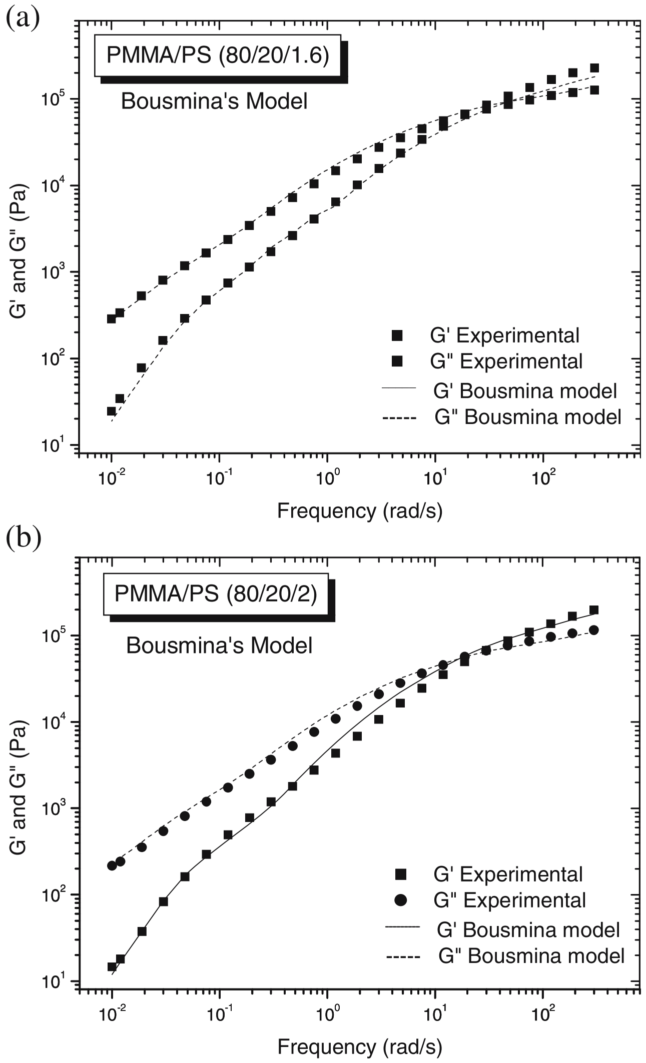

Fig. 6 Rheological behavior of PMMA/PS (80/20) blends with the addition of random copolymer. Comparison between experimental data and the predictions of Bousmina's model. **a** Composition (80/20/1.6); **b** composition (80/20/2)

The experimental data were, therefore, fit to the generalized version of Palierne's model to infer Γ and β. However, fitting the experimental data to the model resulted in a large variation of Γ and β according to the interval of frequencies used for the fit even when ranges of lower frequencies (below 1 rad/s) were considered. To see if Palierne's generalized model corroborates the data, the values of Γ and β found using Jacobs et al. (1999) analysis (see Table 3) were used in Eqs. (1–3) to predict the rheological behavior of the compatibilized blends. Figure 8

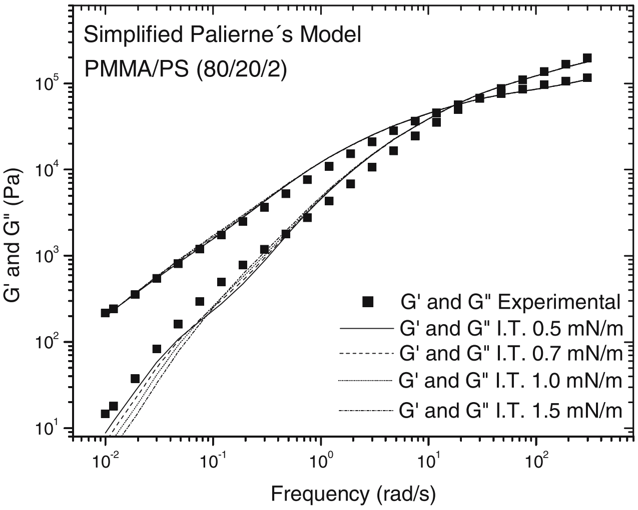

Fig. 7 Rheological behavior of PMMA/PS (80/20/2) blend at 200 °C. Comparison between experimental data and predictions of the simplified version of Palierne's model

shows a typical comparison between the experimental data and the predictions of Palierne's generalized model. In this case, it is shown that the rheological behavior of the 90/10 blend to which 1.6 wt% of random copolymer has been added. The symbols represent the data points, and the two curves represent the predictions of Palierne's model for Γ= 0.91 mN/m and β=0.072 mN/m and Γ=0.91 mN/m and β= 0.00 mN/m, respectively. It can be seen that when a nonzero value of β is considered, the quality of the fit increases considerably. Similar behavior has been shown by Asthana and Jayaraman (1999).

It can be seen from Table 4 that within experimental error, the interfacial tension values found using the three different analyses corroborate. The results presented in Table 4 show that Γ is independent of blend concentration for the blends without the addition of copolymer indicating that no coalescence occurred during the experiments (Calvão et al. 2005). It can be also seen that Γ decreases with an increasing amount of random copolymer added to the blend. Also, when the concentration of copolymer increases, β increases. Similar behavior has been seen by Riemann et al. (1997), Jacobs et al. (1999) and Van Hemelrijck et al. (2004, 2005). Such a behavior was explained by the highest resistance of the compatibilizer layer at the interface to shear deformation. In the case of the blends studied here, the random copolymer probably locates itself at the interface, and although it may not be as efficient as a block copolymer to be used as a compatibilizer, (Lee et al. 1997) arises an interfacial elasticity. The results presented in Table 4 also indicate that Bousmina's model gives a fairly good estimate of the value of interfacial tension for compatibilized blends.

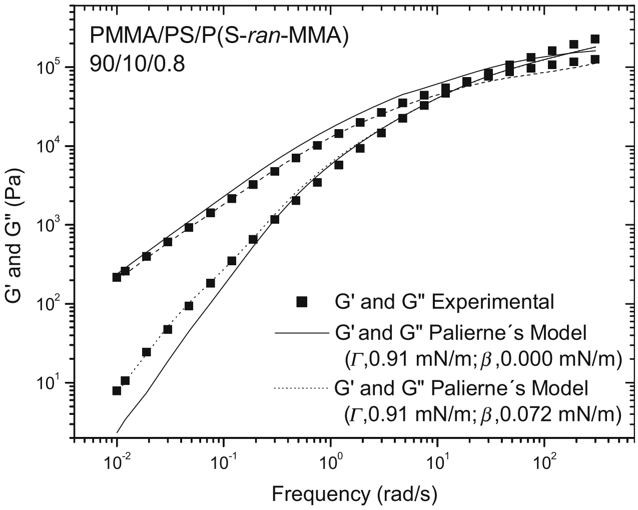

Fig. 8 Rheological behavior of PMMA/PS (90/10/0.8) blend. Comparison between experimental data and the predictions of Palierne's generalized model

Conclusions

The rheological behavior of PMMA/PS blends of different concentrations (95/05, 90/10, 85/15, 80/20), to which a random copolymer has been added when submitted to small amplitude oscillatory shear, has been studied in this work. The relaxation spectra of the blend were inferred. The rheological behavior of the blends was compared to Palierne's and Bousmina's emulsion models. The experimental results and analyses of relaxation spectra showed that the addition of random copolymer leads to a raise of interfacial elasticity. The relaxation spectra of the blends, to which the random copolymer was added, show the presence of four relaxation times: two corresponding to the phases of the blend, one corresponding to the relaxation of the shape of the dispersed phase when sheared and a fourth one that can be attributed to the presence of the copolymer at the interface. This fourth relaxation time is visible experimentally only for the lower blend (90/10 and 95/05) and higher copolymer concentrations (above 0.4 wt%). For larger blend and lower copolymer concentrations, the fourth relaxation occurs at longer times. The values of interfacial tension (Γ) and interfacial complex shear modulus (β) found using the experimental values of third and fourth relaxation times were shown to stay constant (Γ) and to decrease (β) when the blend concentration was increased and to decrease (Γ) and increase (β) when the concentration of random copolymer increased. These trends indicate that the random copolymer behaves in a similar fashion than a compatibilizer, as its addition results in a decrease in interfacial tension and increase in resistance of interfacial layer to shear deformation. The use of the values of Γ and β, found analyzing the spectra, were found to lead to a good fit when the experimental data were compared to the generalized version of Palierne's model. The values of interfacial tension, found analyzing the relaxation spectra and Bousmina's emulsion model, were in good agreement.

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References

Asthana H, Jayaraman K (1999) Rheology of reactively compatibilized polymer blends with varying extent of interfacial reaction. Macromolecules 32:3412–3419

Bousmina M (1999) Rheology of polymer blends: linear model for viscoelastic emulsions. Rheol Acta 38:73–83

Calvão PS, Yee M, Demarquette NR (2005) Effect of composition on the linear viscoelastic behavior of PMMA/PS and PMMA/PP blends. Polymer 46(8):2610–2620

Choi SJ, Schowalter WR (1975) Rheological properties of non-dilute suspensions of deformable particles. Phys Fluids 18(4):420–427

Carreau PJ, De Kee D, Chhabra R (1997) Rheology of polymeric systems principles and applications. Carl Hanser, Munich, Germany

Dermaquette NR (2003) Evaluation of experimental techniques for determining interfacial tension between molten polymers. Int Mater Rev 48:247–269

Fahrländer M, Bruch M, Menke T, Friedrich C (2001) Rheological behavior of PS-melts containing surface modified PMMA-particles. Rheol Acta 40:1–9

Graebling D, Muller R, Palierne JF (1993) Linear viscoelastic behavior of some incompatible polymer blends in the melt interpretation of data with a model of emulsion of viscoelastic liquids. Macromolecules 26:320–329

Gramespacher H, Meissner J (1992) Interfacial tension between polymer melts measured by shear oscillations of their blends. J Rheol 36:1127–1141

Honerkamp J, Weese (1993) A nonlinear regularization method for the calculation of relaxation spectra. Rheol Acta 32:65–73

Iza M, Bousmina M, Jérôme R (2001) Rheology of compatibilized immiscible viscoelastic polymer blends. Rheol Acta 40:10–22

Jacobs U, Fahrlander M, Winterhalter J, Friedrich C (1999) Analysis of Palierne's emulsion model in the case of viscoelastic interfacial properties. J Rheol 43:1495–1509

Lee HM, Park OO (1994) Rheology and dynamics of immiscible polymer blends. J Rheol 38:1405–1425

Lee MS, Lodge TP, Macosko CW (1997) Can random copolymers serve as effective polymeric compatibilizer. J Polym Sci Part B Polym Phys 35(17):2835–2842

Macaúbas PHP, Demarquette NR, Dealy MJ (2005) Nonlinear viscoelasticity of PP/PS/SEBS blends. Rheol Acta 44:295–312

Moan M, Huitric J, Médéric P, Jarrin J (2000) Rheological properties and reactive compatibilization of immiscible polymer blends. J Rheol 44(6):1227–1245

Palierne JF (1990) Linear rheology of viscoelastic emulsions with interfacial tension. Rheol Acta 29:204–214

Palierne JF (1991) Linear rheology of viscoelastic emulsions with interfacial tension-correction. Rheol Acta 30:497

Riemann R-E, Cantow H-J, Friedrich C (1996) Rheological investigation of form relaxation and interface relaxation process in polymer blends. Polym Bull 36:637–643

Riemann R-E, Cantow H-J, Friedrich C (1997) Interpretation of a new interface-governed relaxation process in compatibilized polymer blends. Macromolecules 18:5476–5480

Shi D, Ke Z, Yang J, Gao Y, Wu J, Yin J (2002) Rheology and morphology of reactively compatibilized PP/PA6 blends. Macromolecules 35:8005–8012

Souza AMC, Demarquette NR (2002) Influence of composition on the linear viscoelastic behavior and morphology of PP/HDPE blends. Polymer 43:1313–1321

Underwood EE (1970) Quantitative sterology. Addison Wesley, Reading MA

Utracki LA (1995) History of commercial polymer alloys and blends (from a perspective of the patent literature). Polym Eng Sci 35:2–17

Utracki LA (1998) Commercial polymer blends. Chapman & Hall, London

Van Hemelrijck E, Van Puyvelde P, Velankar S, Macosko CW, Moldenaers P (2004) Interfacial elasticity and coalescence suppression in compatibilized polymer blends. J Rheol 48:143–159

Van Hemelrijck E, Van Puyvelde P, Velankar S, Macosko CW, Moldenaers P (2005) The effect of block copolymer architecture on the coalescence and interfacial elasticity in compatibilized polymer blends. J Rheol 49:783–798

Van Puyvelde P, Velankar S, Moldenaers P (2001) Rheology and morphology of compatibilized polymer blends. Curr Opin Colloid Interface Sci 6:457–463

Velankar S, Puyvelde PV, Mewis J, Moldenaers P (2001) Effect of compatibilization on the breakup of polymeric drops in shear flow. J Rheol 45:1007–1019

Velankar S, Puyvelde PV, Mewis J, Moldenaers P (2004) Steady-shear rheological properties of model compatibilized blends. J Rheol 48:725–744

Vinckier I, Moldenaers P, Mewis J (1996) Relationship between rheology and morphology of model blends in steady shear flow. J Rheol 40(4):613–631

Wang J, Velankar S (2006) Strain recovery of model immiscible blends: effects of added compatibilizer. Rheol Acta 45:741–753

Xing P, Bousmina M, Rodrigue D, Kamal MR (2000) Critical experimental comparison between five techniques for the determination of interfacial tension in polymer blends: model system of polystyrene/polyamide-6. Macromolecules 33 (21):8020–8034