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Effect of composition on the linear viscoelastic behavior and morphology of PMMA/PS and PMMA/PP blends

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Abstract

Here, the effect of concentration on the morphology and dynamic behavior of polymethylmethacrylate/polystyrene (PMMA/PS), for PS with two different molecular weight, and polymethylmethacrylate/polypropylene (PMMA/PP) blends was studied. The blends concentrations ranged from 5% to 30% of the dispersed phase (PS or PP). The dynamic data were analyzed to study the possibility of inferring the interfacial tension between the components of the blend from their rheological behavior using Palierne [Palierne JF. Rheol Acta 1990;29:204–14] [1] and Bousmina [Bousmina M. Acta 1999;38:73–83] [2] emulsion models. The relaxation spectrum of the blends was also studied. The dynamic behavior of 85/15 PS/PMMA blend were studied as a function of temperature. It was possible to fit both Palierne and Bousmina's emulsion models to the dynamic data of PMMA/PS blends, to obtain the interfacial tension of the blend. This was not the case for PMMA/PP. The relaxation spectrum of both blends was used to obtain the interfacial tension between the components of the blends. The values of interfacial tension calculated were shown to decrease when the concentration of the blends increased. It was shown using morphological analysis that this phenomenon can be attributed to the coalescence of the dispersed phase during dynamic measurements that occurs for large dispersed phase concentration. When the 'coalesced' morphology is taken into account in the calculations the interfacial tension inferred from rheological measurement did not depend on the concentration of the blend used. The values of interfacial tension found analyzing the dynamic behavior of one of the PMMA/PS blend were shown to decrease with temperature.

Keywords: Polymer blends; Interfacial tension; Linear viscoelasticity

1. Introduction

For the last 15 years, several researchers have investigated the linear viscoelastic behavior of blends [1–8] and emulsion models were developed to estimate this behavior [1,2], these theoretical models relate the dynamic response of polymer blends to their morphology, composition and interfacial tension between the components. Using these models, it is possible to infer the interfacial tension between the components of the blends or quantify the morphology from the dynamic behavior of the blends. The most common emulsion models are Palierne's and Bousmina's models [1, 2], which provide a constitutive equation for the complex modulus of a blend, with a droplet dispersion type of morphology, as a function of volume fraction of minor phase, volume average radius, interfacial tension and viscosity ratio. In another approach, Gramespacher and Meissner [3] suggested the use of the analysis of the relaxation spectrum of the blend to infer the interfacial tension between the components of the blends or quantify their morphology. These three analyses of linear viscoelastic behavior of blends are briefly reviewed below. More details can be found in Demarquette's review on the evaluation of interfacial tension between molten polymers models [9].

Palierne's [1] model considers an emulsion of incompressible viscoelastic fluids and takes into account the viscoelasticity of the phases and the polydispersity in size and nature of the inclusions. Assuming that small strains, undergone by the blend during small amplitude oscillatory shear (SAOS) do not alter the morphology of the blends, that the interfacial tension between the polymers is independent on the local deformation of the interface and

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Table 1
Comparison between the calculations of frequency at which the secondary plateau occurs (λ_D) and the magnitude of the storage modulus at the plateau (G_p) using Palierne and Bousmina's models (where α is the interfacial tension, ϕ is the volume fraction of minor phase, R_v is the volume-average radius and K is the viscosity ratio)

	Palierne		Bousmina	
G_p	$20\dfrac{\alpha}{R}\dfrac{\phi}{(2K+3-2\phi(K-1))^2}$	(4a)	$25\dfrac{\alpha}{R}\dfrac{\phi(1-\phi)}{\left(1+\frac{3}{2\phi}\right)(2K+3-2\phi(K-1))^2}$	(5a)
λ_D	$\dfrac{R\eta_m}{\alpha}\dfrac{((19K+16)(2K+3-\phi(K-1))}{10(K+1)-2\phi(5K+2)}$	(4b)	$\dfrac{R\eta_m}{\alpha}\dfrac{\left(K+\frac{3}{2}-\phi(K-1)\right)}{1-\phi}$	(5b)

the size distribution of the dispersed phase is not too broad ($R_v/R_n<2.3$), Palierne's model results in the following equation [4] for the complex modulus of the blend:

$$G*(\omega)=G*_m(\omega)\frac{1+3\sum_i\phi_iH_i(\omega)}{1-2\sum_i\phi_iH_i(\omega)} \tag{1}$$

$$H_i=\frac{\left\{4\left(\frac{\alpha}{R}\right)[2G*_m(\omega)+5G*_i(\omega)]+[G*_i(\omega)-G*_m(\omega)][16G*_m(\omega)+19G*_i(\omega)]\right\}}{40\left(\frac{\alpha}{R}\right)[G*_m(\omega)+G*_i(\omega)][2G*_i(\omega)+3G*_m(\omega)][16G*_m(\omega)+19G*_i(\omega)]}$$

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

$$R_v=\frac{\sum_i R_i\phi_i}{\sum_i\phi_i} \tag{2}$$

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

Bousmina [2], based on the Kerner's model [10], developed another constitutive equation taking into account the effect of the interfacial tension and analyzing the circulation of the fluid inside the dispersed drop. The equation for the complex modulus is given by:

$$G*=G*_m\times\frac{2\left(G*_d+\frac{\alpha}{R_n}\right)+3G*_m+3\phi\left(G*_d+\frac{\alpha}{R_n}-G*_m\right)}{2\left(G*_d+\frac{\alpha}{R_n}\right)+3G*_m-2\phi\left(G*_d+\frac{\alpha}{R_n}-G*_m\right)} \tag{3}$$

where: G^*, G^*_m, G^*_d are the complex shear moduli of the blend, matrix and disperse minor phase, respectively; α is the interfacial tension between the components of the blend; ϕ is the volume fraction of minor phase; and R_v is the volume-average radius, given by Eq. (2). Although based on different hypotheses, both models are quantitatively very similar [2].

The dynamic behavior of blends can be fitted to either Eqs. (1) and (3) to infer interfacial tension between the components of the blend or quantify the morphology of the blend, but the range of frequencies used for the fitting can lead to a large variation of results. The interfacial tension or quantification of the morphology can be determined more easily if a secondary plateau, which corresponds to the relaxation of the droplets of the dispersed phase is observed. More details about the emulsion parameters that influence the presence of the plateau can be found in Graebling et al. [8] and Bousmina [2].

According to Palierne and Bousmina, the frequency at which this plateau occurs (λ_D) as well as the magnitude of the storage modulus at the plateau (G_p) are given in Table 1.

Gramespacher and Meissner observed that the relaxation spectra of a blend can be considered as a sum of the relaxation spectra of the pure phases of the blends and an additional relaxation time that corresponds to the relaxation time of the shape of the dispersed droplets when sheared. Based on this observation, they developed a constitutive equation, following the work of Choi and Scholwalter [5] and using an empirical mixing rule. They obtained the following equation for the storage and the loss moduli of the blend.

$$G'(\omega)=\eta\frac{\omega^2(\tau_1-\tau_2)}{1+\omega^2\tau_1^2}=\frac{\eta}{\tau_1}\left(1-\frac{\tau_2}{\tau_1}\right)\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2} \tag{6}$$

$$G''(\omega)=\eta\frac{(\omega^3\tau_1\tau_2-\omega)}{1+\omega^2\tau_1}=\frac{\eta}{\tau_1}\left(1-\frac{\tau_2}{\tau_1}\right)\frac{\omega^2\tau_1}{1+\omega^2\tau_1^2}+\omega\eta\frac{\tau_2}{\tau_1} \tag{7}$$

with:

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

$$\tau_1=\tau_0\left[1+\phi\frac{5(19K+16)}{4(K+1)(2K+3)}\right] \tag{9}$$

$$\tau_2=\tau_0\left[1+\phi\frac{3(19K+16)}{4(K+1)(2K+3)}\right] \tag{10}$$

Table 2
Properties of the polymers

Polymers	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Melt index	η_0 (Pa s) (200 °C)
PMMA DHAF	65,100	2	11.5 (230 °C/3.9 Kg)	24,000
PS1 (N2380)	244,300	2	1.8 (200 °C/5 Kg)	11,700
PS2 (N1841)	198,700	2	10.4 (200 °C/5 Kg)	3200
PP (HY 6100)	–	–	1.5 (230 °C/2.16 Kg)	3700

$$\tau_0 = \frac{\eta_m R}{\alpha} \frac{(19K + 16)(2K + 3)}{40(K + 1)} \tag{11}$$

where: η, η_m, η_d are the blend, matrix, disperse phase Newtonian viscosity, respectively; $K = \eta_d/\eta_m$; α is the interfacial tension, R is the average radius of disperse phase, ϕ is the volume fraction of disperse phase and τ_1 corresponds to the form relaxation time. It is inversely proportional to interfacial tension and proportional to R. The identification of a third relaxation time in the relaxation spectrum of the blend can therefore enable the evaluation of interfacial or blend morphology.

Some studies have shown that there might be an influence of blend composition on the determination of interfacial tension between the components of the blend using dynamic data [11–16]. Lacroix et al. [11] observed that the values of interfacial tension obtained fitting Palierne's model to linear viscoelastic data of blends of polyethylene terephthalate copolymer(PETG)/ethylene vinyl acetate (EVA) depended on blend composition. Huitric et al. [12] studied the effects of composition of PE/PA12 blends on the rheological properties and concluded that Palierne's model can be used to estimate the interfacial tension between the components of the blend only for a limited volume fraction. The same conclusion was obtained by Peón et al. [13] who noticed that Palierne's model described the linear viscoelastic behavior of ethylene/vinyl acetate copolymer (EVAc)/polyethylene (PE) blends accurately only at both ends of the phase diagram. De Sousa and Demarquette [14] using both Palierne and Gramespacher and Meissner's analysis concluded for polypropylene (PP)/high-density polyethylene (HDPE) blends that there is a range of compositions for which is possible to use the linear viscoelastic behavior to evaluate the interfacial tension between the components of the blends. Similar behavior was obtained by Sung et al. [15] for polypropylene (PP)/styrene-acrylonitrile (SAN) blends.

Here, the effect of blend composition on their morphology and linear viscoelastic behavior was addressed. Two polymer pairs presenting a large difference of interfacial tension were studied: PMMA/PS [3] and PMMA/PP [17] in order to get a better understanding of why the emulsion models are valid only for certain concentrations. In the case of PMMA/PS blend two samples of polystyrene to vary the viscosity ratio of the blend were used.

2. Experimental section

2.1. Materials

Commercial polymethylmethacrylate (PMMA) from Metacril S.A., polystyrene (PS) from InNova S.A. and polypropylene (PP) from Polibrasil were used in this study. The characteristics of the polymers are reported in Table 2. PMMA was used as matrix and either PS or PP were used as dispersed phase.

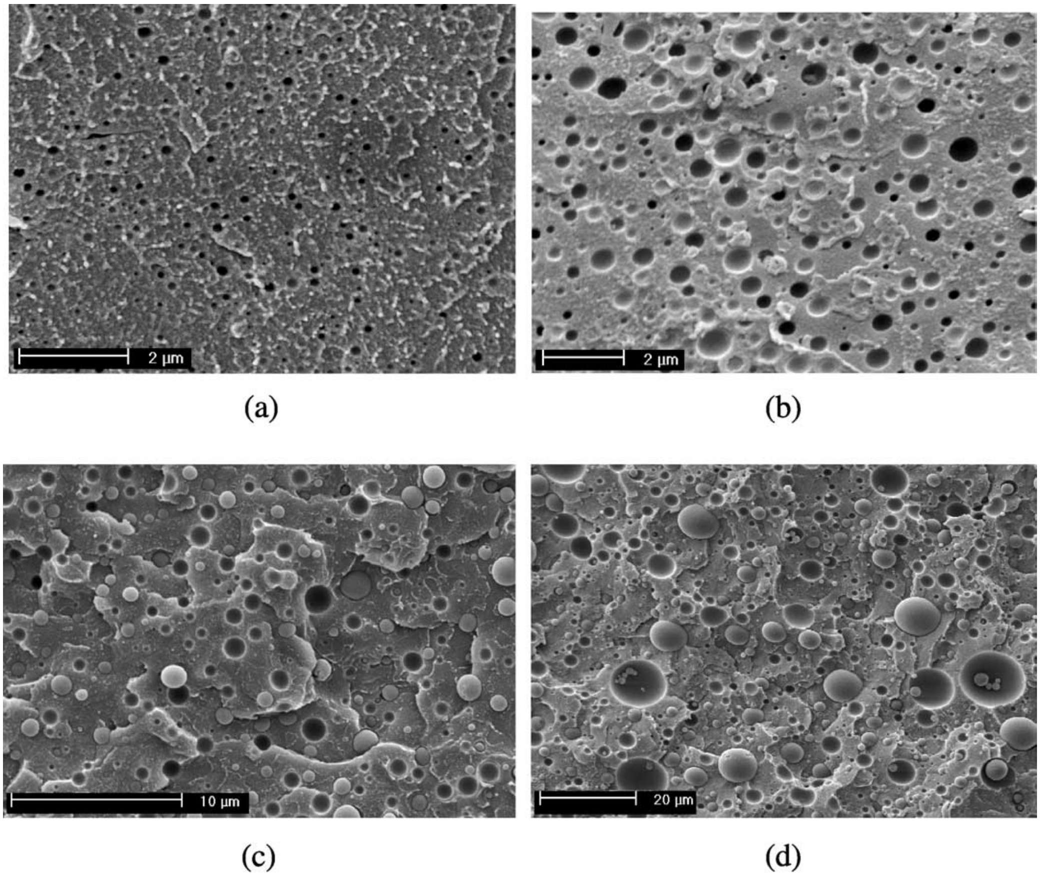
2.2. Blending

Blends of PMMA/PS and PMMA/PP were prepared in different weight concentration (95/5, 90/10, 85/15, 80/20, 75/25, 70/30) using a Haake PolyLab 900/Rheomix 600p. The temperature of the experimental chamber was 200 °C and the velocity of the rotors was 50 rpm. The blends were prepared in two steps: first the minor phase was processed for 5 min and after grinding, this material was mixed with the matrix for 7 min to form the blend. This procedure was adapted to compare the results obtained in this work to others obtained with compatibilized blends [18].

2.3. Rheological measurements

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

The rheological characterization of the samples was carried out 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 a plate diameter of 25 mm. Time sweep tests were performed to evaluate the thermal resistance of the polymers used in this work. Stress sweeps 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 measurements were performed 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 Carreau model [19].



(a) (b)

(c) (d)

Fig. 1. Morphology of PMMA/PS blends: (a) 90/10, (b) 80/20 and PMMA/PP blends: (c) 90/10, (d) 80/20.

2.4. Morphological characterization

The morphology of the blends was 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 case of PMMA/PS blend, the minor phase (polystyrene) was extracted using acetic acid at room temperature, under continuous stirring for 10 h. In the case of PMMA/PP blend no solvent extraction was performed.

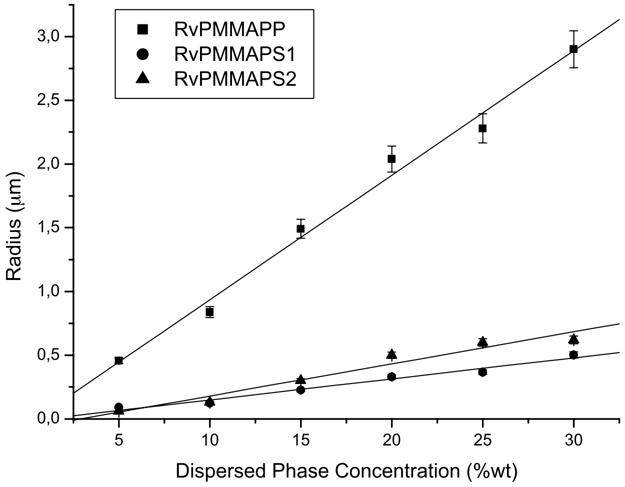


Fig. 2. Volume average radius (R_v) of the dispersed phase as a function of dispersed phase concentration for both PMMA/PS (1 and 2) and PMMA/PP blends.

The morphology was quantified using an appropriate software (KS 300). The average diameter and volume fraction of the minor phase was calculated after analysis of the SEM photomicrographs. About 1000 particles were considered to calculate these parameters. For the calculation of the average size of the minor phase Saltikov's [20] correction was used. This correction takes into account the polydispersity of the droplet sizes and the fact that the fracture in the samples does not always occur at the maximum diameter of the droplets of the dispersed phase.

3. Results and discussion

3.1. Morphology

Fig. 1 shows micrographs of the cryogenically fractured surfaces for the PMMA/PS1 and PMMA/PP blends after compression molding. In the case of PMMA/PP blend the minor phase was not removed by solvent extraction and the holes that can be observed in the micrographs originate from

Table 3
Volume average radius (R_v) and polydispersities (R_v/R_n) of the dispersed phase for both PMMA/PS (1 and 2) and PMMA/PP blends with different compositions

Blend Composition	PMMA/PS1		PMMA/PS2		PMMA/PP	
	R_v (μm)	R_v/R_n	R_v (μm)	R_v/R_n	R_v (μm)	R_v/R_n
95/5	0.09	1.8	0.06	1.8	0.45	2.4
90/10	0.12	2.0	0.13	1.8	0.84	3.0
85/15	0.23	2.3	0.24	2.5	1.49	3.4
80/20	0.33	1.8	0.5	2.0	2.04	3.2
75/25	0.36	1.8	0.6	1.9	2.28	2.6
70/30	0.50	1.9	0.62	2.4	2.9	3.1

the sample's fracture. A droplet dispersion morphology type can be observed. This type of morphology was observed for all blends. From Fig. 1 it can be seen that the size of the dispersed phase increases as a function of increasing concentration of PS1 and PP for both PMMA/PS1 and PMMA/PP. Similar results were obtained for PMMA/PS2 blend.

Fig. 2 shows the volume average radius (R_v) (given by Eq. (2)) as a function of concentration for three blends studied in this work. The experimental values of R_v and polydispersity R_v/R_n are reported in Table 3. It can be seen that the volume average radius of the dispersed phase increases as a function of increasing concentration of the dispersed phase for three blends. This expected increase is most likely due to an increase of coalescence of dispersed phase when the dispersed phase concentration increases. This behavior has already been observed by other researchers [21,22].

The results presented in Fig. 2 indicate that the increase of the droplet size of PMMA/PS blend as a function of concentration for both blend (PMMA/PS1 and PMMA/PS2) is of the same order or magnitude. It can also be seen that the PMMA/PP blend shows a marked increase of the droplet size whereas PMMA/PS does not. This can be explained through the differences of magnitude of coalescence that undergo both blends. As explained by Wallheinke et al. [22] and De Sousa and Demarquette [14], coalescence depends essentially on: (a) the probability of two droplets to collide and (b) the rheological and thermodynamical ability of the blend to drain the film of matrix phase entrapped between two droplets of the dispersed phase until the critical thickness for coalescence to occur is reached [23]. When the probability of two droplets to collide is high and the drainage of the film is easy, coalescence can occur. The probability of two droplets to collide depends on the morphological characteristics of the blend, being higher for larger dispersed phase concentration and inversely proportional to the droplet size [23]. In turns, film drainage is facilitated by high values of interfacial tension between the components of the blend and high viscosity ratio [22]. When comparing PMMA/PS2 and PMMA/PP (both blend having the same viscosity ratio within experimental error) blends it can be seen that coalescence is lower for PMMA/PS2 than PMMA/PP. The droplet size in the case of PMMA/PS2 is much lower than the one of PMMA/PP however in the case of PMMA/PS2 blends, the interfacial tension between the polymers is smaller than the one for PMMA/PP (around 1.5 and 7.5 mN/m, respectively), showing that the film drainage and in particular the high value of interfacial tension is a predominant phenomenon to explain the coalescence in the

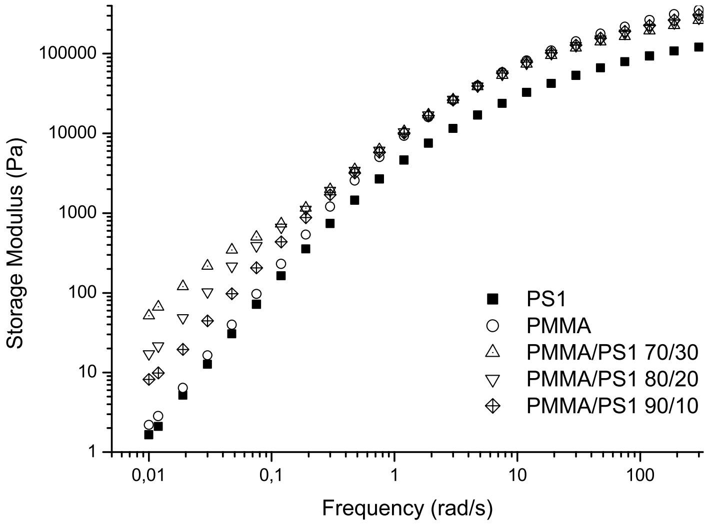


Fig. 3. Storage moduli of the PMMA/PS1 blends with different compositions and of the pure phases at 200 °C.

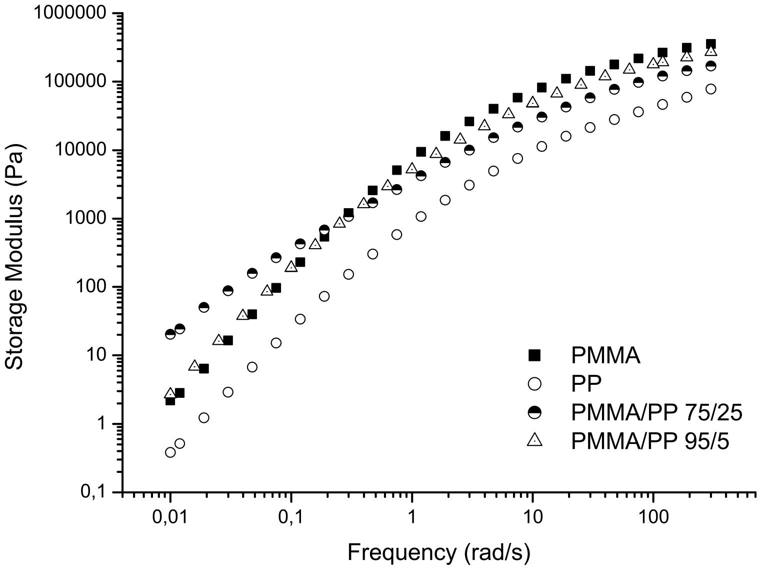


Fig. 4. Storage moduli of the PMMA/PP blends with different compositions and of the pure phases at 200 °C.

case of those two blends. Similar behavior was observed by De Souza and Demarquette [14] when they compared their data to the ones of Wallheinke et al. [22].

From Table 3 it can also be observed that for PMMA/PS blends, the polydispersity (R_v/R_n) of the inclusions does not exceed the value of 2.3, that is a necessary condition if one wants to use the viscoelastic data of the blend to determine the interfacial tension between its components by Palierne's and Bousmina's models [8]. However, PMMA/PP blends showed high values of polydispersity that can affect the applicability of Palierne's and Bousmina's models to evaluate interfacial tension between those two polymers.

3.2. Rheological measurements

Figs. 3 and 4 show the storage (G') moduli for PMMA/PS1 and PMMA/PP blends with different compositions. Data for only three compositions are presented for the sake of clarity of the figures. It can be seen that for low frequencies the storage modulus (G') of the blends for each composition is larger than those for the pure phases and is increasing when the dispersed phase concentration is increasing. This increase of elasticity [2–4,11,24] can be attributed to the form relaxation process of the dispersed phase droplets when slightly sheared. When the dispersed phase concentration increases, the diameter of the dispersed phase increases and the relaxation process of the dispersed phase becomes longer, leading to an increase of the storage modulus. It can also be seen from Figs. 3 and 4, that for blends with low dispersed phase concentration (5% and 10% of dispersed phase contents), no well defined secondary plateau can be distinguished in the storage modulus curves (G'). A small shoulder can be observed for the blends with higher dispersed phase concentration. This behavior corroborates the predictions of Graebling et al. [8] who studied the influence of dispersed phase concentration on presence of the secondary plateau. The authors observed that increasing the dispersed phase concentration increases both G_p and the width of the secondary plateau. Similar behavior was observed for PMMA/PS2 blend.

In order to compare the ability of the models to predict the linear viscoelastic behavior of both PMMA/PS and PMMA/PP blends, Palierne's and Bousmina's emulsion models were fit to the experimental data for the different blends compositions studied. The adjustment was done preferentially over a limited frequency range located around the position of small shoulder of storage modulus (secondary plateau), that corresponds to the form relaxation of the dispersed phase droplets. It was observed that for PMMA/PP it was not possible to obtain a good agreement

Table 4
Form relaxation times of the dispersed droplets obtained analyzing the relaxation spectra calculed using the nonlinear regression method-Rheometrics [26] (τ_{1A}) and the Honerkamp and Weese method [25] (τ_{1B}); and interfacial tension of PMMA/PS1 blend with different compositions obtained analyzing the relaxation spectra (α^1), using Palierne's (α^2) and Bousmina's (α^3) models

Blend composition	τ_{1A} (s)	α^{1A} (mN/m)	τ_{1B} (s)	α^{1B} (mN/m)	α^2 (mN/m)	α^3 (mN/m)
85/15	6.7	1.5	5.6	1.9	1.6	1.9
80/20	11.5	1.4	11.5	1.5	1.4	1.3
75/25	22.0	0.9	22.0	0.9	0.8	0.8
70/30	26.6	1.0	39.3	0.7	0.9	0.7

Table 5
Form relaxation times of the dispersed droplets obtained analyzing the relaxation spectra calculated using the nonlinear regression method-Rheometrics [26] (τ_{1A}) and the Honerkamp and Weese method [25] (τ_{1B}); and interfacial tension of PMMA/PS2 blend with different compositions obtained analyzing the relaxation spectra (α^1), using Palierne's (α^2) and Bousmina's (α^3) models

Blend composition	τ_{1A} (s)	α^{1A} (mN/m)	τ_{1B} (s)	α^{1B} (mN/m)	α^2 (mN/m)	α^3 (mN/m)
90/10	2.7	2.0	2.9	1.9	1.7	1.8
85/15	4.7	2.4	4.5	2.5	2.0	2.3
80/20	8.2	3.2	8.2	3.2	1.6	1.8
75/25	13.8	2.5	16.3	2.0	1.4	1.8
70/30	23.8	1.6	24.2	1.6	1.0	1.6

Table 6
Form relaxation time of the dispersed droplets obtained analyzing the relaxation spectra calculed using the nonlinear regression method-Rheometrics [26] (τ_{1A}) and the Honerkamp and Weese method [25] (τ_{1B}); and interfacial tension of PMMA/PP blend with different compositions obtained analyzing the relaxation spectra (α^1)

Blend Composition	τ_{1A} (s)	α^{1A} (mN/m)	τ_{1B} (s)	α^{1B} (mN/m)
90/10	3.3	10.9	2.5	14.5
85/15	5.7	12.7	6.2	11.6
80/20	12.8	8.6	10.5	10.4
75/25	14.9	9.0	14.7	9.1
70/30	21.5	8.7	36.0	5.2

between experimental data and the emulsion models, most likely due to the higher polydispersity of the morphology of those blends. Also, it was observed that Palierne's emulsion model showed a better fit than Bousmina's model in the case of PMMA/PS blends.

Fitting the emulsion models to the experimental data for the PMMA/PS blends, it was possible to obtain the interfacial tension between the polymers of the blends at different compositions. Tables 4 and 5 show these values of interfacial tension.

Figs. 5 and 6 show the weighted relaxation spectra of PMMA/PS1 and PMMA/PP blends, respectively with different compositions and of the pure phases. The relaxation spectra were calculated using two methods: the Honerkamp and Weese method [25] and the nonlinear regression method available in the stress rheometer SR-5000 software package from Rheometrics [26]. Qualitatively both methods lead to similar results. In the relaxation spectrum of both blends it was possible to identify two peaks: one related to the relaxation times of the blend phases (PMMA, PS and PP) that are superposed, and a second that can be associated to the form relaxation time of the dispersed droplets. Similar results were obtained for PMMA/PS2 blend. In the figures, the results obtained with the stress Rheometer SR-5000 software package from *Rheometrics* are shown.

Tables 4–6 shows the form relaxation times obtained from the relaxation spectra of both PMMA/PS and PMMA/

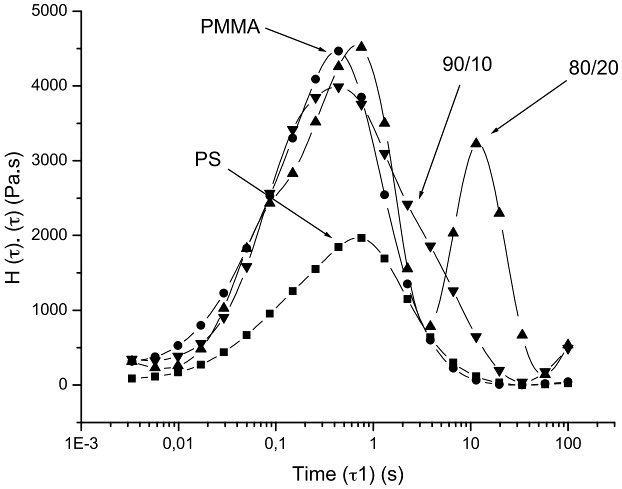


Fig. 5. Weighted relaxation spectra calculed using the method available in the software package from Rheometrics for PMMA/PS1 blends with different composition at 200 °C.

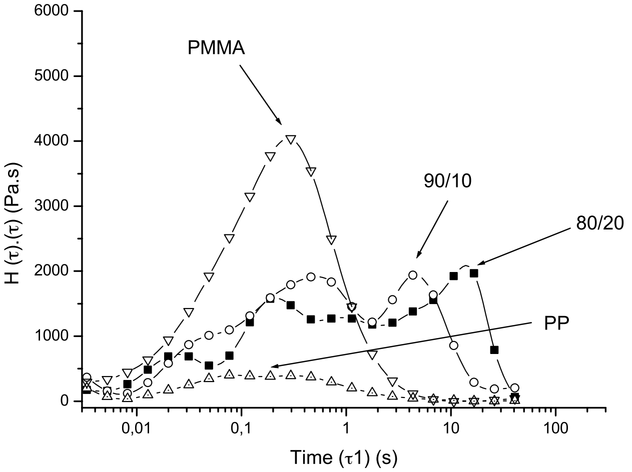


Fig. 6. Weighted relaxation spectra calculated using the method available in the software package from Rheometrics for PMMA/PP blends with different composition at 200 °C.

Table 7
Values of experimental relaxation time ($\tau_{1\mathrm{Exp}}$) obtained analyzing the relaxation spectra calculed using the nonlinear regression method-Rheometrics [26] and the ones calculated for PMMA/PS (1 and 2) and PMMA/PP using Palierne's and Bousmina's models with values of interfacial tension of 1.5 and 7.5 mN/m, respectively

Blend composition	PMMA/PS1			PMMA/PS2			PMMA/PP		
	$\tau_{1\mathrm{Exp}}$ (s)	$\tau_{1\mathrm{Pal}}$ (s)	$\tau_{1\mathrm{Bous}}$ (s)	$\tau_{1\mathrm{Exp}}$ (s)	$\tau_{1\mathrm{Pal}}$ (s)	$\tau_{1\mathrm{Bous}}$ (s)	$\tau_{1\mathrm{Exp}}$ (s)	$\tau_{1\mathrm{Pal}}$ (s)	$\tau_{1\mathrm{Bous}}$ (s)
90/10	–	–	–	2.7	3.0	4.0	3.3	4.0	5.2
85/15	6.7	6.9	8.8	4.7	5.9	7.9	5.7	7.5	10.0
80/20	11.5	10.6	13.7	8.2	13.0	18.0	12.8	10.8	14.9
75/25	22.0	12.4	16.5	13.8	16.4	23.7	14.9	12.7	18.0
70/30	26.6	17.7	24.5	23.8	16.6	26.8	21.5	16.9	25.3

PP blends, respectively for different concentrations of the dispersed phase using both calculation methods. It can be seen that the form relaxation times of the dispersed droplets increase when the dispersed phase concentration increases, which can be easily understood, as the shape relaxation time is directly proportional to the size of the dispersed phase. It can also be seen that the results obtained using both methods corroborate except for 70/30 concentration for both PMMA/PS1 and PMMA/PP blends.

The value of the form relaxation times of the dispersed droplets for each blend were used to evaluate the interfacial tension using Gramespacher and Meissner analysis [3]. The calculated values of the interfacial tension are reported in Tables 4–6.

Tables 4–6 shows the values of interfacial tension obtained for both PMMA/PS and PMMA/PP blends, respectively studied at different compositions. In the case of PMMA/PS blends the values of interfacial tension obtained using the three different methods corroborate within experimental error. For the PMMA/PP blends, only Gramespacher and Meissner analysis was used to infer the interfacial tension because it was not possible to obtain a good agreement between the rheological data and the emulsion models of Palierne and Bousmina.

It can be seen from Tables 4–6 that the values of interfacial tension for the three blends, infered from rheological measurements decrease when the concentration of the dispersed phase increases. The opposite effect was observed by de Sousa and Demarquette [14] who observed that, for PP/HDPE blends, the interfacial tension increases with the increase of the volume fraction. In order to check if the relaxation times obtained experimentally from the analysis of the rheological data can be associated to the relaxation of the dispersed phase of the blends, they were compared to the ones predicted by Palierne's and Bousmina's models. The zero shear viscosities and radii of dispersed phase necessary for the calculations are reported in Table 2. The values of interfacial tension used were obtained from the literature and were set equal 1.5 mN/m [3] and 7.5 mN/m [17], respectively. The relaxation times calculated are reported in Table 7. The values obtained using Bousmina's model are larger than the ones obtained using Palierne's model although the magnitudes are similar. The differences between the values obtained using both models are larger for higher concentrations. This can be explained by the larger influence that the volume fraction of the dispersed phase (ϕ) plays in expression 5b than in expression 4b.

It can be seen that the calculated values of relaxation times only corroborate the experimental values for 15% and 20% of PS contents in the case of PMMA/PS1 blend and for 15% of PP in the case of PMMA/PP and PMMA/PS2 blends. For larger concentrations of the dispersed phase the experimental values of relaxation times are larger than the calculated ones. Since the relaxation time is directly proportional to R_v/α, and α is a thermodynamic constant

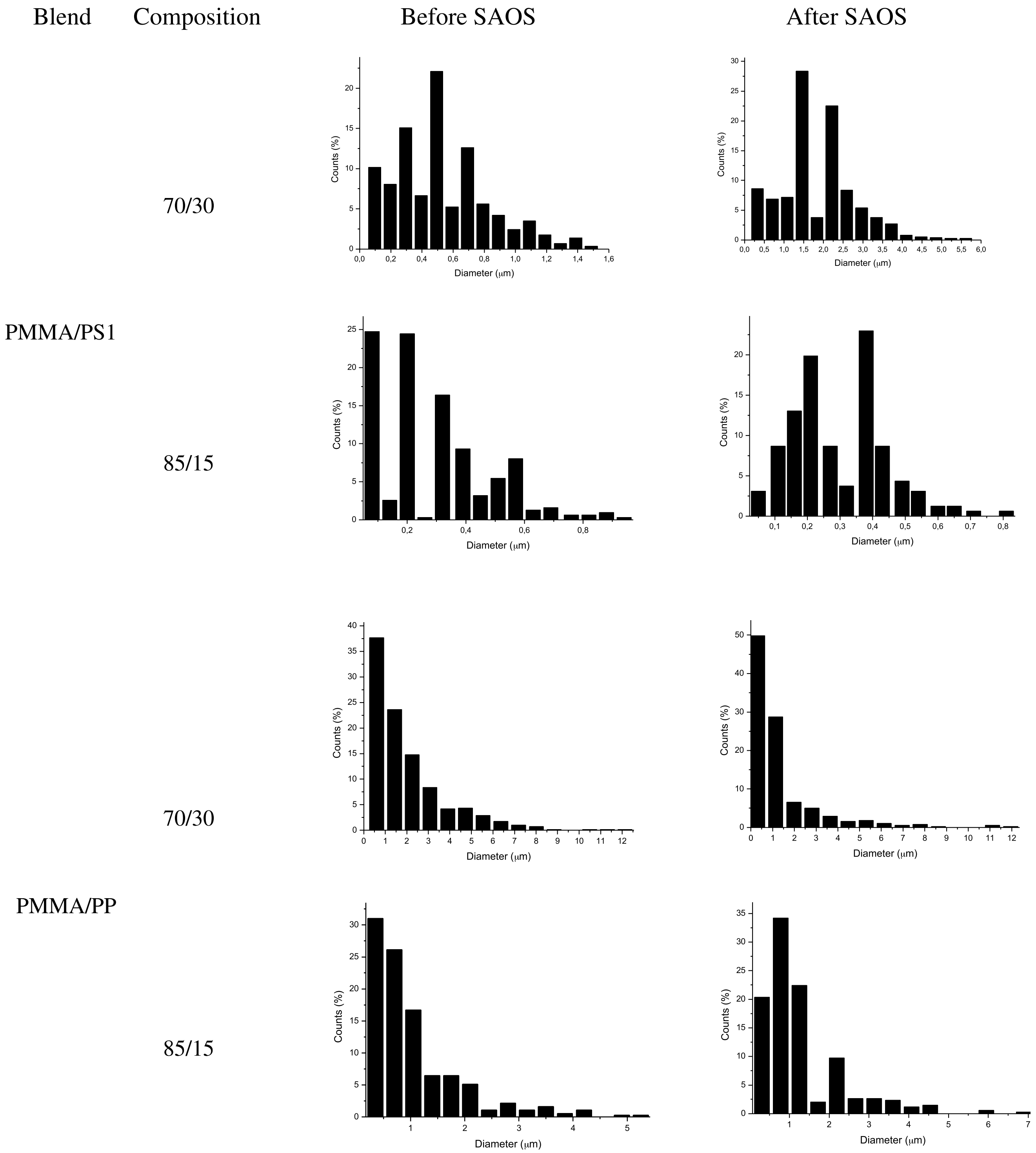


Fig. 7. Drop size distribution of PMMA/PS1 and PMMA/PP 70/30 and 85/15 blends after and before the test of SAOS.

that does not depend on the concentration of the blend, but solely, on the physico–chemical interaction between the components of the blend, these results could indicate that during the Small Amplitude Oscillatory Shear (SAOS) tests, some coalescence might have occurred. In order to check such an hypothesis, PMMA/PS and PMMA/PP samples with a concentration of 70/30 were frozen in situ in the rheometer to visualize and quantify their morphology just after the SAOS. The same experiment was performed with the 85/15 concentration blend to see if coalescence also occurs at lower concentration. Fig. 7 shows the histograms of the quantitative analysis for both PMMA/PS1 and PMMA/PP blends (for 85/15 and 70/30 concentrations) before and after shear. Table 8 presents the values of the

Table 8
Morphology characterization of PMMA/PS (1 and 2) and PMMA/PP blends before and after SAOS

Blends	Composition	Before SAOS		After SAOS	
		R_v (μm)	R_v/R_n	R_v (μm)	R_v/R_n
PMMA/PS1	85/15	0.2	2.3	0.2	1.7
	70/30	0.5	1.9	1.5	1.9
PMMA/PS2	85/15	0.3	3.0	0.3	2.3
	70/30	0.62	2.4	0.88	2.3
PMMA/PP	85/15	1.5	3.4	1.8	3.3
	70/30	2.9	3.1	4.0	0.74

average radius for both blends before and after the SAOS. It can be seen that for both blends the average radius of the dispersed phase increased in the case of 70/30 composition but kept at a constant value within experimental error for the 85/15 blends. These results indicate that coalescence occured for the 70/30 blend whereas it did not for the 85/15 blend during SAOS experiment.

Table 9 presents the values of interfacial tension inferred from the rheological behavior of the 70/30 blends using the morphological characterization of the blends after SAOS. It can be seen that when the average radius of the dispersed phase after coalescence is taken into account, the value of interfacial tension obtained using the rheological data of the 70/30 blends corroborates the ones obtained for the 85/15 blends and by other authors [27]. This can be explained by the fact that in order to reach the range of frequencies for which the relaxation of the droplets is observed, it takes more than two thirds of the time of the SAOS experiment (independently if during the experiment the frequency is decreased from 300 to 0.01 rad/s or increased from 0.01 to 300 rad/s) leading to coalescence.

These results indicate that rheological data of high dispersed phase concentration blends can be used to infer interfacial tension between the components of the blends only if coalescence is taken into account.

Blends with a composition 85/15 were used to evaluate the interfacial tension between PS and PMMA as a function of temperature. Table 10 shows the values of interfacial tension obtained using the three types of analysis of this work. Fig. 8 shows the interfacial of the PMMA/PS blends as a function of temperature. The values were obtained by averaging the values of interfacial tension obtained from fitting Palierne's and Bousmina's emulsion models to the experimental data and from the weighted relaxation spectra of PMMA/PS blends. The symbols represent the experimental data and the straight line represent the best fit obtained by linear regression. It can be seen that the interfacial tension decreases linearly with increasing temperature following the equation below:

Table 9
Interfacial tension obtained analyzing the relaxation spectra (α^1), Palierne's (α^2) and Bousmina's (α^3) models for both PMMA/PS (1 and 2) and PMMA/PP 70/30 blends using the morphological characterization of the blends after SAOS

	α^1 (mN/m)	α^2 (mN/m)	α^3 (mN/m)
PMMA/PS1	2.0	2.3	1.5
PMMA/PS2	2.3	2.0	2.3
PMMA/PP	7.0	–	–

$$\alpha = 10.38 - 0.04T \quad (r^2 = 0.99) \tag{12}$$

where α is the interfacial tension and T is the temperature. Similar results have already been obtained by other researchers for other polymer pairs [28].

4. Conclusion

In this work the influence of composition on the morphology and dynamic behavior of PMMA/PS and PMMA/PP blends was investigated. The results indicated that film drainage and in particular the high value of interfacial tension is a predominant phenomenon to explain the coalescence in the studied blends. Both families of blends showed an increased elasticity when compared to the pure phase. This increased elasticity can be attributed to the relaxation of the dispersed phase when slightly sheared.

The dynamic data were used to infer the interfacial tension between the components of the blend using emulsion models (Palierne or Bousmina's models) and the

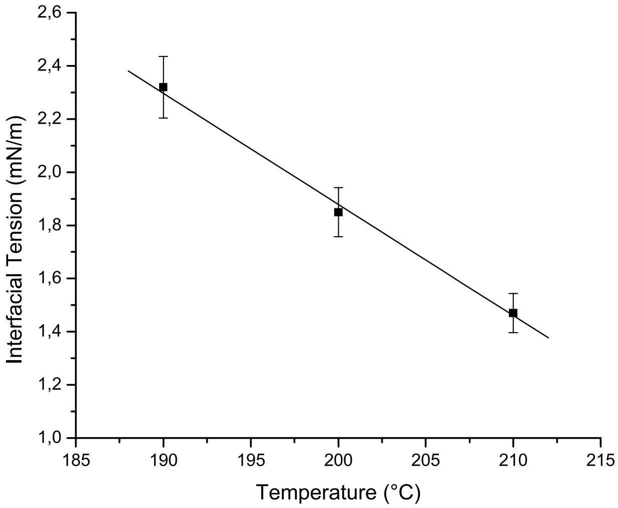


Fig. 8. Interfacial tension between PS1 and PMMA as a function of temperature.

Table 10

Interfacial tension between PS and PMMA as a function of temperature obtained analyzing the relaxation spectra (α^1), Palierne's (α^2) and Bousmina's (α^3) models for both PMMA/PS 85/15 blend

Temperature (°C)	α^1 (mN/m)	α^2 (mN/m)	α^3 (mN/m)	Average
190	1.88 ± 0.40	2.9 ± 0.7	2.2 ± 0.6	2.32 ± 0.50
200	2.07 ± 0.17	1.6 ± 0.3	1.9 ± 0.4	1.85 ± 0.23
210	1.72 ± 0.20	1.2 ± 0.5	1.2 ± 0.4	1.47 ± 0.26

analysis of the relaxation spectrum of the blends. The results obtained using the three methods corroborated within experimental error for PMMA/PS blends. It was not possible to fit the emulsion model to the rheological behavior of PMMA/PP blends but it was possible to infer the interfacial tension between PMMA and PP using the analysis of the relaxation spectrum of the blends. The values of interfacial tension evaluated using the dynamic data were shown to depend on the concentration of the blend used for the rheological measurement and decrease when the concentration of the blend increases. It was shown that this behavior can be attributed to the coalescence of the dispersed phase in the case of large dispersed phase concentrations. When this coalescence is taken into account the interfacial tension evaluated using rheological measurements does not depend on the blend's concentration.

The interfacial tension between PS and PMMA was evaluated as a function of temperature and shown to decrease with an increase of temperature.

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