The effect of interfacial properties on the deformation and relaxation behavior of PMMA/PS blends

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Synopsis

This work aims at studying the role of interface properties on the rheological behavior of non-compatibilized and compatibilized polymer blends. Blends of polymethylmetacrylate (PMMA) with polystyrene (PS) and PS functionalized with oxazoline (PSOX) with concentrations of up to 20w/w of the dispersed phase were used. It was observed that until a critical concentration is reached the increase in PSOX content leads to a significant increase in (a) the elasticity at low frequencies and (b) the relaxation time after cessation of flow, both in shear and extension. This points to a likely significant role played by interface elasticity. Since no chemical reactions occur between PMMA and the oxazoline groups of PSOX, the latter is probably caused by the partial miscibility between PMMA and PSOX. Beyond this critical concentration, the amount of

PSOX does not have a significant influence on the rheological behavior of the blends. In order to gain an insight into the relaxation dynamics of the droplets and interface, and their relationship with the rheological behavior of the blends, small angle light scattering (SALS) was used in diluted blends (1 wt % of the dispersed phase) during step shear. SALS shows a slight deformation of dispersed phase in the vorticity direction for the 99PMMA/1PSOX blend while the droplets of the 99PMMA/1PS blend deforms in the flow direction only. This result confirms the large increase in the interfacial elasticity for the 99PMMA/1PSOX blend.

INTRODUCTION

Blending polymers allows for the development of materials with enhanced proprieties with much less effort than that required to synthesize a completely new polymer, and blends already represent a large fraction of all plastics produced. For example, in 2001 approximately 10% of all thermoplastics and 75% of all elastomers were processed as blends [Ehrenstein (2001)], and these numbers have grown further in recent years. The properties of the blends depend strongly on the properties of the components, on the interfacial properties, and on the final morphology, as most polymer blends of industrial interest are generally immiscible. Usually, the immiscible blends reveal poor interfacial adhesion, their morphology is coarse and unstable, and consequently the mechanical properties are bad. To overcome these difficulties and develop materials with the required properties, compatibilization is often required.

Compatibilization can be achieved by different methods, such as through the addition of a pre-synthesized copolymer or by creating chemically and in situ, during the blending process, a third component, often called an interfacial agent, emulsifier, or compatibilizer [Datta and Lohse (1996a, 1996b); Utracki (1994)]. This component can be a graft or block copolymer, which tends to be located at the interface between the two components of the blend. The first method, ex situ, has the advantage of better control of the molecular architecture of the compatibilizer. However, it requires specific chemical routes and reaction conditions. In the second method, also called reactive blending or in situ compatibilization, the generation of the compatibilizer is performed in situ at the interface directly during blending. Another strategy to enhance the compatibility of the immiscible blends is by increasing specific interactions between polymers, such as van der Waals interactions, hydrogen bonding, ion-dipole interaction, and ion-ion interactions [He et al. (2004); Koning et al. (1998)].

Compatibilization increases the interfacial adhesion between the components of the blend [Van Puyvelde et al. (2003)], produces a finer morphology, and delays the coalescence of the dispersed phase [Van Hemelrijck et al. (2004); Van Puyvelde et al. (2001)]. As could be expected, these differences in the interfacial proprieties and morphology induce different rheological responses of the blends, when subjected to flow. For example, when submitted to small-amplitude oscillatory shear, immiscible binary blends show a higher elasticity in the low frequency range than that of the combined individual components. The higher value of elasticity of the blends can result in the presence of a secondary plateau at low frequencies in the storage modulus vs frequency curve. That phenomenon is due to the relaxation of the shape of the dispersed phase when shear deformed [Graebling et al. (1993); Oosterlinck et al. (2005)]. In the case of compatibilized blends, there are several experimental studies that present evidence for an additional relaxation time. This relaxation time can be attributed to the relaxation of Marangoni stresses tangential to the interface between the dispersed phase and the

matrix [Riemann et al. (1997); Van Hemelrijck et al. (2004)]. They are caused by a gradient in interfacial tension, induced by a gradient in compatibilizer concentration at the interface [Van Hemelrijck et al. (2004); Van Puyvelde et al. (2003)]. A generalized version of the Palierne model [Jacobs et al. (1999)], which includes an interfacial shear modulus, predicts this additional relaxation time in compatibilized blends. Several authors [Yee et al. (2007); Huo et al. (2007); Shi et al. (2002); Asthana and Jayaraman (1999)] used this model and obtained good agreement with the experimental data of the compatibilized blends. However, Sailer and Handge (2007), studying blends of PA 6/SAN compatibilized with styrene-acrylonitrile-maleic anydrid terpolymer (SAN-MA), concluded that the generalized Palierne model could not be fitted to the experimental data for reasonable values of interfacial tension and interfacial shear modulus.

In what concerns the behavior of immiscible polymer blends when subjected to extensional flows, some studies are available in the literature, but in much less quantity than for shear flows. The elongation and subsequent recovery of poly(methylmethacrylate)polystyrene (PMMA/PS) blends, as well as the evolution of the morphology, were studied by Gramespacher and Meissner (1997) and, more recently, by Mechbal and Bousmina (2004) and Handge and Potschke (2004). In terms of recovery after melt elongation, the results suggest that, as in shear flows, there is a fast molecular recovery related to each component and a slow one associated with interfacial tension. In terms of elongational flow, Mechbal and Bousmina (2004) observed that the behavior of a PMMA/PS (95/5) blend is mainly dominated by the matrix. Oosterlinck et al. (2005), while also studying PMMA/PS blends subjected to uniaxial elongational flows, verified that the extra stress due to droplet deformation can, in principle, be deduced from extensional rheological measurements.

Experimental studies about the behavior of compatibilized blends in extensional flows are even less abundant. Mechbal and Bousmina (2007) studied the effect of the diblock copolymer addition on the rheology and morphology development during uniaxial elongation and during relaxation after cessation of flow on a PMMA/PS blend with a viscosity ratio lower than 1 . They observed that when the concentration of the copolymer is above a critical concentration, the interface becomes saturated, the droplets are less deformed, and the relaxation is slower. They postulated that this behavior is due to local entanglements, which resist deformation. Moreover, it was observed that if the molecular weight of copolymer is smaller than the critical molecular weight of entanglement of both PS and PMMA, then the copolymer does not affect the stress relaxation behavior. Also, rheological transient shear experiments have shown that the compatibilization has an important effect on rheological properties [Iza et al. (2001); Macaúbas et al. (2005); Silva et al. (2007)], which suggest a large contribution of the modified interface to the overall behavior.

In the previous work by the present authors [Silva et al. (2007)], it was shown that the relaxation behavior after both shear and extensional deformations of blends of polyamide-6 (PA6) and highly elastic ethylene-propylene copolymer (EPM) varied markedly between non-compatibilized and compatibilized blends. Although all materials showed a two-step relaxation process, the difference in time scale of the second slower process between the non-compatibilized and the compatibilized was very large (nearly two orders of magnitude). Morphological analysis showed that the dispersed EPM droplets were not elongated in the non-compatibilized blend, but were slightly elongated in the highly compatibilized one, despite the fact that the viscosity ratios were very high in both cases (in excess of 10 for the compatibilized blend and of 100 for the

noncompatibilized one). Although at the time the second relaxation process was attributed to the relaxation of the EPM droplets, the role of the compatibilizer at the interface on the relaxation mechanism still remains unanswered. Thus, the main aim of this work is to complement the previous one through the study of the linear and non-linear viscoelastic and rheo-optical behavior of PS/PMMA and oxazoline functionalized polystyrene (PSOX)/PMMA model polymer blends. It is neither known nor expected a priori that any chemical reaction between oxazoline and PMMA occurs. Nevertheless, it is expected that the oxazoline groups promote new physical interactions, such as hydrogen bonds, that change the dynamics of the interface and increase miscibility with the PMMA matrix.

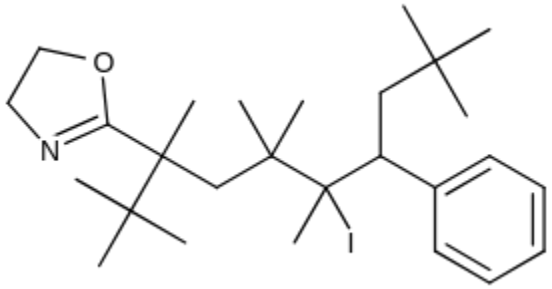


FIG. 1. Schematic of a PS chain functionalized with oxazoline.

Thus, the characteristics of the interface and the subsequent deformation and relaxation mechanisms will be investigated.

EXPERIMENTAL

A. Materials

The blend components are commercial grades of PMMA (Altuglas VSE UVT, MFI 27 g/10 min at 230 °C with 3.8 kg) and PS (Solarene G116, MFI 2.3 g/10 min at 200 °C with 5 kg). The PSOX (Epocros RPS-1005, 6 – 10 g/10 min at 200°C with 5 kg) (Fig. 1) was provided by Nippon Shokubai. In the PSOX, the weight of oxazoline groups corresponds to 1.9% of the total weight. This means that in PSOX, 2.9% of the PS "monomers" are funcionalized with oxazoline.

The main reason for this choice of polymers was that it is expected that they will allow the relative effect of interface structure to be studied in detail since they are both optically transparent, which is essential for rheo-optical measurements. The components are also relatively inelastic, while still showing relatively high viscosity ratios (between 2 and 4 at the relevant shear and extension rates) [see Figs. 2(a) and 2(b)] so that the dispersed phase deformation is still relatively small.

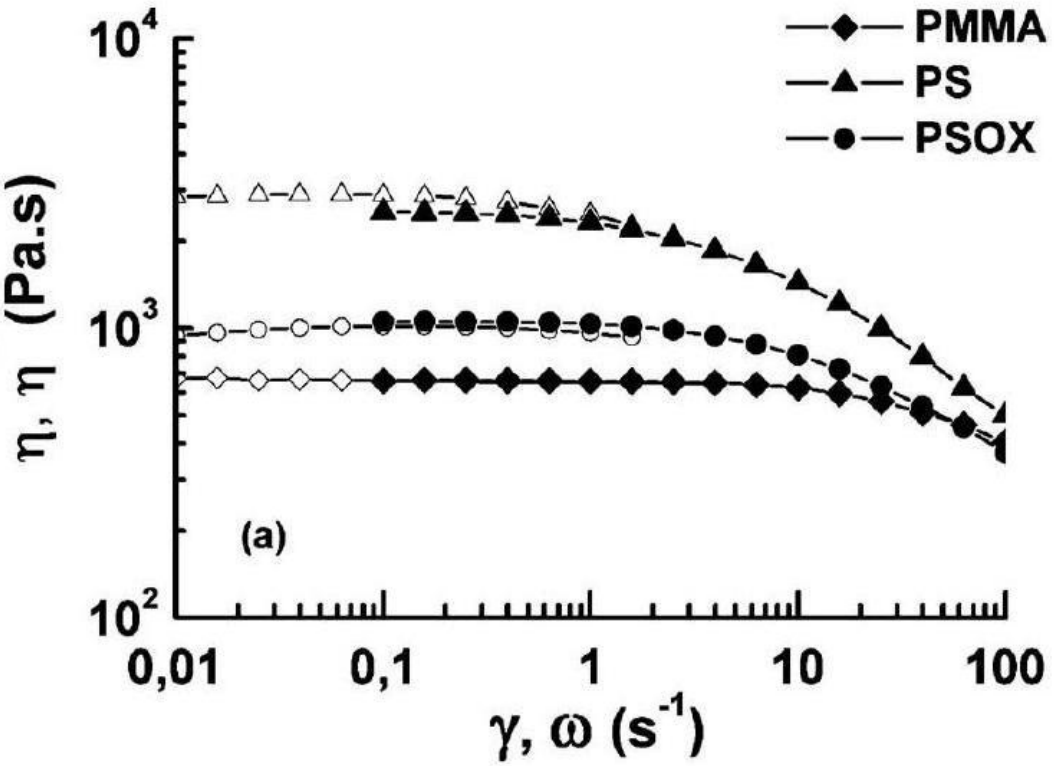
B. Compounding

A series of blends of PMMA/PS/PSOX was prepared in this work. The concentration of the PMMA matrix was keep constant (80w/w), while those of PS and PSOX were varied systematically from only PS and no PSOX (80/20/0 PMMA/PS/PSOX) to the opposite situation, i.e., 20w/w of PSOX and no PS (80/0/20 PMMA/PS/PSOX). Moreover, two diluted blends (99/1/0 PMMA/PS/PSOX and 99/0/1 PMMA/PS/PSOX) were also prepared. A Haake batch mixer at a set temperature of 210°C and a rotor speed of 80 rpm was used to compound the blends. The sample was removed from the mixer after a mixing time of 600 s .

Morphology

The morphology of all the blends was analyzed by scanning electron microscopy (SEM). The samples were fractured in liquid nitrogen and then the PS/PSOX phase was removed in cyclohexane at 50°C during 1 h . The morphology of the blends was studied, after gold plating the samples, using a Jeol JSM 6310F scanning electron microscope.

The volume (R_v) and number (R_n) average radii of the dispersed phase were determined from SEM micrographs using an automatic method of image analysis (IMAGETOOL); the results were obtained after studying typically 300 particles.


PMMA
PS
PSOX
10^4
10^3
10^2
η, η^* (Pa.s)
(a)
0,01
0,1
1
10
100
γ, ω (s^{-1})

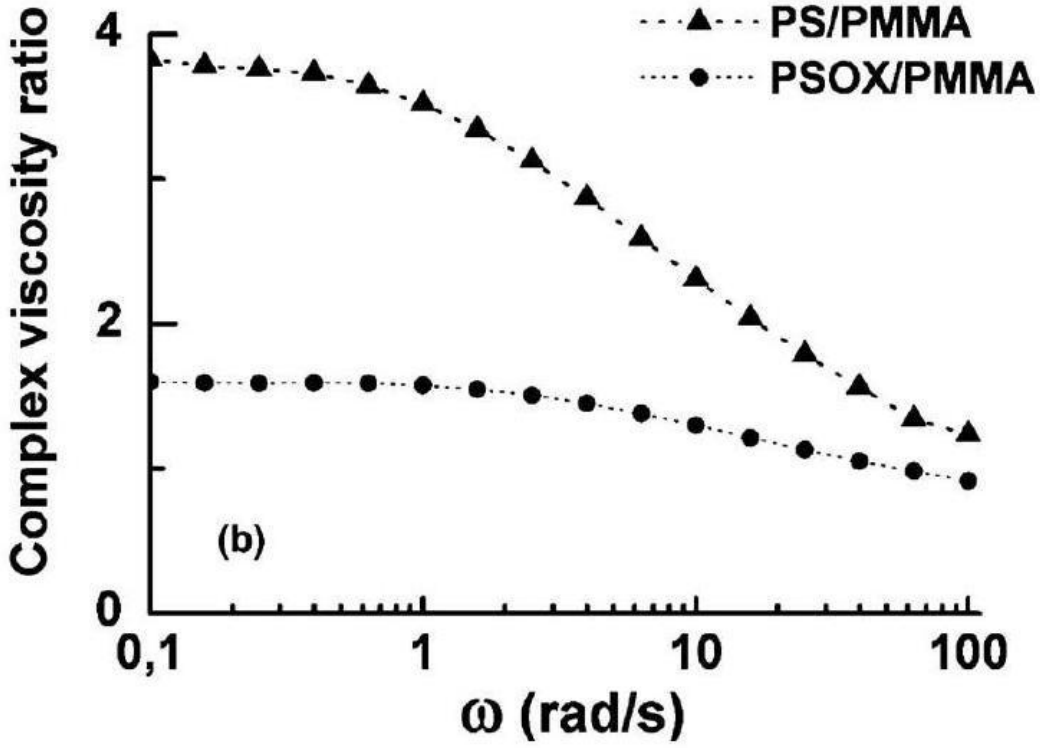

PS/PMMA
PSOX/PMMA
Complex viscosity ratio
4
2
0
(b)
0,1
1
10
100
ω (rad/s)

FIG. 2. (a) Viscosities of the pure components at 230°C. The open symbols are the steady shear viscosity; the full symbols are the complex viscosity. (b) Viscosity ratios at 230°C.

Rheometry

The rheological measurements were performed on circular disks (previously hotpressed) in the linear viscoelastic region in an ARES rheometer (TA Instruments). Samples were vacuum dried at 80°C for 12 h before each rheological experiment. Since degradation may occur during blend preparation, in order to have comparable results for the pure components and the blends, the former were also subjected to the same processing conditions in the mixer.

Oscillatory tests were performed for the pure components and blends at 230 °C, using a parallel-plate geometry with a 1.0 mm gap. For the samples with lowest moduli, 50 mm plates were used in order to increase the signal, while for the remainder, 25 mm diameter plates were used. Stress relaxation after applying a shear rate of 0.1 s^{-1} during a time interval of 250 s , which is enough to reach the steady state, was also investigated.

The extensional rheological measurements were performed on the modified rotational rheometer developed by Maia et al. (1999) at 205°C (the highest temperature at which the sample yielded a strong enough signal to be measurable). For both extensional start-up and relaxation extensional experiments, samples with rectangular cross-section (about 3×2 mm^2), prepared by compression molding, were used in order to increase the signal (force) measured by the rheometer. Upon loading onto the rheometer, residual stresses were first allowed to relax; once the measured torque decayed to zero, any existing slack was removed and once again the stresses were allowed to relax. The effective length of each sample was 40 mm and the diameter varied between 2 and 3 mm , thus yielding an aspect ratio, L/D, ranging between approximately 20 and 13. This has been shown [Barroso et al. (2002)] to be high enough for shear-related end-effects to be negligible. During all experiments, the samples were immersed in silicone oil at the test temperature for the dual purpose of temperature control and sagging prevention. The particular details on the experimental technique to measure the stress relaxation after an extensional step strain are given in Barroso and Maia (2002) and Barroso et al. (2003).

E. Small angle light scattering

Small angle light scattering (SALS) measurements were performed to study the deformation of the droplets and the interface. Light emerging from a He -Ne laser ($\lambda = 633$ nm) is sent through the sample that is contained within a Linkam shear cell (CSS 450). The anisotropy of the SALS patterns can be quantified calculating a second moment tensor from the measured light intensity on the two-dimensional charge coupled device array. Then, the anisotropy, ε, is given by the difference between the eigenvalues of this tensor [van Egmond et al. (1992); Vermant et al. (1998)]:

$$\varepsilon(\dot{\gamma},t) = \frac{\left[\left(\int d\vec{q} q_x q_x I(q,\dot{\gamma},t) - \int d\vec{q} q_y q_y I(q,\dot{\gamma},t)\right)^2 + 4\int d\vec{q} q_x q_x I(q,\dot{\gamma},t)^2\right]^{0.5}}{\int d\vec{q} I(q,\dot{\gamma},t)}, \qquad (1)$$

where I is the light intensity and q is the scattering vector with x and y corresponding to running coordinates in two perpendicular directions.

This calculation was done using in house developed salssoftware from K. U. Leuven. To avoid multiple scattering only the diluted blends (99/1/0 and 90/0/1) were used in the SALS experiments. The experiments were performed at 230 °C.

RESULTS AND DISCUSSION

A. Viscosity of the pure components

Figure 2(a) shows the steady state and the complex viscosities of the pure components as functions of shear rate and frequency, respectively. These materials are thermorheologically simple and thus the Cox-Mertz rule is valid. Figure 2(b) shows the viscosity ratios between the two polystyrenes (with and without oxazoline) and the PMMA matrix at 230 °C. At low frequencies, the viscosity ratios between PS and PMMA and PSOX and PMMA are 3.8 and 1.6, respectively. They decrease as the frequency (shear rate) increases reaching the values approaching unity at high frequencies. This behavior means that the stress relaxation experiments (which were performed after the imposition of a shear rate of 0.1 s^{-1}) were performed in blends of relatively high viscosity ratios.

B. Blend morphology

The morphology of the blends after the mixing process was analyzed by SEM. Figures 3(a) and 3(b) depict the micrographs of PMMA/PS (80/20/0) and PMMA/PSOX (80/0/20) blends, respectively, which exhibit the same morphology type, i.e., droplets of PS or PSOX dispersed in a PMMA matrix. However, it is possible to observe a difference in particle size, which is smaller for the blend with PSOX. The values of R_n and R_v obtained after particle size quantification were 0.30 and 0.50μ m for PMMA/PS and 0.12 and

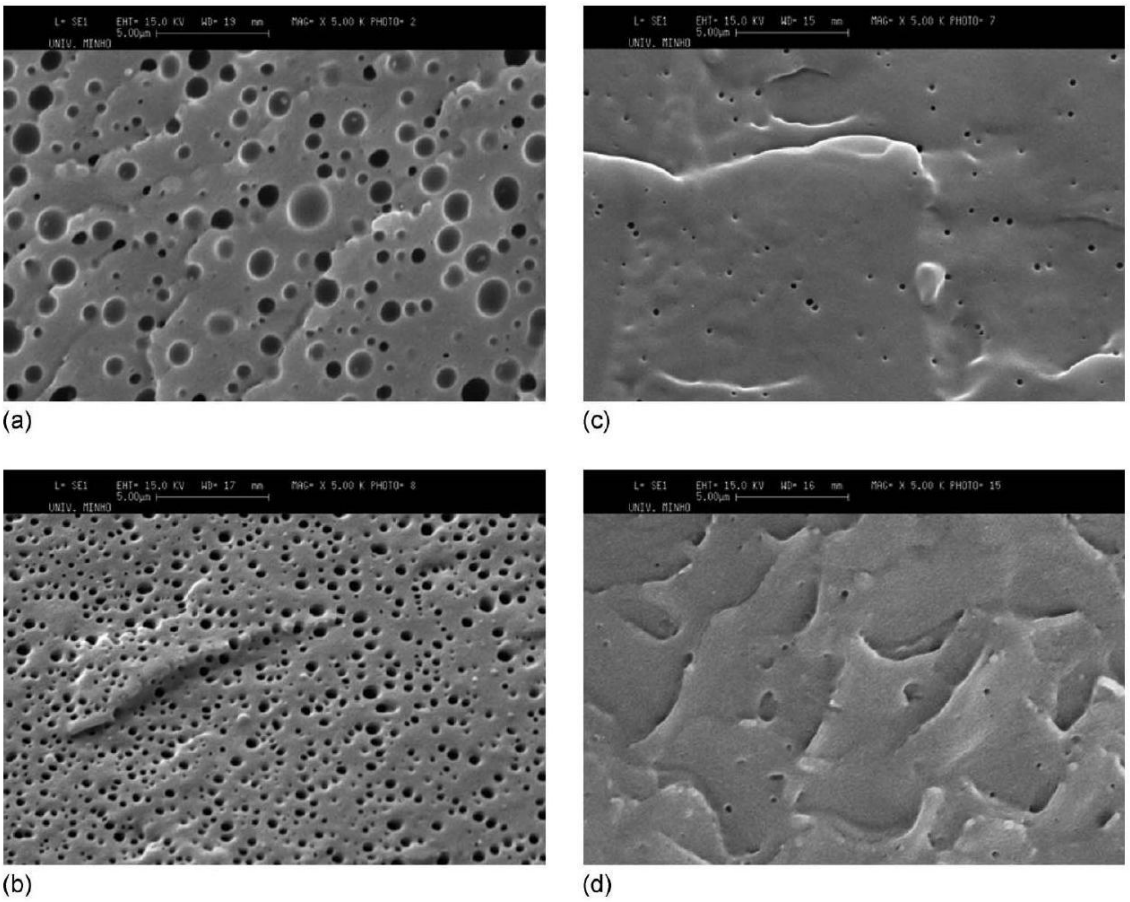


FIG. 3. SEM micrographs of the (a) 80/20/0, (b) 80/0/20, (c) 99/1/0, and (d) 99/0/1 blends.

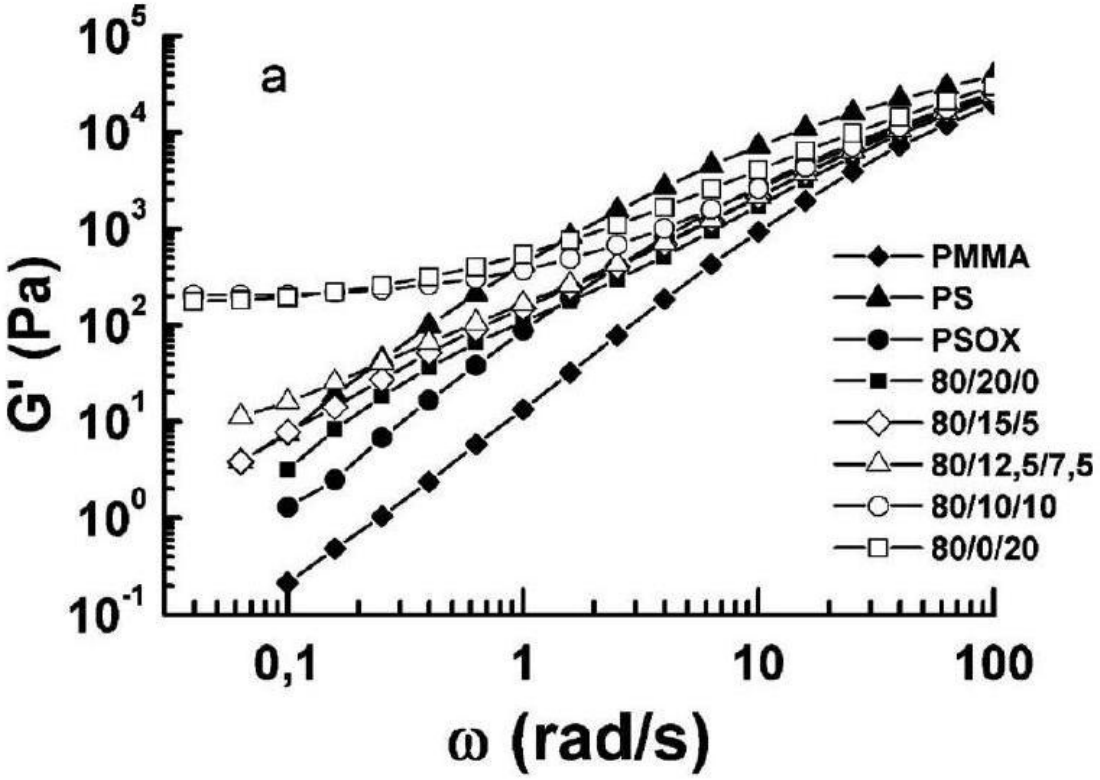
0.17μ m for PMMA/PSOX, respectively This difference can be explained by the expected miscibility difference between PMMA/PS and PMMA/PSOX; the presence of the oxazoline groups increases the interactions between both polymers which results in lower interfacial tension and consequently smaller particles size. Furthermore using the morphological data, the volume fraction of the dispersed phase was calculated for each blend as being approximately 17% for PMMA/PS and 9% for PMMA/PSOX. The fact that the latter is significantly lower than the original amount of 20% is a clear indication that there is at least partial miscibility between PMMA and PSOX.

The dilute blends (with 1% of dispersed phase) also show droplet-matrix morphology with similar dimensions but with smaller droplet sizes. In these cases, $R_n = 0.09\mu$ m for both 99/0/1 and 99/1/0 and $R_v/R_n = 1.2$ and 1.1 for 99/1/0 and 99/0/1, respectively [Figs. 3(c) and 3(d)].

Since the mixing conditions were the same for all blends, the differences in the morphology of the diluted and concentrated blends is due to the fact that the former are less prone to coalescence than the latter (in the non-compatibilized blends) because the probability of collision of two droplet is lower and because the dynamic equilibrium is established at lower droplet sizes [Grizzuti and Bifulco (1997); Vinckier et al. (1998)].

Linear viscoelastic behavior

The dynamic storage and loss moduli of the three pure components and the concentrated blends, at 230 °C, are shown in Figs. 4(a) and 4(b), respectively. The PMMA/PS blend shows a behavior typical of immiscible polymer blends, with the dynamic moduli


a
G' (Pa)
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
0,1
1
10
100
ω (rad/s)
PMMA
PS
PSOX
80/20/0
80/15/5
80/12,5/7,5
80/10/10
80/0/20

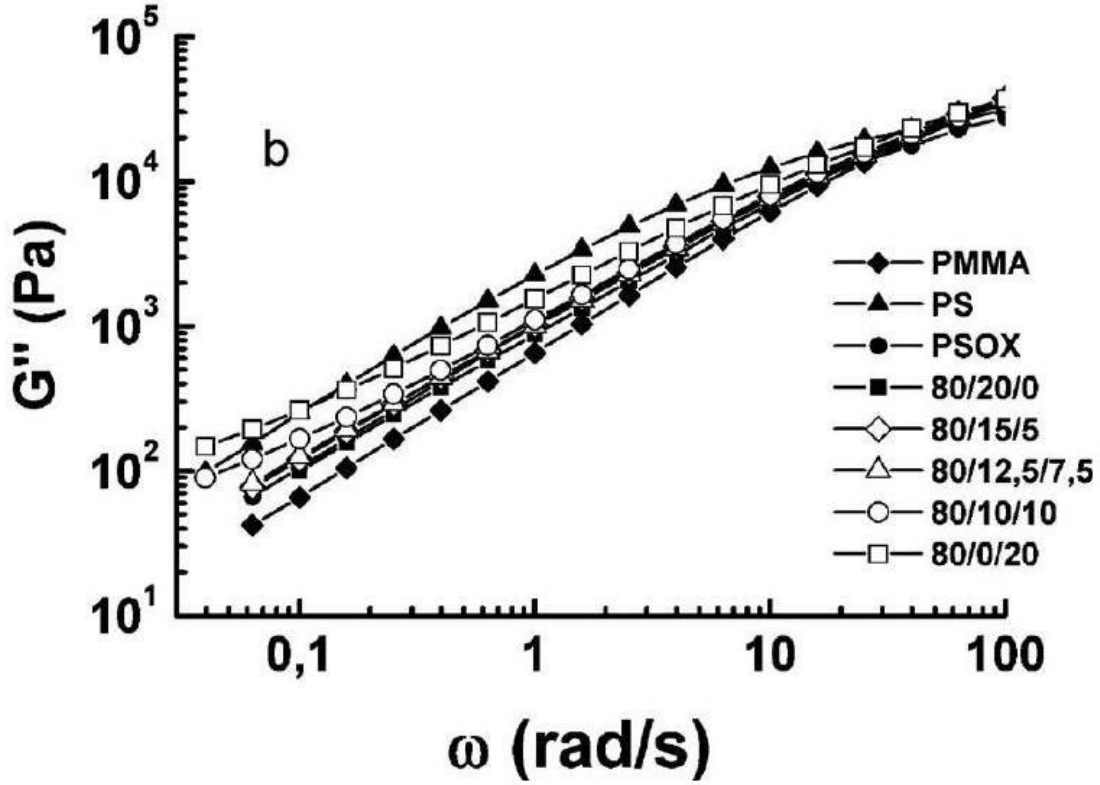

b
G'' (Pa)
10^5
10^4
10^3
10^2
10^1
0,1
1
10
100
ω (rad/s)
PMMA
PS
PSOX
80/20/0
80/15/5
80/12,5/7,5
80/10/10
80/0/20

FIG. 4. Moduli for PMMA, PS, PSOX, and the blends at 230°C. (a) Storage and (b) loss moduli.

being able to be fitted to the Palierne model [Palierne (1990)]. In the blends containing modified polystyrene, it was observed that the increase in PSOX concentration causes a very large increase in the dynamic moduli at low frequencies (more than two orders of magnitude in G', for example), giving rise to the appearance of a large shoulder in G' at frequencies below approximately 1rad/s. In G' this increase is particularly large when the PSOX concentration goes from 7.5 to 10% wt and remains nearly constant thereafter, thus indicating that there may exist a critical concentration of PSOX above which there are no significant changes in rheological behavior as a function of %PSOX added. Moreover, the observed plateau [also previously observed by other authors in compatibilized blends, e.g., Yee et al. (2007), Sailer and Handge (2007), and Fahrländer et al. (2001)] suggests that the presence of interactions at the interface, which increases the interfacial thickness and decreases the interfacial tension, plays a crucial role in the rheological behavior. Thus, in agreement with the morphological results, the presence of oxazoline groups results in partial miscibility of the polymers and changes the nature of the interface.

This behavior cannot be explained by the relaxation of droplets of the dispersed phase only. For example, if one tries to fit any form of the Palierne model [Palierne (1990)] to the data of the blends with higher concentrations of PSOX, the obtained values of the interfacial tension are totally unrealistic.

The elongational measurements, the results of which are depicted in Fig. 5 for the

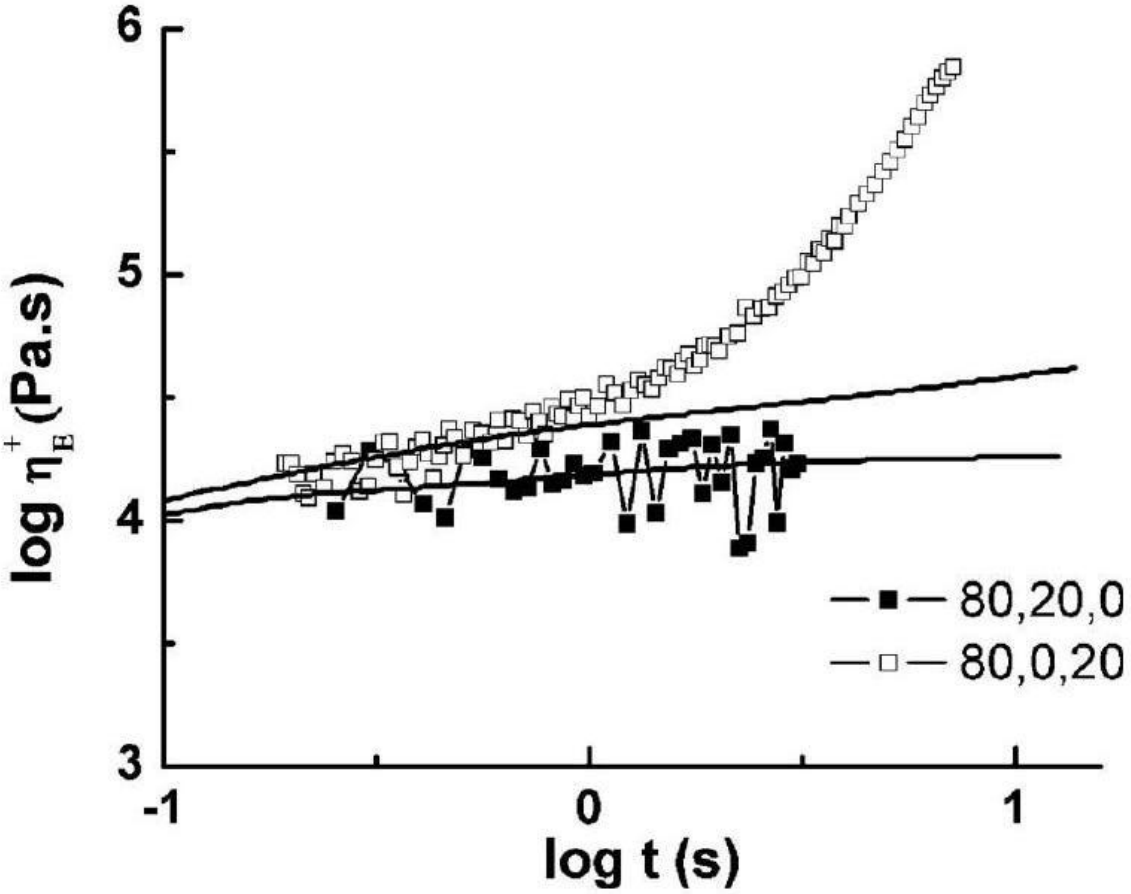


FIG. 5. Transient uniaxial extensional viscosity at 205°C for 80/20/0 and 80/0/20 blends (strain rates of 0.46 and 0.24 s^{-1}, respectively) and corresponding curves (solid lines) for the linear viscoelastic regime.

samples with highest concentrations of PS and PSOX, show that while the 80/20/0 blend follows linear viscoelastic behavior, the 80/0/20 blend exhibits strong strain hardening, which is in agreement with the results in oscillatory shear. The results above indicate that the presence of the oxazoline groups change the interfacial properties and the corresponding rheological behavior dramatically.

It is known that oxazoline groups react with carboxylic acids, acid anhydrides, and phenolic hydroxyls. However, no chemical reaction is known to occur between oxazoline and methacrylate groups, but to verify whether the introduction of PSOX leads to formation of new chemical species, Fourier Transform Infrared Spectroscopy (FTIR) was used.

FTIR and interfacial tension

After compression of a small sample of each blend (80/20/0 and 80/0/20), FTIR spectra were recorded in transmittance mode (Fig. 6). These are very similar, indicating that no reaction took place when oxazoline groups were present. Thus, from FTIR it is possible to state that during blending there was no formation of new chemical species at the interface, or the amount that could be formed was so low that cannot be detected by this technique.

However, it is known that specific interactions between polymer chains may result in a decrease in the mixing enthalpy, resulting in a decrease in the interfacial tension and increase in the interphase thickness [Koning et al. (1998)]. Thus, it is likely in view of the morphological and dynamical shear results that such interactions between the acetate groups of PMMA and the oxazoline groups of PSOX indeed exist and result in physical compatibilization and at least partial miscibility of the polymers; if this is the case, then the interfacial tension between the polymers should also be lower.

Figure 7 shows the evolution of interfacial tension for both PMMA/PS and PMMA/ PSOX measured through the pendant drop technique at 210°C. The interfacial tension measurements were performed using an OCA 15 system from DataPhysics. PMMA was introduced in a needle, which was then heated to 205°C. This PMMA drop was injected in PS or PSOX, which were placed in an optical transparent glass cell. The system was maintained at 205°C at all times and the evolution of drop profile was analyzed by SCA

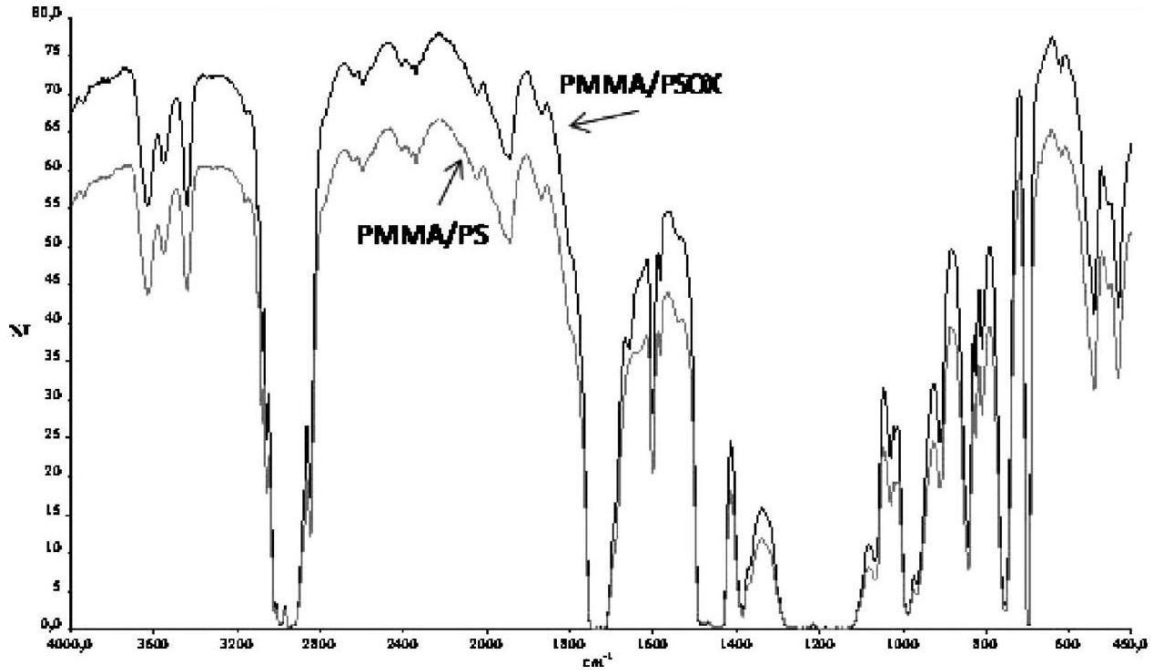


FIG. 6. FTIR spectra of PMMA/PS and PMMA/PSOX blends.

software using the Laplace-Young fit. Typically, the drop shape stabilizes after 6 h . The results confirm the hypothesis above; in both cases the shape of the drop becomes nearly constant after some time but an approximately 15% lower value of interfacial tension is observed for PMMA/PSOX (3.0mN/m) than for PMMA/PS (3.5mN/m). The values are themselves higher than those in the literature for PMMA/PS, which are closer to 1.2mN/m at 190 °C [Ellingson et al. (1994)] and 0.9mN/m at 200 °C [Carriere et al. (2000)], obtained using the embedded drop retraction method. We cannot offer an obvious explanation for these differences, although it is possible that due to the long times involved, material degradation may have started to affect our data. However, our values were reproducible, show clear differences between materials, and are compatible with the rheological and morphological results, so it was decided to utilize them nonetheless.

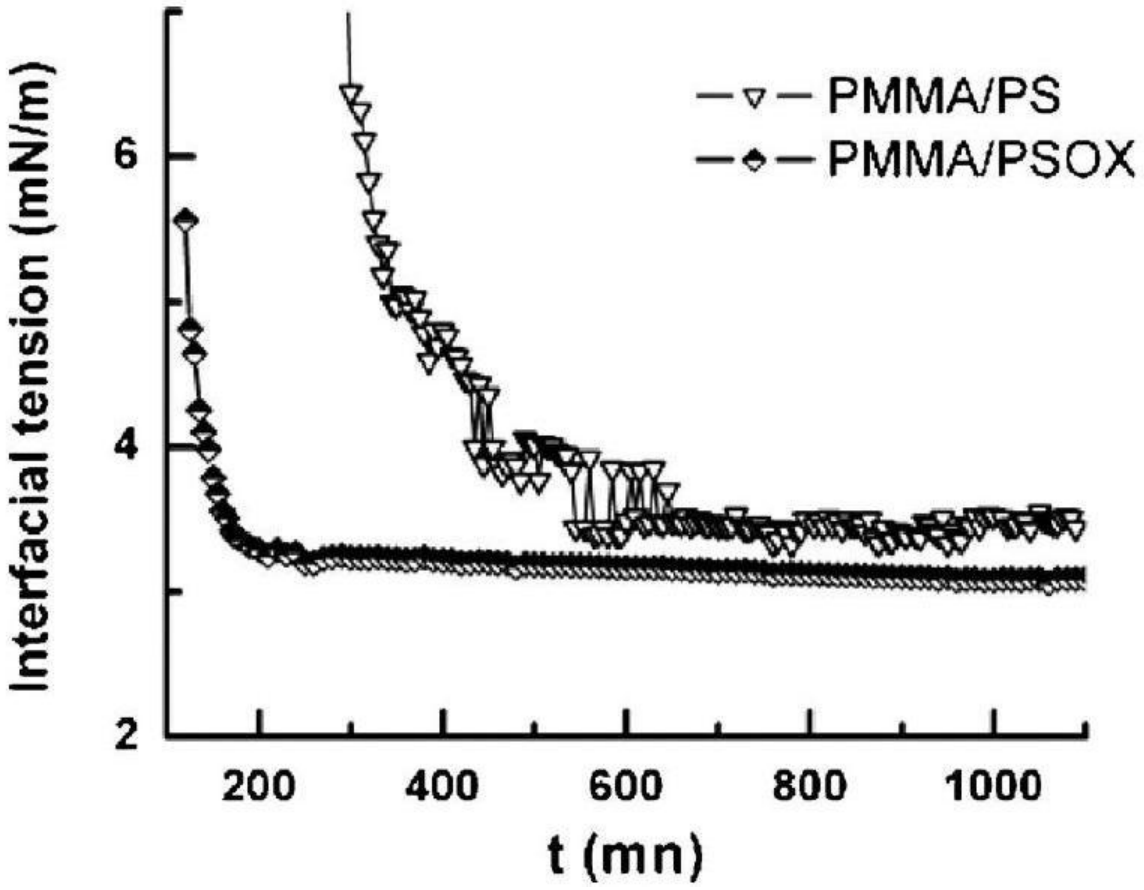


FIG. 7. Evolution of interfacial tension as measured by pendant drop method at 210°C.

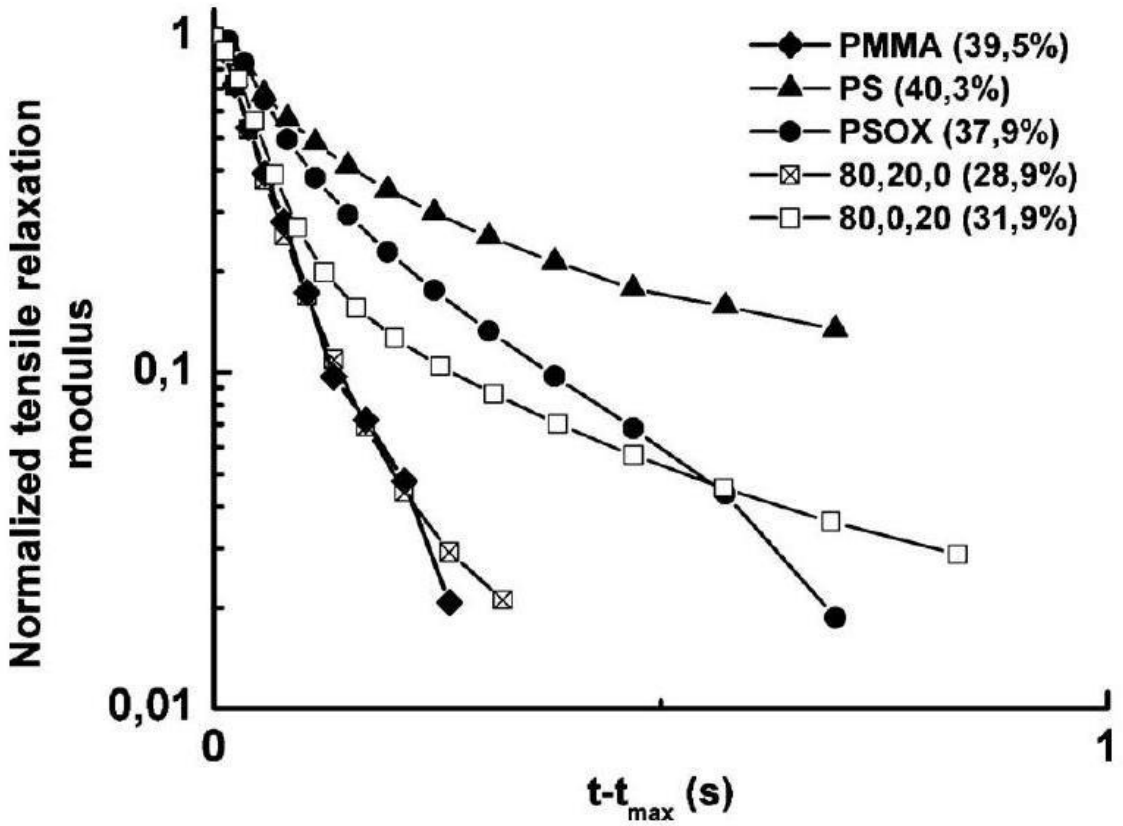


FIG. 8. Normalized transient extensional stress for concentrated blends of PMMA/PS/PSOX, and their individual components, at 205°C, after a step extension. The difference between actual time and time corresponding to maximum stress is represented in x-axis. The stress is normalized by its maximum. The Hencky strains, in percentage, applied to each sample are indicated.

Although we are not certain of what these physical interactions may be, among the best candidates are the formation of hydrogen bonds and van der Waals interactions between PMMA and PSOX.

E. Relaxation after cessation of flow

Although partial miscibility between PMMA and PSOX is now established, at this point it is not clear whether the plateau at low frequencies in G′ and strain hardening behavior in extension observed for 80/0/20 blend is due to a larger deformation of the droplets and/or to existence of strong physical interactions at the interface of the 80/0/20 blend that are not present in the 80/20/0 blend. One way to determine for sure whether these results are really due to interfacial effects is to perform stress relaxation experiments after flow and compare the relaxation kinetics of the PMMA/PS blend and the blends containing PSOX.

The aim is to test the elasticity of the interfaces while deforming the disperse phase droplets as little as possible. This can be better achieved in extension than in shear, namely, by resorting to stress relaxation experiments after a step ($\varepsilon \sim 30\%; t < 0.15$ s) uniaxial extension. The results for the tensile stress relaxation modules normalized by its

highest, i.e., initial, value are depicted in Fig. 8 and show that the 80/20/0 blend follows essentially the relaxation of matrix, as expected, while the blend with PSOX shows a second relaxation process, inasmuch as after a short time in which the blend follows the relaxation of the matrix, a much slower relaxation process is observed. At long times the relaxation modulus of the 80/0/20 blend even becomes higher than the relaxation modulus of the PSOX dispersed phase. This effect was attributed previously [Silva et al. (2007)] to the slow relaxation of the highly elastic disperse phase in PA6/EPM-g-MA blends, but clearly the present results indicate that this alone cannot explain the phenomenon and that the interface may play at least a similar role because the droplets undergo very little deformation. Mechbal and Bousmina (2007) investigating compatibilized blends observed that much slower stress relaxation is obtained at higher copolymer compatibilizer concentrations, i.e., above a critical concentration of saturation of the interface. This effect was attributed to entanglements in the interfaces.

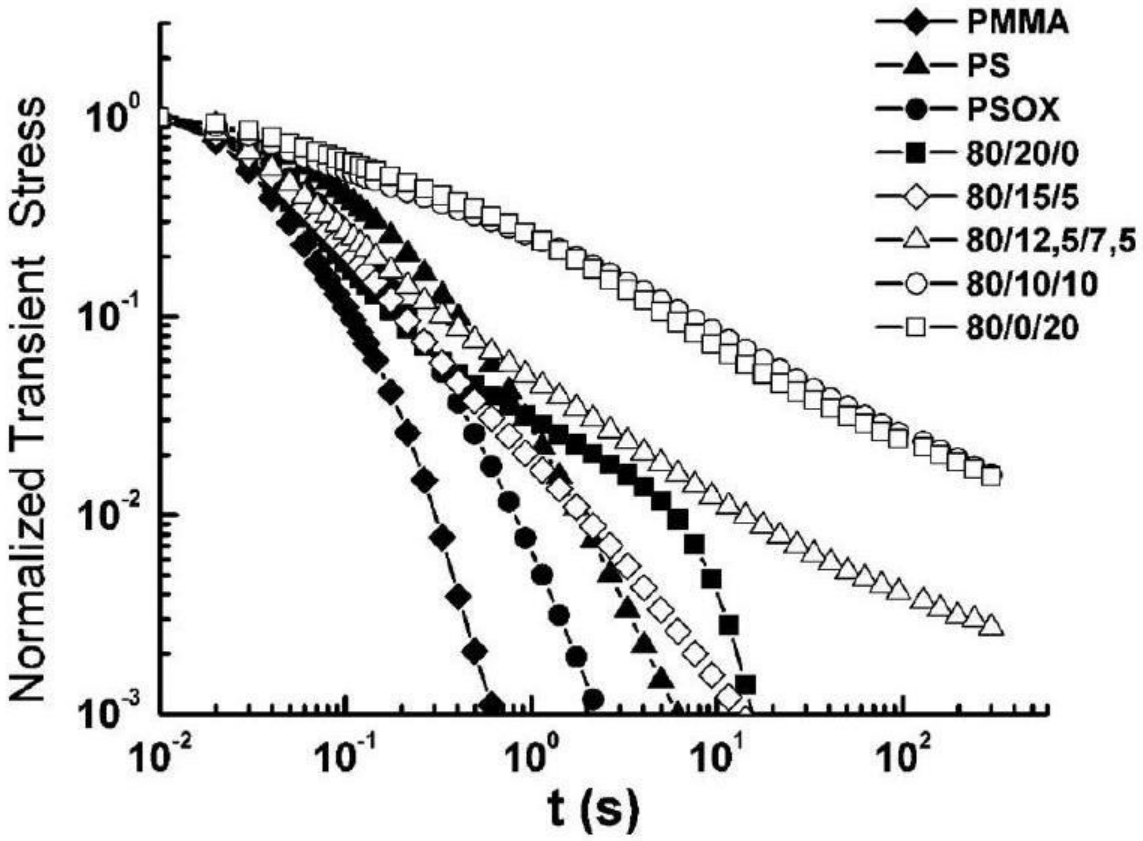


FIG. 9. Normalized transient stress for concentrated blends of PMMA/PS/PSOX and their components after cessation of a steady shear flow of 0.1 s^{-1} for 250 s , at 230 °C.

Since stress relaxation experiments after a step strain in shear were not conclusive due to the low measured signals, the next set of experiments performed was that of stress relaxation after steady shear, i.e., when a finite droplet deformation is expected, with the results being depicted in Fig. 9 for a number of blends with varying PS and PSOX ratios. These indicate clearly that at long times all blends relax slower than the pure components. The blend without PSOX (80/20/0) shows a well-defined two-step relaxation process: a first fast relaxation due to the molecular relaxation of the PMMA matrix followed by a second step probably related to the relaxation of the PS droplets

With the introduction of the PSOX, the two-step relaxation becomes less evident. In fact, the shape of the curves and the increase in the relaxation times indicate that there is a fundamental change in relaxation mechanisms that at the moment is still not clear. This effect has been seen before, e.g., by Van Hemelrijck et al. (2004) and Van Puyvelde et al. (2001) that predicted indirectly an additional relaxation time from the calculation of the relaxation spectra of compatibilized blends.

Figure 10 shows the time necessary for the reduced relaxation modulus to decrease to

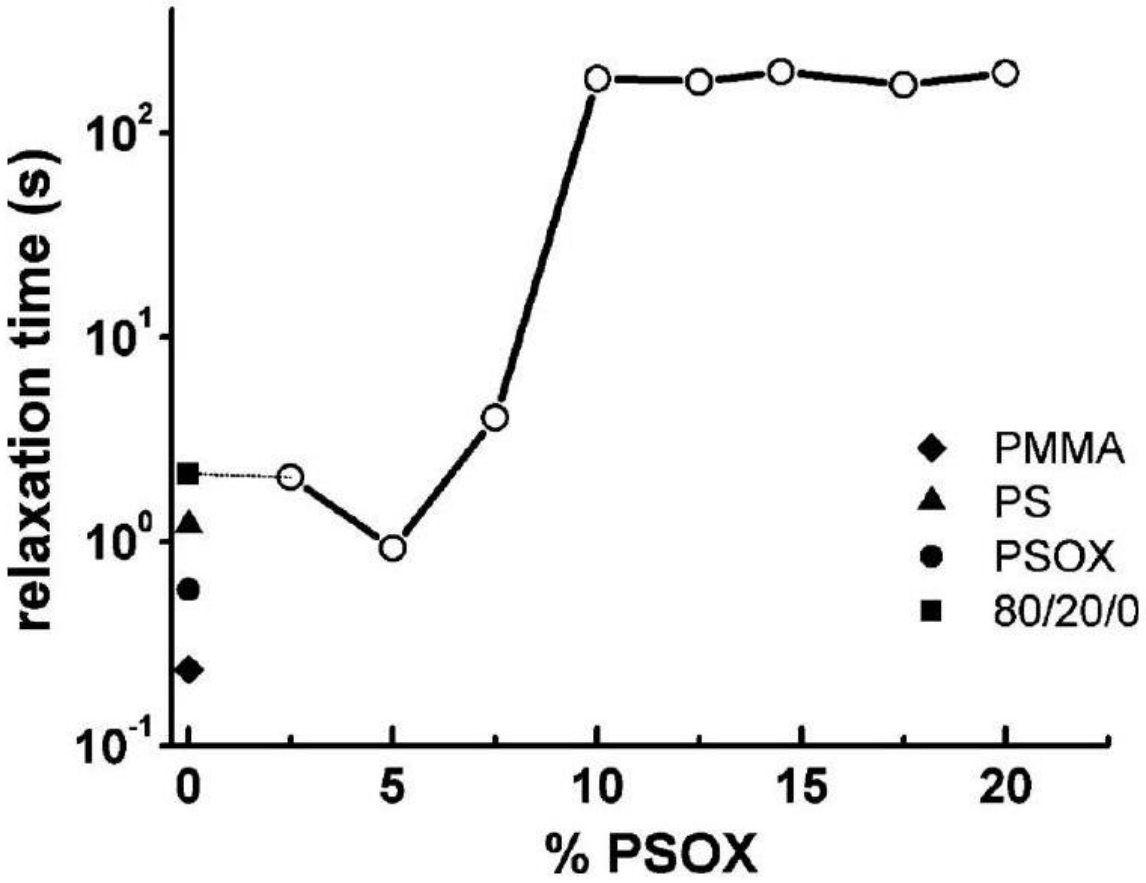


FIG. 10. Time taken by the blends and their components to relax the stress to 2% of the initial value.

2% of the original value vs the concentration of PSOX. This time was dubbed, for simplicity, "relaxation" time, although it was chosen arbitrarily as a point at which the differences between the different sets of data were evident and are not a true relaxation time. From the figure, it is clear that the increase of the "relaxation" time with increase of concentration of PSOX is not linear. At very low PSOX concentrations, the relaxation decreases slightly relatively to that of the immiscible blend, which can be explained by the faster relaxation of the PSOX droplets due to the improved adhesion to the less elastic PMMA matrix relatively to the PS. However, it then increases rapidly between 5 and 10 w/w%, at which point it becomes independent of the concentration of PSOX in the dispersed phase, as had already been observed in the storage modulus [Fig. 4(a)]; this is entirely consistent with the existence of a critical concentration for PSOX that leads to a saturation of the interactions at the interface, as predicted by Mechbal and

Bousmina (2007). Moreover, the blends above the critical concentration exhibit a very slow relaxation process lasting of the order of several minutes that, again, are consistent with the plateau in G' observed in the linear viscoelastic measurements.

These results not only confirm that PSOX is indeed acting as a compatibilizer, albeit a physical one, but also constitute the first real indication that the characteristics of the interface are very important because the amount of oxazoline group has a crucial role in the relaxation behavior role. In order to confirm this, SALS experiments were performed on dilute compatibilized and non-compatibilized blends at 1%w/w of PS or PSOX.

F. SALS

As mentioned before, in order to avoid the problems associated with multiple scattering, dilute samples (1 wt % of PS or PSOX in PMMA) were prepared for SALS investigations. In these experiments, samples being sheared at 2.5 s^{-1} were, after 800 s , submitted to a shear rate step to 70 s^{-1}, at which they are maintained for 250 s . After this time, the shear is suddenly removed and the sample is allowed to relax in time.

Figure 11 shows the results for the 99/1/0 blend and, as expected, the SALS pattern deforms highly in the neutral direction, thus indicating that the dispersed phase is being deformed in the flow direction. Moreover, the anisotropy shows an overshoot characteristic of orientation and/or break-up of the droplets. When the flow is stopped, the SALS pattern takes about 5 s to recover the isotropic shape, which is within the same time scale observed in stress relaxation experiments in shear (Fig. 9) and with the form relaxation times predicted from the Palierne model [Palierne (1990)], although the latter are derived for small-amplitude oscillatory shear and should be lower (which they are) and, thus, not directly comparable to the former.

Figure 12 depicts the results for the 99/0/1 blend and it too shows the existence of an overshoot in the anisotropy, but much smaller than for the 99/1/0 blend. Initially the droplets deforms in the flow direction as was observed for PMMA/PS blend. However, at long times the anisotropy pattern appears slightly deformed in flow direction, a trait that is present even upon the cessation of flow, which is an indication that dispersed phase is slightly deformed in the vorticity direction. This effect was seen before by several authors, e.g., Hobbie and Migler (1999), Lin et al. (2005), Mighri and Huneault (2006), and Migler (2000), and attributed to deformation of the dispersed phase in the vorticity direction in blends when droplets are more elastic than the matrix. All the above authors agree that this phenomenon depends critically on the difference in the elasticity of the components; thus, it cannot single handedly explain the observed behavior in our systems because the elasticity ratio between the PSOX and PMMA is relatively low and is even lower than that between PS and PMMA, as seen from Figs. 4(a) and 8(b). Additionally,

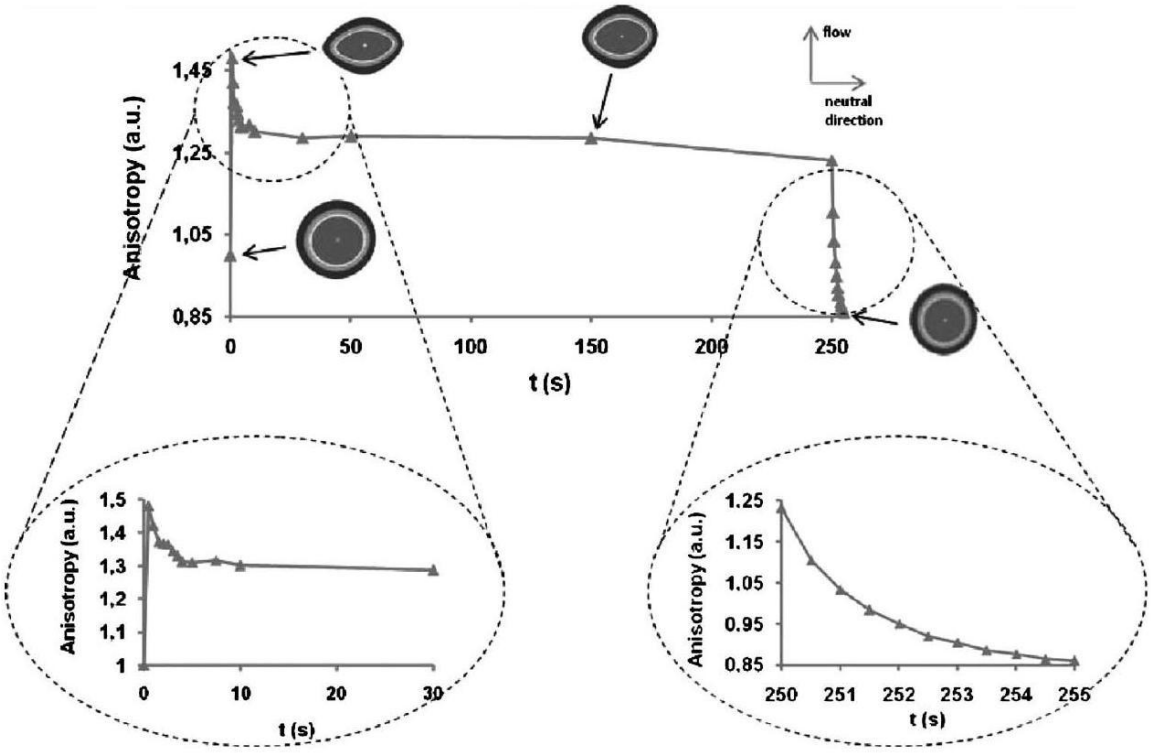


FIG. 11. Anisotropy as a function of time for the 99/1/0 blend. A step-up in shear from 2.5 to 70 s^{-1} is performed and the flow is stopped 250 s later. Representative SALS patterns are shown for each stage.

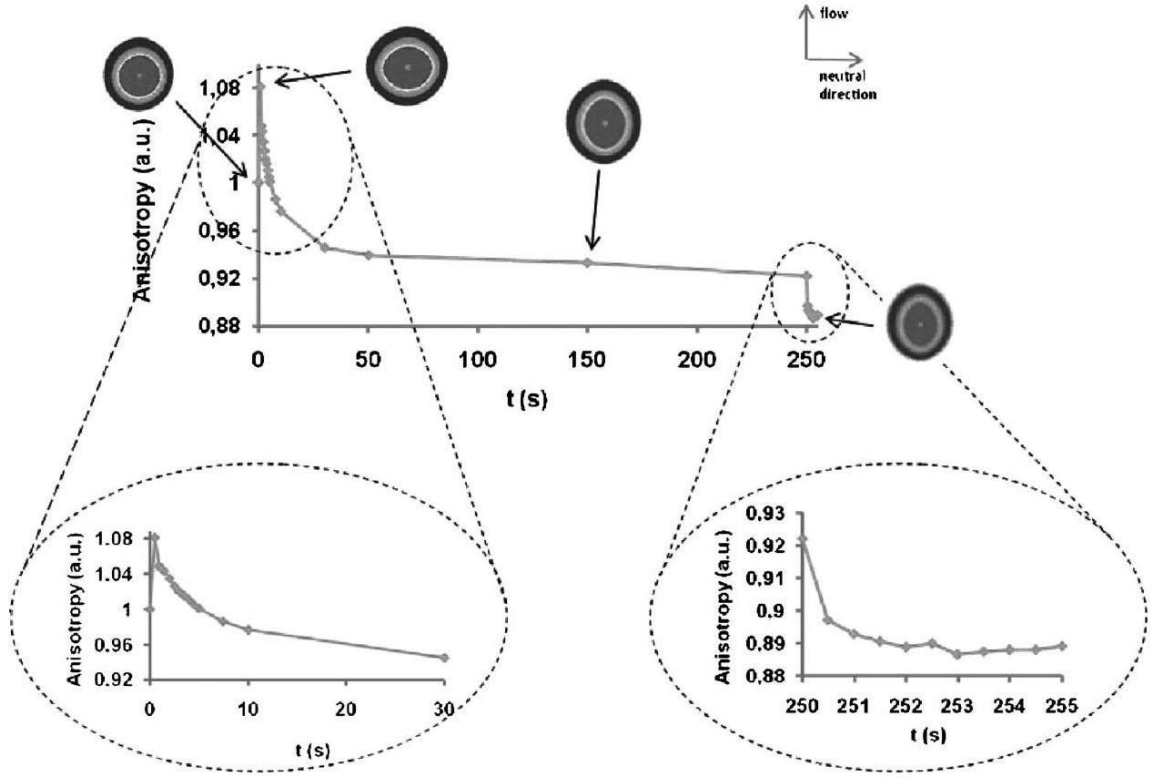


FIG. 12. Anisotropy as a function of time for the 99/0/1 blend. A step-up in shear from 2.5 to 70 s^{-1} is performed and the flow is stopped 250 s later. Representative SALS patterns are shown for each stage.
the dispersed phase remains slightly elongated in the vorticity direction during a long time, much higher than would be expected for structural relaxation of any of the materials per se. The only remaining feasible explanation for these results, which is consistent with all the data, is that of an increase in elasticity at the interfaces caused by the introduction of the oxazoline groups, with the consequent very slow relaxation upon cessation of flow.

CONCLUSIONS

In this work, we studied the role of the interface in the rheological behavior of polymer blends. With this purpose and in order to minimize the contribution of the deformation of the dispersed phase without making it so viscous that no deformation occurred, PMMA/PS and PMMA/PSOX blends with viscosity ratios slightly higher than 1 were used. Although no chemical bonds between PMMA and PSOX could be detected, the rheological results show that in blends containing PS modified with oxazoline, the interfaces have a different behavior. In particular, it was observed that the introduction of oxazoline leads to an increase in the relaxation times of the blends. Moreover, above a critical concentration of PSOX the rheological behavior of the blends almost does not change, which is an indication that at this concentration the interface becomes saturated with oxazoline groups. The SALS experiments indicated that the addition of PSOX increases the interfacial elasticity leading to droplet deformations in the vorticity direction at high enough shear rates. This increase in interfacial elasticity is due to additional interactions that result from introduction of oxazoline groups. Moreover, the results show that these additional interactions slow down the relaxation of the dispersed phase.

As a more general conclusion this work showed that even in the case of blends with viscosity ratios higher than 1 and high elasticity ratios, as many blends of industrial interest are, the behavior and characteristics of the interface are crucial to the rheological behavior and therefore these emulsions cannot be treated as suspensions of hard spheres.

ACKNOWLEDGMENTS

The authors thank the Foundation for Science and Technology (FCT) for awarding J.S. with a Ph.D. Fellowship (Ref. BD/12833/2003) within the framework of Programa Operacional "Ciência, Tecnologia, Inovação" (POCTI) and Programa Operacional Sociedade da Informação (POSI) of the Quadro Comunitário de Apoio III (2000-2006). The authors also wish to thank Loic Hilliou for helpful discussions and Peter van Puyvelde for the help with the training of J.S. in SALS equipment.

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