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# Deformation and Relaxation of PMMA/PS and PMMA/PSOX blends

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**Abstract.** In this work we study the role of the interfaces in the rheological behavior of blends of PMMA with PS and PS functionalized with oxazoline (PSOX). The blends here studied are concentrated (20 w% of dispersed phase) and have viscosity ratios higher than 1. Linear and non-linear (both in shear and extension) experiments were performed. In terms of relaxation, the cessation of flow after steady shear experiments reveal the appearance of second very slow relaxation mechanism in the PMMA/PSOX blend as do those upon cessation of a step uniaxial extension. Small Angle Light Scattering (SALS), performed on 1 w% dispersed phase blends, was used during step shear to infer about the relaxation of the droplets and/or interface and the patterns show that this behavior is not due to a higher deformation of the PSOX droplets, but should be attributed to a relaxation of the interfaces. The reason for the very high elasticity of the interface is not a priori obvious, but is probably related with the existence of extra physical entanglements at the interface in the PMMA/PSOX blends since the chemical analysis does not indicate any type of chemical interaction between the oxazoline groups and the PMMA.

**Keywords:** Polymer blends, Interface, PMMA/PS blends, stress relaxation.

## INTRODUCTION

Usually, immiscible blends have poor interfacial adhesion, their morphology is coarse and unstable and consequently the mechanical properties are bad. To overcome these difficulties and develop competitive materials with good properties compatibilization is often required. Compatibilization increases the interfacial adhesion between the components of the blend [1], produces a finer morphology, delays the coalescence of dispersed phase [2-3], and increases the interfacial elasticity.

Compatibilization can be achieved by different methods, such as through the addition of a pre-synthesized copolymer or by creating in situ, during the blending process, a third component, often called an interfacial agent, emulsifier, or compatibilizer. 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 [4-5].

The main aim of this study is to complement the literature about the deformation and relaxation of the dispersed phases and interfaces (p.e.[6]) through the analysis of the linear and non-linear viscoelastic and rheo-optical behavior of PS/PMMA and PSOX/PMMA polymer blends. In particular we aim to investigate the influence of the introduction of the oxazoline groups in the PS chain on the characteristics of the interface and the subsequent deformation and relaxation mechanisms. The reasons for the choice of the polymers were that they are both optically transparent, which facilitates rheo-optical measurements, they are relatively inelastic, thus allowing disperse phase elasticity to be largely neglected but still show relatively high viscosity ratios (between 2 and 4 at the relevant shear and extension rates).

## MATERIALS AND EXPERIMENTAL PROCEDURE

The blend components are commercial grades of poly-methylmethacrylate (PMMA, Altuglas VSE UVT, MFI 27g/10min at 230°C with 3.8Kg) and polystyrene (PS, Solarene G116, MFI 2.3g/10min at 200°C with 5Kg). The oxazoline functionalized polystyrene (PSOX, Epocros RPS-1005, 6-10 g/10 min at 200°C with 5Kg) was provided by Nippon Shokubai. The amount of the oxazoline in PSOX is 1.9 wt%.

Both dilute (1 wt.% of dispersed phase) and concentrated blends (20 wt.% of dispersed phase) of PMMA/PS/PSOX were prepared in this work. All blends were prepared in a Haake batch mixer at a set temperature of 210 °C and a rotor speed of 80 rpm. After mixing for 600 s the total sample was removed. (TABLE 1).

TABLE (1) Composition of the blends.

	Blend (w/w/w)	PMMA (wt. %)	PS (wt. %)	PSOX (wt. %)
Concentrated blends	80/20/0	80	20	0
	80/10/10	80	10	10
	80/0/20	80	0	20
Diluted blends	99/1/0	99	1	0
	99/0/1	99	0	1

The morphology of all the blends was analysed by SEM (Scanning Electron Microscopy). The samples were fractured in liquid nitrogen and then the PS phase was removed in cyclohexane at 50°C during 1h. The morphology of the blends was studied, after gold plating the samples, using a Jeol JSM 6310F Scanning Electron Microscope.

The rheological measurements were performed in an ARES rheometer (TA Instruments). Samples were vacuum dried at 80°C during 12h 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 was also subjected to the same processing conditions in the mixer. The oscillatory tests were performed for the pure components and blends at 230°C, using a parallel-plate geometry with a  $1000 \pm 1 \mu\text{m}$  gap. For the samples with lowest moduli 50 mm plates were used in order to increase the signal, whilst for the remainder 25 mm diameter plates were used.

The stress relaxation experiments in shear were performed at 230 °C again using a parallel-plate geometry (diameter=25 mm) with a  $1000 \pm 1 \mu\text{m}$  gap; a shear rate of  $0.1 \text{ s}^{-1}$  during 250 s was applied and the evolution of the shear stress upon cessation of flow was measured.

The extensional rheological measurements were performed on the MRR (Modified Rotational Rheometer) developed by Maia et al. [7] at 205 °C (the highest temperature at which the sample yielded a strong enough signal to be measured). To experimental details see Silva et al. [8].

Small angle light scattering measurements (SALS) have been used to study the deformation of the droplets and the interface. Light emerging from a He-Ne laser ( $\lambda = 633 \text{ nm}$ ) is sent through the sample that is contained within a Linkam shear cell (CSS 450). 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.

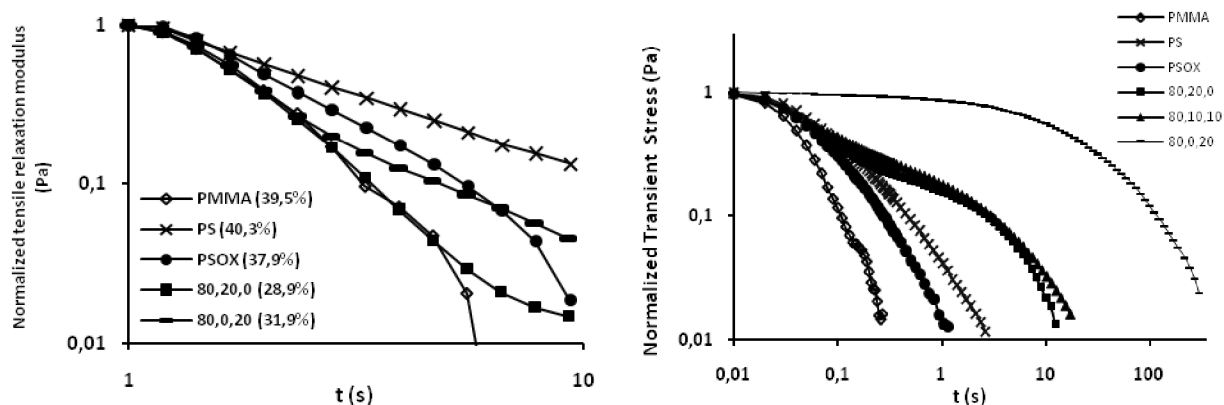
## RESULTS AND DISCUSSION

The concentrated blends containing PSOX show a finer morphology than the 80/20/0 blend. In terms of dynamic moduli, the blend with more oxazoline groups, exhibits a large elastic plateau in the storage modulus, suggesting that the extra interactions at the interface play a crucial role in the rheological behavior, inclusively being more important than the average size and size distribution of the dispersed phase. Since it was no found any evidence of some chemical reaction in the interface, the occurrence of hydrogen bonds and van der Waals interactions, between PMMA and PSOX for example, was attributed as the cause of the compatibilization effects of the oxazoline.

The relaxation experiments after a step extension results (see FIGURE 1a) show that the 80/20/0 blend follows essentially the relaxation of matrix, as expected, while the blends with PSOX shows a second relaxation process; at long times the relaxation modulus of the 80/0/20 blend becomes higher then the relaxation modulus of the PSOX dispersed phase. Thus, this clearly shows that there is strong stress build-up at the interface in these systems that may even surpass that inside the droplets.

The results for the relaxation behavior after steady shear (FIGURE 1b) indicate that all blends relax slower than the isolated components. For example, although PS, PSOX and PMMA show very quick (under 3 seconds) and

uniform relaxation processes the 80/20/0 and 80/10/10 blends show a two-step relaxation process: a first fast relaxation due to the molecular relaxation of the PMMA matrix followed by a second one slower related with the shape relaxation of the PS droplets.



**FIGURE 1.** (a) Normalized transient extensional stress for concentrated blends of PMMA/PS/PSOX and their components after cessation of a step extension, at 205°C. The time is normalized by that corresponding to maximum stress and the stress is normalized by its maximum. (b) Normalized transient stress for concentrated blends of PMMA/PS/PSOX and their components after cessation of a steady shear flow of  $0.1\text{ s}^{-1}$  for 250s, at 230°C.

The SALS experiments in the diluted blends, which have the same morphology, evidence that the droplets in blend without oxazoline are more deformed than the droplets of the 99/0/1 blend. For other hand the relaxation in 99/0/1 blend is slower appearing a pattern deformed in the flow direction which is probably caused by the anisotropy of the interface.

## CONCLUSIONS

Despite the chemical tests did no confirm any additional interaction between PMMA and PSOX, the morphological and rheological results show that PS modified with oxazoline has a different interfacial behavior. At enough amounts the presence of oxazoline groups in the interfaces has several effects: increase of interfacial elasticity, retard the deformation of the droplets and increase the relaxation time of the blend. The results indicate that the very slow relaxation observed in blend with more oxazoline groups is due to more strong entanglements in the interface that resist to deformation and causes a slower relaxation when flow is stopped.

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