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TESTING

## Material Properties

## Effect of the chemical structure on the linear viscoelastic behavior of acrylic and styrenic polymer blends

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## ABSTRACT

It was investigated the influence of chemical structure on the linear viscoelastic rheological behavior of polymer blends comprising acrylic and styrenic polymers. Fourier transform infrared spectroscopy revealed a different bands characteristic of the chemical structures of the polymers. The chemical compositions of the styrenic copolymers contain acrylonitrile at levels of 25 and 21%, respectively, which are within the miscibility window for PMMA/SAN and PMMA/ABS blends. Differential scanning calorimetry revealed the glass transition temperature for the polymers and for the elastomeric phase present in an elastomeric-particle-containing poly (methyl methacrylate) that are different to that of the elastomeric phase of ABS. The rheological data obtained at low frequencies in the linear viscoelasticity region, revealed significant changes in the rheological behavior of acrylic homopolymer, when compared to an acrylic polymer containing elastomeric particles (core-shell type). It was possible to indicate the miscibility of polymer blends by means of the linear viscoelastic rheological behavior.

## 1. Introduction

Studies into the rheological behavior of homopolymers, copolymers, and polymer blends, in their linear viscoelastic regions, provide important information about these materials, such as their melt molecular structures, molecular-weight distributions, viscoelasticities, and interfacial tensions, among others [1–4].

There are many graphical representations provided in the literature (described below) that can be used to qualitatively or quantitatively infer the rheological behavior of a polymer blend in its linear viscoelastic region. These results can be visualized in the forms of plots of storage modulus ( $G'$ ) or loss modulus ( $G''$ ) as functions of frequency ( $\omega$ ), Cole-Cole plots (imaginary viscosity ( $\eta'' = G''/\omega$ ) vs. dynamic viscosity ( $\eta' = G'/\omega$ )), or Han plots of  $G'$  as functions of  $G''$ , and these graphical data are influenced by the temperature, and variations in polymer composition and miscibility [2–6].

The miscibility window of a pair of polymers influences rheological behavior through interactions in the melt state during the formation of the polymer blend; consequently it is important that the interactions between poly (methyl methacrylate) (PMMA) and polystyrene (PS), styrene-acrylonitrile copolymer (SAN), and acrylonitrile-butadiene-styrene copolymer (ABS) are determined. PMMA/SAN and PMMA/ABS

polymer blends are miscible when the acrylonitrile (AN) content lies between 9 and 33 wt%, where they exhibit lower-critical-solution-temperature (LCST). PMMA is not miscible with either polyacrylonitrile (PAN) or polystyrene (PS), and PS/SAN blends exhibit upper-critical-solution-temperature (UCST) behavior at acrylonitrile volume fractions in the 4–20 wt% range; therefore, PS is miscible with SAN [7–9].

PMMA/SAN and PMMA/ABS blends are miscible as a result of the balance between dipole-dipole forces produced by acrylonitrile (AN) and the optimum concentration of the voluminous group in styrene (S) that transfers macromolecules from the SAN phase by attraction-repulsion effects present in SAN and ABS, thereby providing a means of varying the miscibility of the polymer-polymer pair [10–12].

Immiscible PMMA/PS polymer blends have widely been used by several researchers such as Han and coworkers [13] and Yee and coworkers [14], who showed that the rheological behavior in the linear viscoelastic region is due to low interfacial tension between the components. These researchers studied the rheological properties of pure polymers (PMMA and PS) and PMMA/PS blends by observing their rheologies under oscillatory dynamic testing, using  $\log G'$  and  $\log G''$  vs.  $\omega$ , or  $\log G'$  vs.  $\log G''$  curves. This work revealed that the curves for the pure polymers exhibited different slopes in the terminal zone to that of the PMMA/PS blend.

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In this way, the  $G'$  and  $G''$  analyzes were found to be very sensitive to variations in the morphological state of the polymer blends and showed that the PMMA/PS blend is immiscible, which can be attributed to the form of dispersed-particle relaxation. This plateau was more pronounced with increasing levels of the PS-dispersed phase in the PMMA matrix; however this behavior was not observed for blends containing 2 or 5 wt% PS, because no differences were observed in the rheology and in the morphology of the phases. The PS particle size also increased with increasing PA content due to interfacial tension [13–17].

Several authors [18–25] have studied the dynamic viscoelasticities in PMMA/SAN blends using SAN with different percentages of acrylonitrile (AN). Rheological studies revealed that PMMA/SAN blends are miscible when the acrylonitrile content in the SAN is in the 10–29 wt% range, and are immiscible when the acrylonitrile content lies outside of this range. These rheological observations on the melt state of these PMMA/SAN blends were characterized using  $\log G'$  vs.  $\log G''$  plots; these plots for miscible blends afforded straight lines with slopes of 2; however straight lines were not observed for the immiscible blends, suggesting that this characterization technique can be used to determine polymer-blend miscibilities.

Rheological studies on PMMA/ABS blends are important since it is known that the miscibility window for these blends lies between 9.5 and 33 wt% acrylonitrile content [12,26,27]. Kim and coworkers [12] performed a microrheological study on ABS/PMMA blends and showed correlations between the morphologies observed by transmission electron microscopy (TEM) and the corresponding complex viscosity ( $\eta^*$ ) curves as functions of frequency ( $\omega$ ). They observed that the AN percentage influences the miscibility of the PMMA/ABS blend; however, when the butadiene particles were grafted into the SAN matrix they did not affect the miscibilities of the PMMA/ABS blends, and the miscibility behavior was the same as that expected for PMMA/SAN blends. For PMMA/ABS blends with 24–27 wt% AN, miscibility was observed in both the morphological and dynamic-oscillatory rheological properties. ABS blends containing 35 wt% AN were observed to be immiscible.

Studies into the rheological behavior of polymer blends in the linear viscoelastic region have used dynamic-oscillatory rheological assays, as they are sensitive to changes in the chemical structures of the polymers, as previously shown by several researchers. This technique is an important method for the analysis of miscibility and the transition to the immiscible state. In addition, it can be used to predict other important properties of polymeric materials [12–29]. The objective of this work was to evaluate the effect of acrylic (PMMA homopolymer and elastomeric-particle-containing PMMA) and styrenic (PS, SAN, and ABS) polymers with different chemical structures on the formation of polymer blends in the melt.

## 2. Experimental

In this work, it was used the LEP-100 poly (methyl methacrylate) homopolymer (PMMA<sub>h</sub>) and the ECP-800 elastomeric-particle-containing poly (methyl methacrylate) (PMMA<sub>e</sub>), which were obtained from the Unigel Company. Polystyrene (PS) N 1921 was obtained from the Innova Company, while the Luran 358N acrylonitrile-styrene copolymer (SAN) and the Terluran GP-35 acrylonitrile-butadiene-styrene copolymer (ABS) were obtained from the Styrolution Company. Prior to any processing, the pure polymers and the polymer blends were dried in a vacuum oven for 12 h at 60 °C. Table 1 displays the MFI values of the polymers used in this study.

### 2.1. Preliminary characterization

#### 2.1.1. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy was performed on a Shimadzu IR Tracer 100 spectrometer. The spectra were used to determine the chemical structures present in the homopolymers and copolymers, and to calculate the percentage of acrylonitrile, butadiene,

**Table 1**  
Composition of pure polymers and PMMA/PS, PMMA/SAN, and PMMA/ABS blends, and their MFI.

Materials	Compositions (wt%)	MFI (g/10 min) <sup>a</sup>
PMMA <sub>h</sub>	100	4.4
PMMA <sub>e</sub>		1.3
PMMA <sub>h</sub> /PS	PMMA <sub>e</sub> /PS 80/20	7.7 3.6
PMMA <sub>h</sub> /SAN	PMMA <sub>e</sub> /SAN 80/20	4.8 2.2
PMMA <sub>h</sub> /ABS	PMMA <sub>e</sub> /ABS 80/20	5.1 2.5
PS	100	37.1
SAN		6.3
ABS		6.6

Measured by the authors: <sup>a</sup>(ASTM D1238: 230 °C and 3.8 kg).

and styrene in ABS using the calibration procedures and constants calculated by Mantovani [30]. The pure polymer samples were pressed into thin films using a hydraulic press at a temperature of 230 °C.

### 2.1.2. Elemental chemical analysis

1108 CHNS-O elemental analyzer was used to determine the nitrogen concentration of the acrylonitrile in the SAN and ABS samples.

### 2.1.3. Differential scanning calorimetry (DSC)

DSC was performed on a NETZSCH 200 F3 Maia differential scanning calorimeter, using a ~6 mg sample of each polymer under a nitrogen flow rate of 50 mL min<sup>-1</sup> and a heating rate of 10 °C min<sup>-1</sup>, from -120 to 150 °C, in a closed aluminum sample holder.

### 2.2. Polymer blends processing

The compositions of the polymer blends used are shown in Table 1. A co-rotational twin screw extruder from AX Plásticos Máquinas Técnicas, with a diameter of 16 mm and an aspect ratio of 40, was used to prepare polymer blends under the same processing conditions; i.e., with a temperature profile of 110, 160, 180, 200, 210, 220, 230, 230 and 220 °C from the feed zone to the die, with a feed rate into the filler of 80 rpm and a screw speed of 220 rpm.

### 2.3. Rheological characterization

Samples for rheological analyses were prepared in a Solab hydraulic press at a temperature of 230 °C, after which these materials were processed at a temperature of 220 °C in an Anton Paar MCR 302 rotational rheometer with parallel plates, in their regions of linear viscoelastic behavior. Rheological experiments for PMMA<sub>e</sub> were also carried out at a temperature of 270 °C, with the aim of evaluating the effect of temperature on the crosslinking storage modulus and the loss modulus of the copolymer.

### 2.4. Morphological characterization

Samples were cryo-fractured in liquid nitrogen and metallized with a thin gold layer. Morphological analyses were performed using a scanning electron microscope with field-emission gun in a Zeiss equipment model Auriga operated at 3 kV with LaB6 filament.

## 3. Results and discussion

### 3.1. Preliminary characterizations

Due to the structural complexities of the components used for the development of these polymer blends, it was necessary to carry out preliminary characterizations on the pure polymers to understand their rheologies.

Fourier transform infrared (FTIR) spectra of the pure polymers were

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