Material Properties

Effect of the chemical structure on the linear viscoelastic behavior of acrylic and styrene 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 styrene polymers. Fourier transform infrared spectroscopy revealed a different bands characteristic of the chemical structures of the polymers. The chemical compositions of the styrene 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 (ω), Cole-Cole plots (imaginary viscosity (η'' = G''/ω) vs. dynamic viscosity (η' = G'/ω)), 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. ω, 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.
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 micro rheological study on ABS/PMMA blends and showed correlations between the morphologies observed by transmission electron microscopy (TEM) and the corresponding complex viscosity (η″) curves as functions of frequency (ω). 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 (PMMAh) and the ECP-800 elastomer-particle-containing poly (methyl methacrylate) (PMMAe), which were obtained from the Unigel Company. Polystyrene (PS) N 1921 was obtained from the Terluran Company 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.

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, 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⁻¹ and a heating rate of 10 °C·min⁻¹, 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, 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 PMMAh 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 measured by the authors: a(ASTM D1238: 230 °C and 3.8 kg).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compositions (wt%)</th>
<th>MFI (g/10 min)</th>
</tr>
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<tbody>
<tr>
<td>PMMAh</td>
<td>100</td>
<td>4.4</td>
</tr>
<tr>
<td>PMMAe</td>
<td>1.3</td>
<td></td>
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<tr>
<td>PMMAe/PS</td>
<td>PMMAe/PS</td>
<td>80/20</td>
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<td>PMMAe/SAN</td>
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</tr>
<tr>
<td>SAN</td>
<td>6.3</td>
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<td>ABS</td>
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Measured by the authors: AASTM D1238: 230 °C and 3.8 kg.
acquired with the objective of identifying the different chemical structures present in the homopolymers and copolymers (Fig. 1).

The FTIR spectra of PMMA_h and PMMA_e exhibit characteristic C=O peaks at 1729 cm⁻¹. The spectra of PS and the styrenic copolymers (SAN and ABS) show absorption bands at 1351 cm⁻¹ attributable to styrene, while the characteristic absorption band of acrylonitrile is observed at 1987 cm⁻¹ in the spectra of the SAN and ABS copolymers. The absorption band observed at 906 cm⁻¹ is characteristic of butadiene and was observed in the spectrum of the ABS copolymer.

According to the literature [31–34] the types of copolymers with elastomers that can be used to toughen PMMA without loss of transparency are MBS, MABS, and PBA-co-PS. Bands corresponding to the C=C bonds of butadiene were not observed in the FTIR spectrum of PMMA_e, which may indicate the presence of another type of elastomer in PMMA_e. The chemical structure of PBA is similar to that of PMMA (Fig. 2); consequently, it is not possible to detect their different FTIR spectroscopy. No differences were observed between the spectra of PMMA_h and PMMA_e (Fig. 1), suggesting that PMMA_e possibly contains PBA in its composition.

Morphological studies performed by Reinaldo and coworkers [35,36] on RuO4-stained PMMA_h (using TEM) revealed the shapes of the core-shell particles of the elastomeric phases in PMMA_h and the presence of PS, since RuO4 preferentially stains the aromatic rings of PS. However, the characteristic absorption bands of the styrene in the PBA-co-PS copolymer in PMMA_e were not detected by FTIR spectroscopy, which is probably due to the shapes of the PBA-co-PS core-shell particles.

The percentages by weight of styrene (S) and acrylonitrile (AN) in SAN, and the percentage by weight of acrylonitrile (AN), butadiene (B), and styrene (S) in ABS, determined by CHNS-O elemental analyses and FTIR spectroscopy, are presented in Table 2. Inspection of Table 2 reveals that AN is present in SAN and ABS at levels of 25 and 21 wt%, respectively. These percentage values are within the miscibility window for mixtures developed with PMMA [12] [37]; consequently, the polymer blends studied in this work are miscible with SAN and the SAN-free phase of pure ABS.

The FTIR results reveal that ABS contains low concentrations of the elastomeric phase, with around 15 wt% of butadiene and a higher (64 wt%) concentration of styrene; the concentration of the elastomeric phase in a copolymer directly influences the rheological analysis results at low shear rates.

Table 2 lists the glass transition temperatures (T_g) of the pure polymers obtained by DSC, which reveals T_g values for the acrylic polymers (PMMA_h and PMMA_e) of around 100 °C; however PMMA_e also showed a T_g value of around ~18.7 °C that is related to the thermal transition of the elastomeric phase. Mina and coworkers [34] studied PMMA_h and observed a T_g value close to that found in this work. The glass transition temperatures for the PS and SAN polymers, as well as the elastomeric phase (polyybutadiene) of ABS were determined; PMMA_h and ABS possess distinct elastomeric phases with T_g values of ~18.7 and ~86.2 °C, respectively. Therefore, the elastomeric phase of PMMA_e used in this work is not methyl methacrylate-butadiene-styrene copolymer (MBS) or methyl methacrylate-acrylonitrile-butadiene-styrene copolymer (MABS), as proposed by other authors [31], but the PBA-co-PS copolymer as corroborated by the FTIR results.

3.2. Rheological behavior of the pure polymers

Fig. 3 displays the rheological dynamic oscillatory results for the pure PMMA_h, PMMA_e, PS, SAN, and ABS polymers at 220 °C in the 628–0.06 rad/s frequency range, which revealed their storage moduli (G’) and loss moduli (G″) of PMMA_h (Fig. 3a) and PS (Fig. 3d) exhibited typical rheological behavior of a homopolymer [2], and SAN (Fig. 3c) (a random copolymer with a single phase) exhibited similar behavior to the homopolymers, while PMMA_e (Fig. 3b) and ABS (Fig. 3f) exhibited different rheological behavior due to the presence of their elastomeric phases.

ABS is a material that is partially composed of rubber; consequently these copolymers exhibit solid-like behavior, where G’ > G″ at low frequencies and G’ is constant in the linear region (Fig. 3f). However, this rheological behavior was not observed at 220 °C for PMMA_e, which also contains an elastomer in its composition (Fig. 3c); its terminal zone displays G’ and G″ curves that are very different to those of PMMA_h (Fig. 3a), indicating that the rubbery phase of PMMA_e influences its rheological behavior.

The rubbery phase causes differences in the G’ = G″ cross-points of the copolymers (where the dissipative feature is equal to the elastic feature at the same frequency), when compared with those of the homopolymers at 220 °C. In the homopolymers and in SAN, the G’ = G″ crosses occur at high frequencies and only at single points. ABS at 220 °C exhibits a band of G’ = G″ crosses (Fig. 3f), rather than a single angular-frequency point as was observed for PMMA_e, PS, and SAN (Fig. 3a, d, and e).

On the other hand, while the rheological behavior of PMMA_e showed a single cross-point at 220 °C (Fig. 3c), two G’ = G″ cross-points
were observed at 270 °C, the first at a high frequency (ω = 160 rad/s) and the second at a low frequency (ω = 0.65 rad/s), confirming that temperature influences the rheological properties at low frequencies, thereby altering the log G′ and log G″ vs. log ω curves. boussmina and Muller [27] and Pakula and coworkers [28] reported similar behavior for other copolymers containing rubber. In these studies, the G′ = G″ cross-points were attributed to network-type structures formed through the association of elastomeric particles; the first crossings at high frequencies were attributed to segmental movements and the second crossings at low frequencies are related to chain orientations or chain relaxations.

Fig. 6a reveals linear plots of ω vs. log G′ and G″ slopes (slope = 2) for the pure polymers, the homopolymers (PMMAh and PS), and the random copolymer (SAN), with the log G′ vs. log G″ curve for the SAN copolymer overlapping with that for the PS-homopolymer. However, the curves for the copolymers containing rubber are not linear.

Viscosity is an important rheological property during the processing of melt polymers, since flow rates, pressure drops, and temperature increases depend directly on this property. Viscosity is indicative of the resistance of a polymer to a given type of flow and can be measured in the steady state η(γ) or in the oscillatory dynamic regime η(ω) [1–3].

PS, SAN, and PMMAh exhibit Newtonian behavior at low frequencies (Fig. 4b), however PMMAe and ABS did not, over the analyzed frequency range. Raha and coworkers [38] claimed that the absence of Newtonian plateaus for copolymers containing rubber phases is attributed to the slow relaxations of these phases.

These multiphase systems exhibit complex rheological behavior mainly in the presence of elastomeric phases that change the behavior of the G′ and G″ vs. ω, η(γ) vs. ω, G′ vs. G″, and η(γ) versus η(ω) plots for blends containing these polymers.

Fig. 5 shows the analysis strategy of the effect of chemical structure on the rheological behavior of the polymer blends; i.e., the effect of the styrene, acrylonitrile, and butadiene monomer concentration in relation to the major, poly (methyl methacrylate), component.

PMMA (the main component of the polymer blend) has excellent optical characteristics and is used in a variety of applications, including glazing, panels, advertising signs, aircraft windows, and decorations, among other applications [39]. In this research were developed polymer blends with styrenic polymers (minority component) using acrylonitrile that provides thermal and chemical resistance, butadiene that provides better resistance and elongation, and styrene that is responsible for brightness, mobility and stiffness, in the polymer blend [40,41].

Correlations between the structures and the properties of the pure polymers and copolymers were observed during preliminary characterizations, in which distinct rheological properties (Figs. 3 and 4) were compared with the various acrylic and styrenic polymer structures (Fig. 5) used in the formation of polymer blends.

3.3. Rheological behavior of the polymer blends

The rheological behavior data for the PMMA/PS, PMMA/SAN, and PMMA/ABS blends were evaluated as functions of storage modulus (G′), angular frequency (ω), and illustrative morphology (Figs. 6–8). PMMA/PS systems containing PMMAh and PMMAe exhibit typical rheological behavior of an immiscible polymer blend (Fig. 6a). Illustrative morphology (Fig. 6b and c) and obtained by SEM (Fig. 6d and e) display the dispersed phases of polystyrene and polystyrene/core-shell particles in PMMA/PS and PMMA/ABS blending.

These polymer blends exhibited G′ values above those of the constituent polymers, which Yee and coworkers [14] claim to be due to interfacial tension between the polymers. The values of G′ for PMMAh show greater differences with increasing PS percentage due to interfacial tension, compared to pure PMMAh, but no significant changes in the G′ vs. ω curves were observed when only 5 wt% of the dispersed PS phase was present. For PMMAh/PS blends with PS phases at 10 wt% levels or higher, significant changes relative to PMMAh were observed; similar behavior was reported by Yee and coworkers [14] and Calvão and coworkers [16]. The G′ values for PMMAh/PS blends were slightly higher than those for PMMAe, however, these increased less with increasing PS concentration when compared to those of the PMMAe/PS blends, which is justified on the basis of the core-shell format of the elastomeric particles observed in PMMAe.

Fig. 7a reveals that the addition of SAN to PMMAh does not influence the storage modulus (G′); i.e., significant changes were not observed upon addition of 20 wt% of SAN when compared to PMMAh. In
addition, SAN contains 25 wt% AN, which is within the PMMA-miscibility window, and corroborates the work of Costa and coworkers [37], which revealed by TEM that a PMMA$_h$/SAN blend containing 24 wt% AN is miscible, and no dispersed phases are formed. The miscibilities of PMMA$_h$ and PMMA$_e$ with the SAN copolymer can be visualized in the illustrative morphologies (Fig. 7b and c) and obtained by SEM (Fig. 7d and e).

Increases in the concentration of SAN in the PMMA$_e$/SAN blend displace the storage modulus ($G'$) curves closer to those of SAN, while decreases in the SAN concentration move the curves toward those of PMMA$_e$; i.e., the $G'$ values of the PMMA$_e$/SAN blends are the weighted means of the $G'$ values of the pure polymers. Han [2] reported that when the $G'$ value of a polymer blend lies between those of the constituent polymers, then these mixtures are considered to be miscible since there is no interfacial tension due to the lack of a second phase. However, when the core-shell particles of PMMA$_e$ are inserted into the PMMA/SAN miscible blend, significant differences in the curves for the PMMA$_e$/SAN blends are observed relative to pure PMMA$_e$.

PMMA/ABS blends exhibited rheological behavior similar to PMMA$_h$/SAN blends (Fig. 8a); that is, the PMMA$_h$/ABS blends, in which the ABS contained 25 wt% AN (which is within the PMMA-miscibility range) were miscible, as evidenced by FTIR spectroscopy and elemental analysis (Table 2). Miscibility occurs between the free SAN present in the ABS and the PMMA to form a single phase (Fig. 8b and d), and corroborates the work of Kim and coworkers [12], in which the polybutadiene phase of ABS was found not to influence the miscibility of PMMA and SAN in PMMA/ABS blends. The PMMA$_e$/ABS blend also exhibited evidence of miscibility between the SAN phases present in the ABS and the PMMA phase of the elastomeric-particle-containing PMMA (PMMA/core-shell particles) (Fig. 8c and e).

3.4. Other rheological studies used to evaluate the miscibilities of polymer blends as function of chemical structure

In addition to the previously reported results, there are other types of plots that can be used to determine the rheological behavior of multiphase systems, such as Han, complex viscosity, and Cole-Cole plots. Han ($G'$ vs. $G''$) plots are used for homogeneous polymer systems, are independent of component or temperature, and can be used to investigate the miscibilities of polymer blends [2].

The log $G'$ vs. log $G''$ plots for PMMA$_h$/PS and PMMA$_e$/PS blends containing 20 wt% of the PS phase lie above those of their pure polymer constituents (Fig. 9), and display typical rheological behavior of immiscible blends. Polymer blends formed by PMMA$_h$ presented linear Han plots, whereas those of polymer blends formed with PMMA$_e$ were not linear due to the greater elasticity of PMMA$_e$.

The PMMA$_h$/SAN blend exhibited an LCST, so it may be miscible depending on the acrylonitrile content, the molecular weight of the PMMA$_h$, the composition, and temperature [2–6]. The Han plot for the PMMA$_h$/SAN blend reveals that the terminal region of the polymer blend containing 20 wt% SAN overlaps with that of PMMA$_h$ (Fig. 9a). This may indicate that the PMMA$_h$/SAN blends used in this work are rheologically miscible, as demonstrated by the preliminary characterizations. Han [2], Yang and coworkers [18] also observed similar rheological behavior for PMMA$_h$/SAN blends using a SAN containing 25.3 wt% acrylonitrile, which they attributed PMMA$_h$/SAN blend miscibility since they did not observe differences in the log $G'$ vs. log $G''$ plots, even with the addition of higher concentrations of the second phase.
Fig. 6. PMMA_h/PS and PMMA_e/PS blends. a) $G'$ vs. $\omega$. b) Illustrative PMMA_h/PS morphology. c) Illustrative PMMA_e/PS morphology. d) PMMA_h/PS morphology obtained by SEM. e) PMMA_e/PS morphology obtained by SEM.

Fig. 7. PMMA_h/SAN and PMMA_e/SAN blends. a) $G'$ vs. $\omega$. b) PMMA_h/SAN illustrative morphology. c) PMMA_e/SAN illustrative morphology. d) PMMA_h/SAN morphology obtained by SEM. e) PMMA_e/SAN morphology obtained by SEM.

Fig. 8. PMMA_h/ABS and PMMA_e/ABS blends. a) $G'$ vs. $\omega$. b) PMMA_h/ABS illustrative morphology. c) PMMA_e/ABS illustrative morphology. d) PMMA_h/ABS morphology obtained by SEM. e) PMMA_e/ABS morphology obtained by SEM.
component.

The PMMAe/SAN blend containing 20 wt% SAN exhibited a non-linear curve closer to and similar to that of PMMAe (Fig. 9b), which is attributable to higher mass concentrations of PMMAe, the miscibility between PMMA and SAN, and the elastomeric particles (core-shell particles) present in PMMAe. Analyses of the curves for the pure polymers and the PMMAe/SAN blends show that the PMMAe/SAN-blend curves lie between those of PMMAe and SAN, revealing miscibility. These results are different to those of the PMMAe/PS blends that showed immiscible phases.

The G’ vs. G” curves for the PMMAe/ABS blends exhibited were similar to those of the PMMAe/SAN blends. The addition of 20 wt% ABS led to typical miscible-blend behavior because its G’ vs. log G” curve is linear and lies between the curves of the pure polymers (Fig. 9a), which indicates that this blend is miscible, even when loaded with 20 wt % ABS. The log G’ vs. log G” curve for the PMMAe/ABS blend is not linear since the two pure polymers did not present linear log G’ vs. log G” plots (Fig. 9b). The PMMAe/ABS blend formed by the two copolymers composed of elastomeric phases presented rheological behavior closer to that of PMMAe than ABS.

Fig. 10 displays the effect adding 20 wt% of the different styrenic polymers (PS, SAN, and ABS) on the complex viscosities of polymer blends containing PMMAh and PMMAe at low frequencies. The differences between the complex viscosity curves of the pure polymers
(PMMAh, PMMAe, PS, SAN, and ABS) are important for evaluating polymer blends. The complex viscosities at low frequencies of the PMMAh/PS blend were above those of pure the polymers (Fig. 10a). Newtonian plateaus at low frequencies were observed under these test conditions for PMMAh/PS blends, but were not observed for the PMMAe/PS blends (Fig. 10a and b), and the complex viscosity behavior of these polymer blends was very close to that of the PMMAh matrix.

The PMMAh/SAN blends showed no significant variations in complex viscosity upon addition of 20 wt% SAN; i.e., the viscosities of the blends were close to that of PMMAh for compositions analyzed at 220 °C (Fig. 10a). Hence, the PMMAh/SAN blends showed behavior similar to PMMAh (Fig. 10b).

The complex viscosity of the PMMAh/ABS blend with 20 wt% ABS was close to that of pure PMMAh (Fig. 10a); i.e., no visible changes in complex viscosity were observed upon addition of 20 wt% ABS, despite the high complex viscosity of ABS compared to the other polymers and polymer blends used. PMMAh/ABS blend with 20 wt% ABS also showed no changes in complex viscosity, which remained close to the complex viscosity of PMMAh (Fig. 10b).

Cole-Cole plots of imaginary viscosity ($\eta''$) vs. dynamic viscosity ($\eta'$) obtained from rheological testing at low shear rates have been used by several authors [42–46] when examining the miscibilities of polymer blends. The formation of semicircles in these plots, even with increasing percentage of the second component of the polymer blend, is an indication of miscibility; however, deviations from semicircle behavior are indicative of immiscibility.

The PMMAh/PS blend with 20 wt% PS exhibits semicircle deviations (Fig. 11a), with a second semicircle formed on the right side of the curve. The formation of semicircles indicates the existence of a second phase due to its longer relaxation time. In addition, the sizes of the particles in the dispersed phase and the interfacial tension also affect the shape of the Cole-Cole plot.

The Cole-Cole plots of the PMMAh/SAN and PMMAe/ABS blends did not show semicircle deviations (Fig. 11a), indicating that these polymer blends are miscible. Kim and coworkers [12] used Cole-Cole plots to analyze the miscibilities of PMMA/ABS blends with three ABS polymers of different acrylonitrile content, the results of which revealed that the miscibilities of these blends depended on the acrylonitrile content.

The Cole-Cole plots of the polymer blends with PMMAh exhibit semicircles with deviations, the presence of shoulder and curve falling away. The polymer blends formed with PMMAh show slight semicircular formations, but curve falling away is not observed; i.e., the final region of each curve increases without the formation of a shoulder. These results are justified when the differences in elasticity caused by the presence of elastomeric particles and the interfaces are considered (Fig. 11b).

Polymers with different chemical structures were observed to exhibit rheological behavior in the linear viscoelastic region that is different to that of PMMAh or PMMAe (Fig. 5). These different chemical structures also influenced the miscibility and rheology of the polymer blends developed in this study. It was also verified that the percentage of AN in the styrene copolymers (SAN and ABS) are responsible for the different miscibility and rheological behavior of polymer blends.

4. Conclusions

The rheological behavior of PMMA/PS, PMMA/SAN, and PMMA/ABS blends was studied in the linear viscoelastic regions using parallel plates at low frequencies, which revealed significant differences when two different types of PMMA were used.

The different rheological behavior is understood on the basis of the behavior of the pure polymers, miscible polymer blends, and immiscible polymer blends.

The rheological properties of the polymer blends were dependent on their chemical structures. Therefore, it was possible to determine that the presence of acrylonitrile in the chemical structures of the SAN and ABS copolymers significantly affected the rheological behavior of these polymer blends by correlating the rheological properties of the polymers with their chemical structures.

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