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Dynamic-mechanical and dielectric relaxations of SBS block copolymer: polyaniline blends prepared by mechanical mixing

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Abstract

Blends of SBS with polyaniline doped with dodecylbenzenesulfonic acid (Pani·DBSA) or its deprotonated form (emeraldine base) were obtained by mechanical mixing and characterized by dynamical–mechanical and dielectric thermal analysis techniques. The dynamic-mechanical characterization revealed that both Pani·DBSA and its non-conducting, deprotonated form exhibits different degrees of interaction with the two phases of the SBS block copolymer. The tan δ peak position on temperature scale corresponding to the T_g of the PB block did not change with the addition of the conducting polymer, but there is progressive drop of peak height with the increase in Pani·DBSA concentration, probably because of the rigidity of this component. The activation energies E_a for glass–rubber transition process for both the phases of SBS were calculated using Arrhenius equation from DMTA results. From dielectric studies, it was possible to detect conductivity relaxations, at temperatures above the glass transition of the PS phase. Concerning the blend with 15 wt% of Pani·DBSA, the relaxations attributed to both Pani·DBSA blend component and PS phase of the SBS copolymer can be observed only when the measurement are performed at frequencies lower than 10^3 Hz. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene–butadiene–styrene; Polyaniline; DMTA

1. Introduction

Conducting polymer systems constituted by a conducting filler dispersed inside an insulating polymer matrix have been extensively studied in the last decades as a way to produce materials that combine the good mechanical properties, thermal stability and processability of the matrix with the electrical properties of the conducting component. These systems are normally characterized by a sharp insulator–conductor transition at a specific volume fraction of the filler. At this point, known as percolation threshold, a continuous conducting network of conducting particles is formed inside the insulating matrix [1]. When a heterogeneous polymer blend is employed as the matrix, the insulator–conductor transition can be achieved at a lower volume fraction of the filler, compared to single polymer matrices, because of the uneven distribution of the filler inside each polymer phase [2–4]. When the filler is preferentially located inside one phase or at the interface of an heterogeneous blend that presents a co-continuous morphology, the probability of the conducting particles touching each other increases significantly, resulting in the formation of conducting pathway with a very low amount of filler [5–7]. Most of the studies concerning heterogeneous polymer matrix are related to carbon black as the extra-conductive filler.

Intrinsically conducting polymer, such as polyaniline, may also present preferential distribution inside one phase of an heterogeneous system. This behavior may also be influenced by the nature of the protonating agent used to impart conducting properties to polyaniline. For example, the protonation with special functionalized acid such as dodecylbenzenesulfonic acid (DBSA) can improve the compatibility of polyaniline with several conventional polymers [8,9].

Among several heterogeneous systems, the one constituted by styrene–butadiene–styrene (SBS) triblock copolymer as the insulating matrix should be advantageous due to its thermoplastic–elastomeric nature, i.e. it presents the unique combination of mechanical properties and processability without a vulcanization process [10]. In addition, it presents a morphology characterized by the two block components segregated into different phases with a typical micro domain structure [11]. This feature is a

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consequence of the thermodynamic incompatibility of polystyrene (PS) and polybutadiene (PB) blocks.

Recently, we have reported some results concerning conducting SBS–polyaniline blends prepared by melt mixing [12] or solution process [13]. Other authors also have studied the electrical conductivity of SBS-based conducting blends by using both polyaniline and polypyrrole as the conducting polymer component in the blend [14–19]. The polyaniline employed in those reports has been doped with DBSA (Pani·DBSA), in order to promote some compatibility with the insulating matrix. In spite of the heterogeneity of the system, the preferential distribution of Pani·DBSA in one of the two phases of the SBS copolymer have not been discussed in all these articles. The introduction of polyaniline in the SBS triblock copolymer may affect not only the electrical conductivity, but also the dynamic-mechanical and dielectric properties of SBS. The alteration of these properties with the blend composition may also provide some information on the selective location of the Pani·DBSA in one of the two phases of SBS block copolymer.

The aim of this work is to study the dynamic-mechanical relaxations of the SBS matrix loaded with different amount of polyaniline and to investigate the preferential location of the conducting component in one of the two SBS phases. The influence of the DBSA on this behavior has also been evaluated by performing dynamic-mechanical analysis in SBS blends containing polyaniline in the protonated, conducting form (Pani·DBSA) and in non-protonating, non-conducting form, called emeraldine base (EB). If polyaniline displays a preferential affinity to one of the two phases of the SBS triblock copolymer, changing the proportion of polystyrene or polybutadiene phases in the SBS copolymer can control the percolation threshold of the conducting blend. Dielectric properties of SBS loaded with polyaniline have also been investigated with the aim to identify the dielectric relaxations, including interfacial polarization, which is common in heterogeneous systems.

2. Experimental

2.1. Materials

Aniline (Ani) (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), hydrochloric acid (HCl) (analytical grade, Merck) and dodecylbenzenesulfonic acid (DBSA) (technical grade, Pro-Química do Brazil) were used. Petroflex S.A. (Rio de Janeiro, Brazil) supplied SBS block copolymer (TR-1061). The SBS sample presents a PB content of 70 wt% and M_w of 120,000.

2.2. Synthesis of polyaniline doped with DBSA (Pani·DBSA)

Polyaniline doped with HCl (Pani·HCl) was prepared by chemical oxidative polymerization of Ani in aqueous acidic medium (1 M HCl) with APS as an oxidant, according to the procedure mentioned in the literature [20]. A molar ratio of Ani/APS corresponding to 1:1 was employed and the reaction was carried out at 0 °C for 2 h. The deprotonation of Pani·HCl samples were performed by stirring the Pani·HCl powder in a 0.1 M aqueous solution of ammonium hydroxide for 24 h at room temperature, thus obtaining the polymer in the EB form. The resulting polymer was then dried under vacuum for 48 h at room temperature. The redoping of the Pani EB with DBSA was performed by mixing the EB with DBSA in a proportion by weight of 1:3 in an agate mortar. The Pani·DBSA obtained by this method presents an electrical conductivity of 0.92 ± 0.2 S/cm and a doping degree of 48 mol% relative to the amount of nitrogen in the Pani chain [21].

2.3. Blend preparation

Blends of SBS with different amounts of polyaniline in the doped or dedoped form (Pani·DBSA or EB, respectively) were prepared in a Berstoff two-roll mill at 60 °C for 10 min. The blends were compression molded at 130 °C and 1.0 MPa pressure for 7 min.

2.4. Characterization

The dynamical–mechanical measurements were made using a thermal dynamical–mechanical analyzer DMTA (Rheometric Scientific, model MK III). The measurements were carried out in a bending mode, at the heating rate of 3 °C/min from − 130 to 130 °C at fixed frequencies of 1, 10, 30 and 100 Hz.

Dielectric relaxation measurements of the SBS triblock copolymer and the blends were made using a Dielectric analyzer DETA (TA Instruments Model 2970) operating with parallel plate electrodes. In the case of pure DBSA, a single surface electrode was employed. The DETA was used to measure the dielectric constant ε' and dielectric loss ε'' on a thin film of the SBS and SBS/Pani blends over the frequency range from 0.3 to 10^5 Hz and the temperature range from − 130 to 150 °C under dry nitrogen gas purging. The blends prepared with protonated polyaniline (Pani·DBSA) were superficially dedoped by treatment of the composite with 0.1 M aqueous NH_4OH for 24 h.

3. Results and discussion

3.1. Dynamical–mechanical properties of SBS/polyaniline blend

Dynamical mechanical analyses were performed in pure

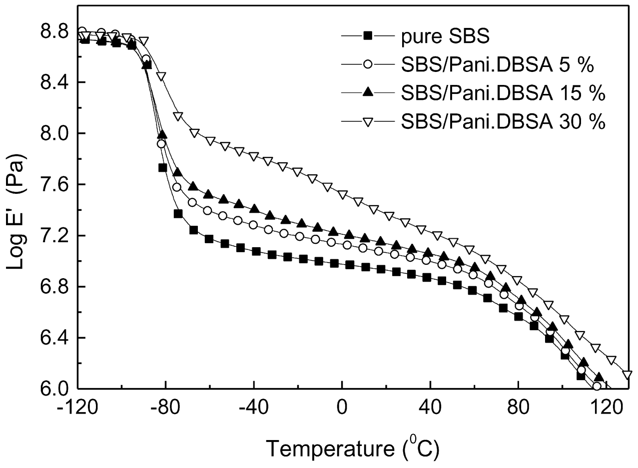

Fig. 1. The variation of bending modulus against temperature for pure SBS and SBS/Pani·DBSA blends at 1 Hz.

SBS and their blends with 5, 15 and 30 wt% of Pani/DBSA. Fig. 1 shows the dependence of bending modulus on temperature. Pure SBS sample displays a sudden fall in the modulus at a temperature around −80 °C, which corresponds to the glass–rubber transition of butadiene segments of the triblock SBS copolymer. The presence of Pani·DBSA in the blends does not change the temperature where the first transition occurs, but exerts strong influence on the modulus in the rubbery region (from −70 to 90 °C). An increase of Pani·DBSA concentration resulted in an increase of modulus probably because of the increase in the rigidity of the system caused by the presence of rigid polyaniline chains.

The dependence of mechanical loss tangent (tan δ) on temperature for these systems, taken at two different frequencies, is shown in Fig. 2. The region corresponding to the relaxation of the PS is highlighted in a separated graphic. As expected for a biphasic system, the pure SBS copolymer displays two distinct transitions: one at −80 °C, which corresponds to the glass–rubber transition of the flexible elastomeric polybutadiene phase and the other at around 110 °C, related to the transition of the hard rigid polystyrene phase. The addition of Pani·DBSA resulted in a significant drop of peak height of the PB transition, but the corresponding temperature where this transition takes place was not affected. Considering the same blend composition, the damping of PB phase in all systems was not influenced

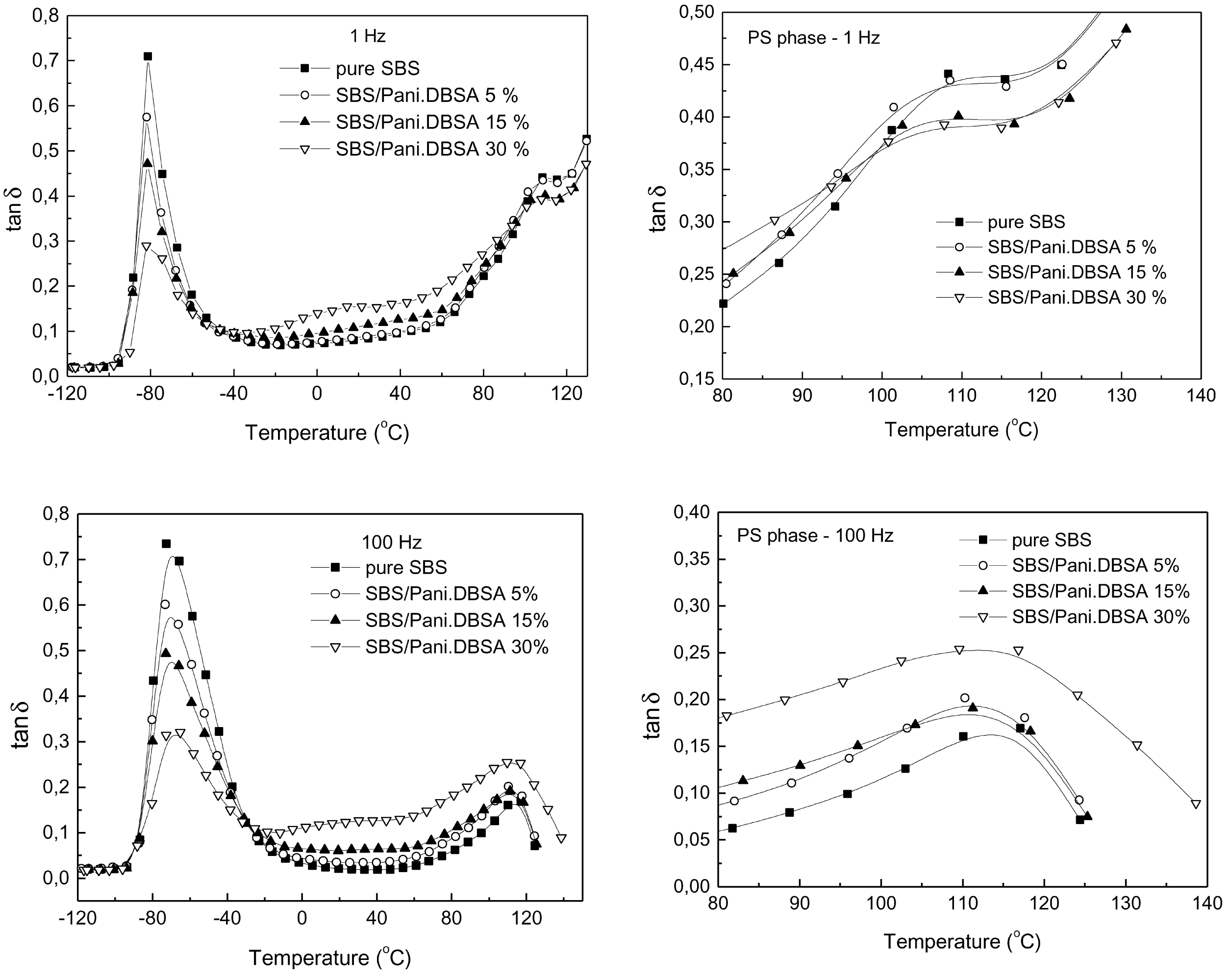

Fig. 2. The variation of tan δ against temperature for pure SBS and SBS/Pani·DBSA blends at 1 and 100 Hz.

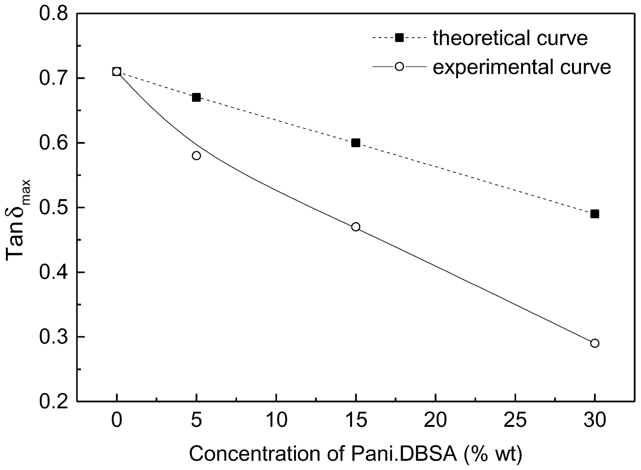

Fig. 3. The dependence of tan δ_{max} with the Pani·DBSA content in the blend: theoretical and experimental curve.

by the frequency of measurement. The effect of Pani·DBSA concentration on damping values of the PB phase is shown in Fig. 3. The dashed line in Fig. 3 represents the theoretical values, calculated by adopting the mixing rule, as follows

$$\tan \delta_{\mathrm{mixture}} = \tan \delta_{\mathrm{SBS}} \times X \qquad (1)$$

where tan δ_{SBS} and tan $\delta_{\mathrm{mixture}}$ are the damping values of PB phase in pure SBS and in the mixture, respectively, and X is the weight fraction of SBS in the mixture. In both theoretical and experimental curves, the damping value decreases as the amount of Pani·DBSA increases due to the decrease of SBS concentration in the blend. However, the experimental values of damping were lower than the theoretical, indicating a decrease of the mobility of the PB phase as a consequence of the presence of rigid polyaniline backbone, which exhibits a glass transition at a temperature much higher than the T_g of the PB segment. A very similar behavior is often found when rigid filler particles are added to flexible elastomer matrices [22,23].

Concerning the transition of the PS segments (separately presented in the right side of Fig. 2), the damping values were not significantly affected by the presence of Pani·DBSA as in the case of PB relaxation. Only a small decrease on damping (around 0.05) with the addition of 15 or 30 wt% of Pani·DBSA can be observed in measurements performed at a frequency of 1 Hz. On increasing the frequency, there is a small decrease on damping because the relaxation ability of the PS segments decreases. This behavior is more accentuated in pure SBS or in blends containing lower amount of Pani·DBSA. As a consequence, the damping value for SBS/Pani·DBSA (70:30 wt%) blend is higher at higher frequency. This behavior may be attributed to the presence of a higher amount of DBSA in this system.

Besides the two transitions related to PB and PS phases, another small relaxation at around 15–20 °C is also present

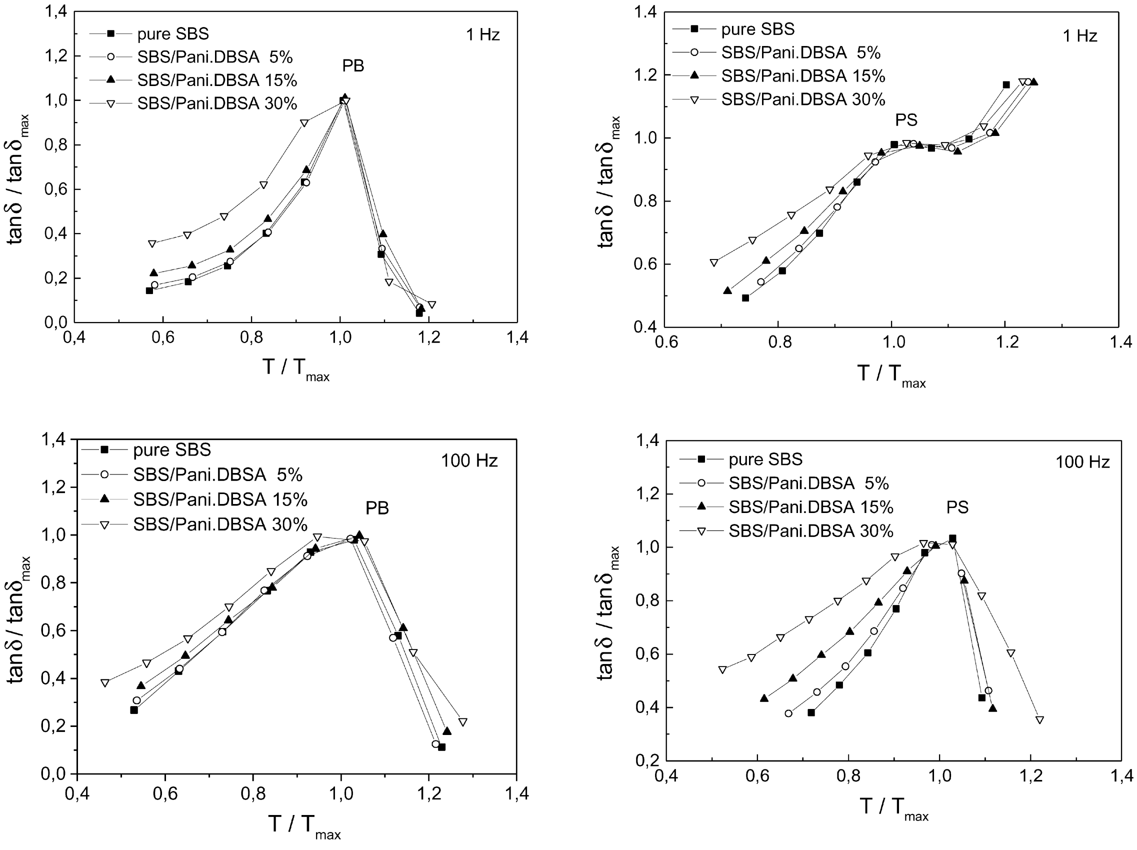

Fig. 4. The normalized plots of tan δ/tan δ_{max} versus T/T_{max} at 1 and 100 Hz for PB and PS block relaxations for pure SBS and SBS/Pani·DBSA blends.

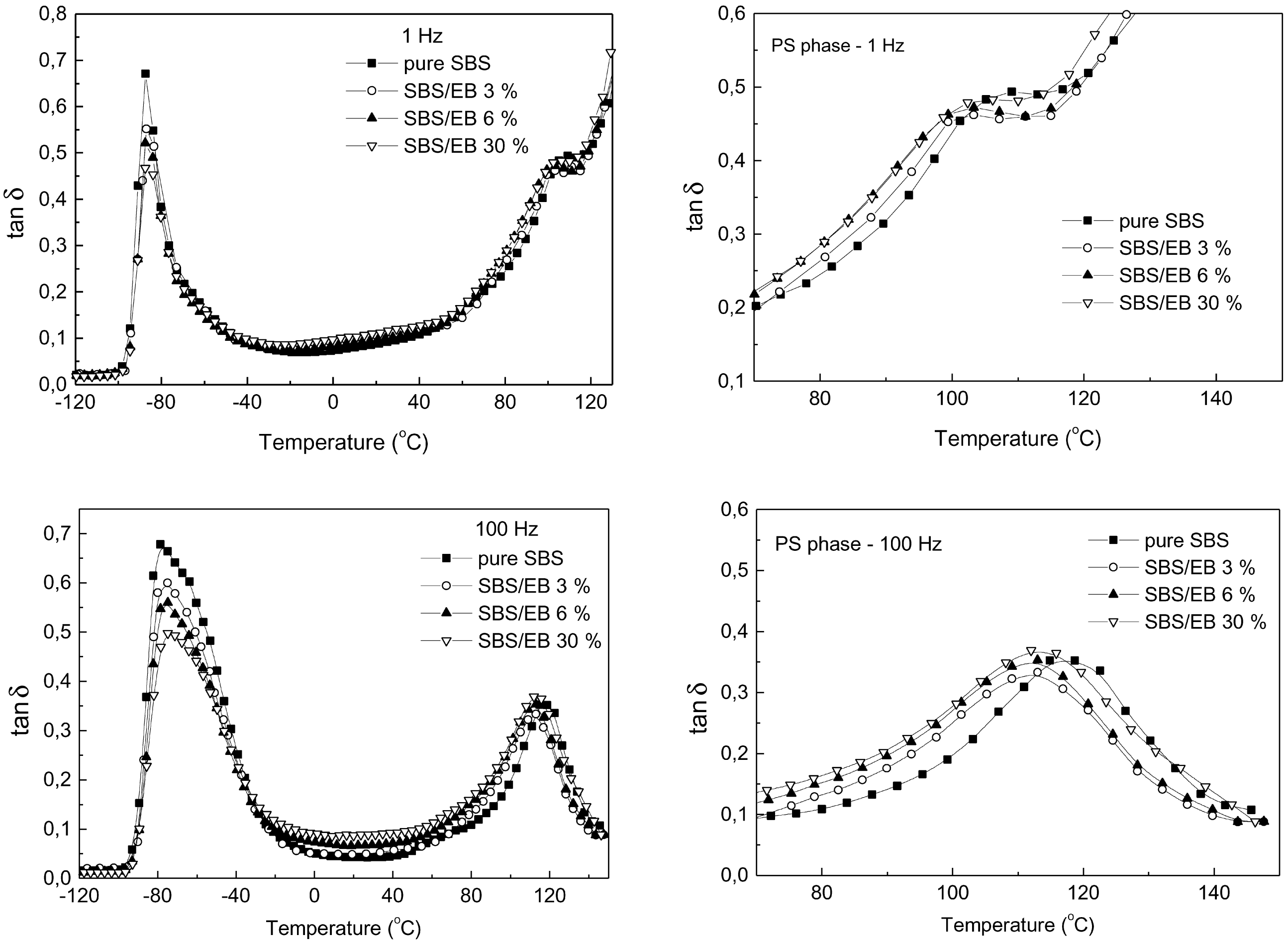

Fig. 5. The variation of tan δ against temperature for pure SBS and SBS/EB blends at 1 and 100 Hz.

in the blend containing 30 wt% of Pani·DBSA, which may be attributed to some specific transition related to the conducting component, probably because of the high amount of DBSA in the sample.

The heterogeneous distribution of Pani·DBSA inside both phases of the SBS matrix can be estimated using the normalized plots of the two relaxation processes associated to the two phases, taken at different blend compositions [23]. The extent of broadening of these plots with the addition of Pani·DBSA can be correlated to the degree of heterogeneity of the corresponding phase, which may be related to the presence of the conducting polymer inside this phase. The normalized plots of tan δ/tan $\delta_{\max}$ against $T/T_{\max}$ for glass–rubber transitions of both PB and PS segments at different blend compositions are presented in Fig. 4, where tan δ represents the value of loss tangent at any temperature T and tan $\delta_{\max}$ represents the loss tangent value at the corresponding $T_{\max}$ temperature. The width of these normalized plots indicates the heterogeneity of the phases. To have a clear understanding of the variation of phase heterogeneity, the normalized plots were built from the data obtained at two different frequencies, 1 and 100 Hz. At a frequency of 1 Hz, the addition of Pani·DBSA resulted in a broadening of the normalized plots for glass–rubber transition of PB and PS segments, which increases as the Pani·DBSA concentration in the blend increases. At higher frequency (100 Hz), the width of the plots related to PB phase does not present any significant change, whereas in the case of PS segment, a continuous broadening is observed as the Pani·DBSA concentration in the blend increases. This behavior suggests that the conducting component is partially distributed in both phases, but a major portion of Pani·DBSA in the blend should be located inside the PS phase, thus affecting the heterogeneity of this phase in a larger extent when compared to that of PB block.

To confirm the role of DBSA on the distribution of the conducting polymer inside the SBS matrix, different amounts of the EB (non-protonated polyaniline) was melt mixed with SBS. The dependence of tan δ on temperature for these SBS/EB blends is shown in Fig. 5. The damping related to the PB glass–rubber transition presents a slight decrease with the addition of EB, but the difference is not as great as that found in SBS/Pani·DBSA systems, and seems to be only related to the difference in the weight fraction of EB in the blend. The damping related to the PS glass–rubber transition does not change with the addition of EB.

The normalized plots of tan δ/tan $\delta_{\max}$ against $T/T_{\max}$ for the relaxation processes of both PB and PS phases of

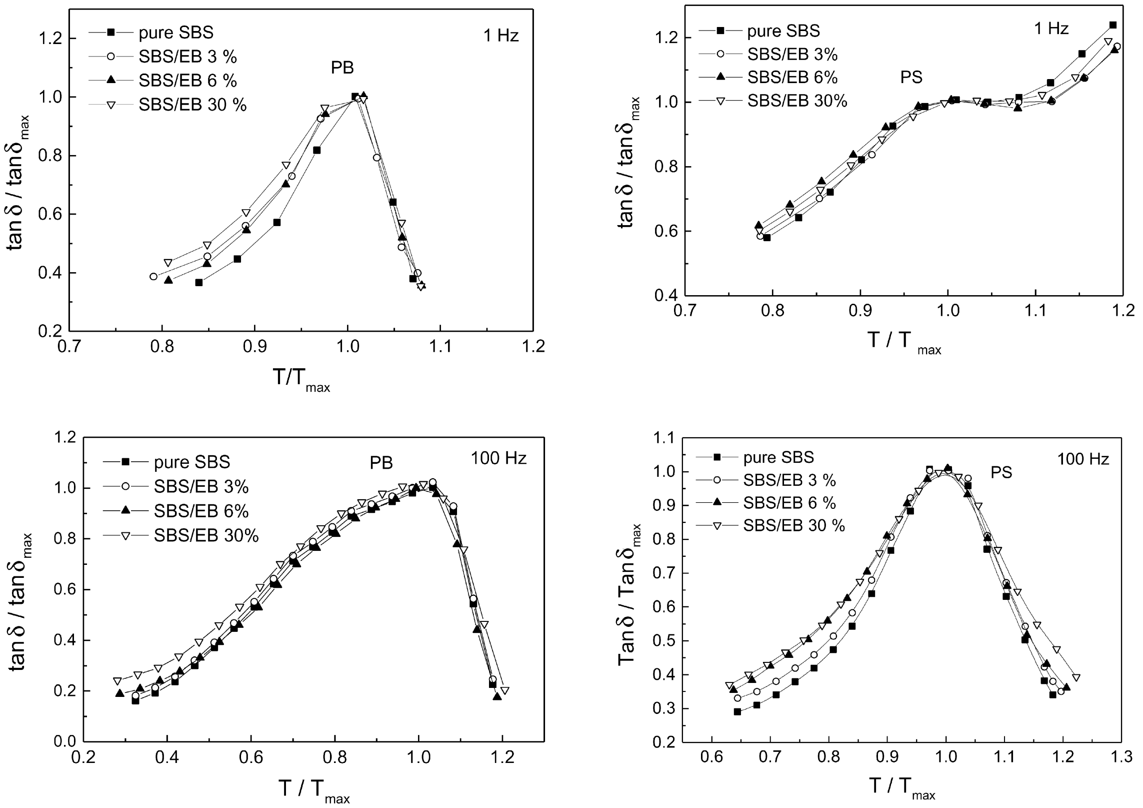

Fig. 6. The normalized plots of tan δ/tan δ_{max} versus T/T_{max} at 1 and 100 Hz for PB and PS block relaxations in the pure SBS and SBS/EB blends.

SBS/EB blends at different compositions are shown in Fig. 6. The profile of the normalized curves related to PB segment presents a slight broadening at a frequency of 1 Hz but there is no considerable change at a higher frequency. PS relaxation is a little broader than PB relaxation at a frequency of 100 Hz, indicating that EB has also a better affinity to the PS phase. By comparing the normalized plots of both SBS/Pani·DBSA and SBS/EB systems, one can suggest that both filler have better affinity towards PS phase but a better interaction can be found with Pani·DBSA probably because of the presence of DBSA moiety in the polyaniline sample, which acts as protonating and surfactant agent, thus promoting a better compatibility with the SBS matrix.

The activation energy, E_a, corresponding to the glass–rubber transition process of PS and PB phases were calculated by performing experiments at different frequencies and relating the transition temperature with the corresponding frequency using Arrhenius equation, which is often applied for such relaxations with some approximations [24]. The equation can be expressed as follows

$$f = f_0\, e^{-E_a/RT} \tag{2}$$

where f is the frequency used in the experiment and T is the corresponding temperature taken at the maximum of damping peak. This temperature may be referred to as glass transition temperature T_g.

The slope of logarithm of frequency of measurement against the inverse of the glass transition temperature ($1/T_g$) expressed in Kelvin scale corresponds to the E_a. Table 1 shows the values of E_a for the glass–rubber transition of PB and PS segments of SBS copolymer as a function of Pani·DBSA or EB concentration. The E_a corresponding to the transition of the PB and PS segments slightly increases with the addition of Pani·DBSA, but the difference is not significant. In the case of SBS/EB blends, the E_a of the PS phase was strongly affected by the presence of as low as

Table 1
Effect of the Pani·DBSA or EB concentration on the activation energy of PS and PB segments of SBS copolymer (E_a determined from DMTA results)

Blend component (wt%)		Activation energy, E_a (kcal mol^{-1})	
SBS	Pani·DBSA	PB	PS
100	0	30.5	111.0
95	5	30.8	112.1
85	15	32.0	110.0
70	30	32.5	114.2
SBS	EB	PB	PS
100	0	30.5	111.0
97	3	31.0	124.4
94	6	29.0	130.0
70	30	27.8	129.2

PB, polybutadiene block; PS, polystyrene block.

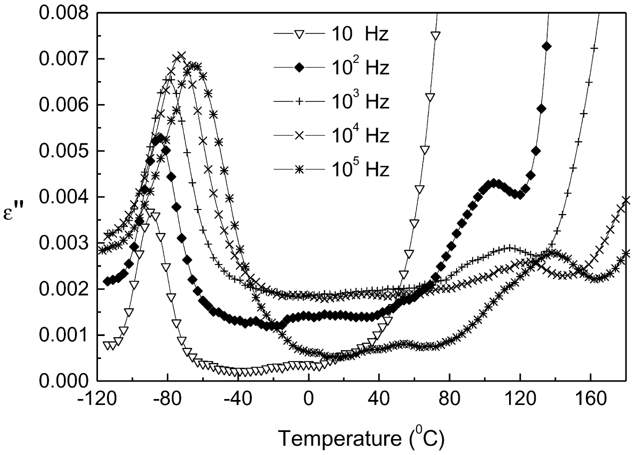

Fig. 7. The variation of dielectric loss factor ε'' against temperature for pure SBS at different frequencies.

3 wt% of EB. These results are also an indication of the better of EB towards PS phase and are in agreement with the data obtained from normalized damping curves.

3.2. Dielectric properties of SBS/Pani·DBSA blend

Dielectric relaxation of pure SBS is presented in terms of the dielectric loss factor (ε'') against temperature at different frequencies in Fig. 7. Two distinct dielectric relaxations can be observed: the first, around −80 to −70 °C, is due to the glass–rubber transition of PB block and the second, around 90–140 °C, corresponds to the glass–rubber transition of PS segment.

The peak related to glass–rubber transition of PS block is only detected at frequency above 10 Hz. Below this frequency, ε'' undergoes a sharp increase with increase in temperature as a consequence of interfacial polarization contribution and/or ionic conductance. The dielectric relaxations of PB and PS segments of SBS copolymer shift towards higher temperatures as the measurement frequency increases. Therefore, the Arrhenius plots can also be used to obtain the activation energy related to PB and PS relaxations from DETA. From DETA, the E_a values for PB and PS have been found as 30.6 and 97.6 kcal mol^{-1}.

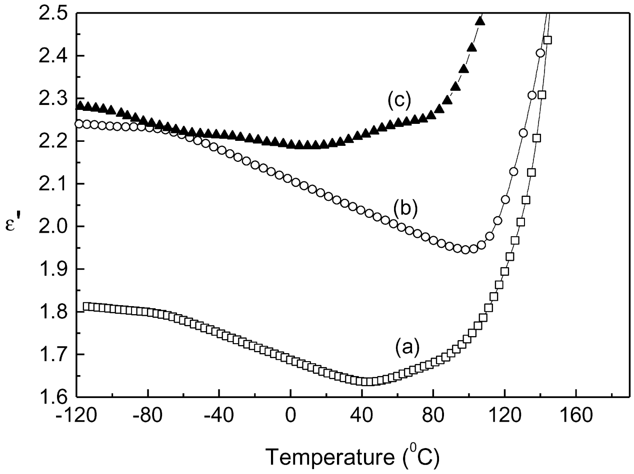

Fig. 8. The variation of dielectric constant ε' against temperature for (a) pure SBS, (b) SBS/Pani·DBSA 95:5 wt% and (c) SBS/Pani·DBSA 85:15 wt% (at a frequency of 10^3 Hz).

The effect of Pani·DBSA on permittivity (ε') for SBS block copolymer was studied at a frequency of 10^3 Hz, and the results are shown in Fig. 8. Pure SBS presents a slow decrease of permittivity from −80 to 45 °C. The change of the slope at −80 °C is indicative of glass–rubber transition of PB segment in SBS copolymer. Beyond 100 °C, there is a sharp rise in permittivity, which is attributed to the glass–rubber transition of the PS segment. The addition of Pani·DBSA resulted in an increase of the dielectric constant even at the lowest temperature of measurement. This is mainly because of the polar nature of Pani·DBSA component. Blends containing Pani·DBSA also display a decrease of permittivity around −80 °C.

Both dielectric constant (permittivity) and loss factor depend upon two factors: (1) dipole density, characterized by the total number of dipole per unit volume and (2) the ability of the dipoles to follow the reversal of polarity with applied electrical field, i.e. the mobility of the dipole in turn depends upon the mobility of the polymer chains to which the dipoles are attached. At very low temperature, the dipolar activity of the polar materials is frozen. As the temperature increases, the volume of the system increases, resulting in a decrease of dipole density. Consequently, the permittivity decreases. This effect explains the decrease of ε' around −80 °C observed in the systems presented in Fig. 8. When the temperature increases, the mobility of the dipole is also increased and permittivity increases. In addition, at further higher temperature, there is also a contribution of interfacial polarization originated from polar–non-polar interface together with some conductivity, which contribute to the sharp increase in permittivity observed in Fig. 8. This phenomenon occurs at lower temperature for blend with 15 wt% of Pani·DBSA because of the higher polarity of this blend.

The variation of dielectric loss factor (ε'') against temperature at a frequency of 10^3 Hz for SBS and their blends with 5 and 15 wt% of Pani·DBSA is shown in Fig. 9. Fig. 9(b) corresponds to the same plot at different ε'' scale, to better observe the transitions of the blend containing 15 wt% of Pani·DBSA (curve c). The first relaxation at −80 °C is related to the PB segment. The addition of 5 wt% of Pani·DBSA to SBS (curve b) does not change the peak position at −80 °C, but increases the peak height. When Pani·DBSA concentration in the blend increases to 15 wt%, this peak is almost masked due to the increase in contribution of the polar Pani·DBSA component. The blend component is also responsible for two new peaks observed in Fig. 9(b): one at around −40 °C, which may be related to the DBSA portion and the other stronger at around 50 °C, which can be attributed to the Pani backbone. The

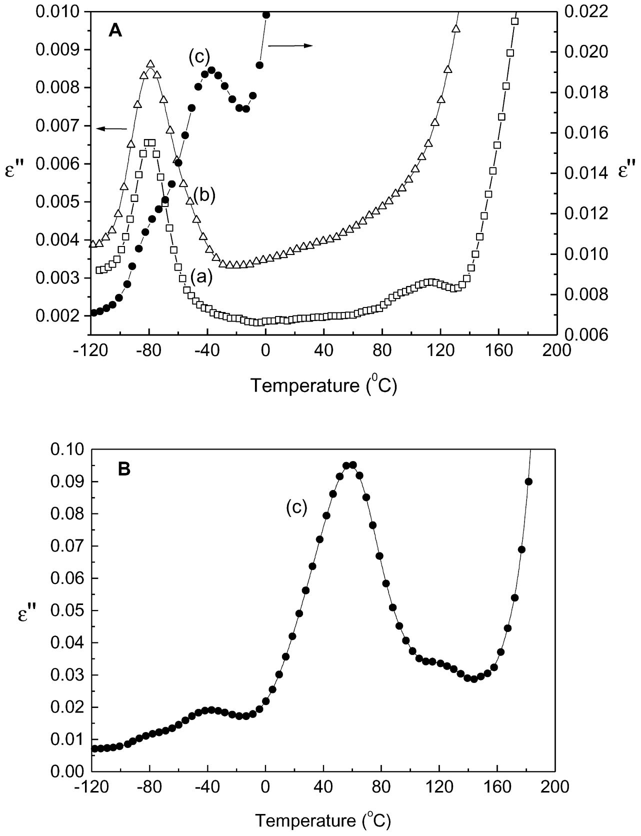

Fig. 9. The variation of dielectric loss factor ε'' against temperature for (a) pure SBS, (b) SBS/Pani·DBSA 95:5 wt% and (c) SBS/Pani·DBSA 85:15 wt% (at a frequency of 10^3 Hz).

loss factor peak due to the PS block is not well defined in SBS/Pani·DBSA blends because of interfacial polarization and ionic conductivity contribution.

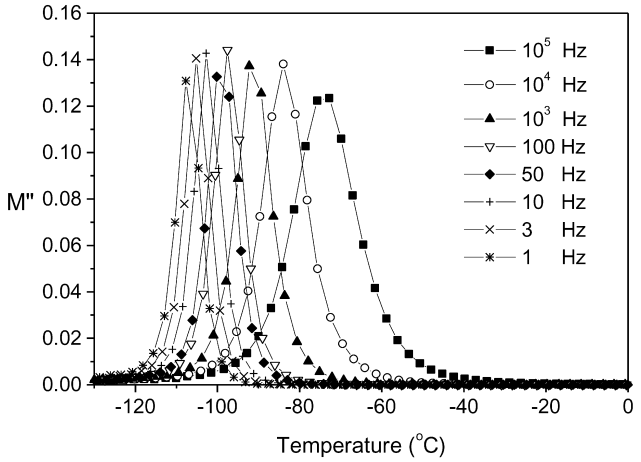

Fig. 10. The variation of imaginary part of the electric modulus M″ against temperature for pure DBSA at different frequencies.

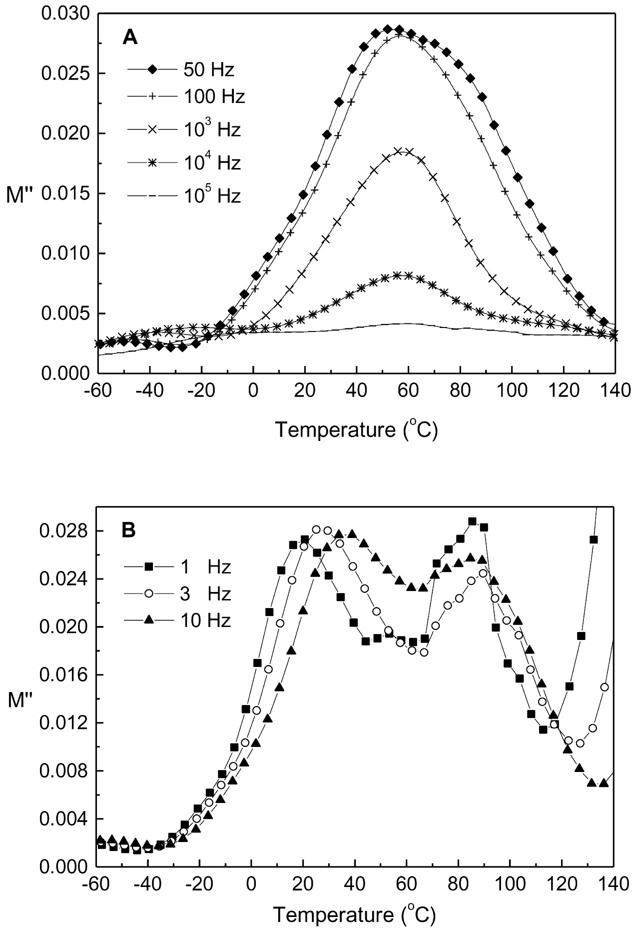

Fig. 11. The variation of imaginary part of the electric modulus M″ against temperature for SBS/Pani·DBSA(15%) at higher frequencies (30–10^5 Hz) and lower frequencies (1–10 Hz).

In order to relate some relaxations observed in the SBS/Pani·DBSA blend, the DETA analysis of pure DBSA was performed. Fig. 10 presents the variation of the imaginary component of electric modulus, M″, with temperature for pure DBSA at different frequencies. The M″ has been employed in this case because the conductive effects of the polar DBSA obscures the dipole alignment of the molecular chain to ε'' at low frequencies [25]. M″ is calculated from dielectric constant, ε', and dielectric loss, ε'', according to the following equation

$$M'' = \frac{\varepsilon''}{(\varepsilon')^2+(\varepsilon'')^2} \tag{3}$$

The transition of this sample occurs at very low temperature (from −110 to −60 °C). Therefore, one may assume that the relaxation at −40 °C in Fig. 9(b) is related to the DBSA portion joined to the Pani backbone.

Fig. 11 shows the dependence of M″ with temperature of SBS-based blend with 15 wt% of Pani·DBSA at different frequencies. At frequencies higher than 10^3 Hz (Fig. 11(a)), only one relaxation peak at around 50 °C can be observed. However, by decreasing the measurement frequency (Fig. 11(b)), it is possible to distinguish two relaxation peaks: the first one at around 20 °C, which may be attributed to Pani·DBSA component and the other at 80 °C related to PS phase. The broad peak that appears at frequencies higher than 10^3 Hz can be attributed to the Pani·DBSA component, because the electric modulus of the PS phase is very low at higher frequencies.

4. Conclusion

The dynamic-mechanical characterization revealed that polyaniline doped with DBSA exhibits different degree of interaction with PB and PS phases of SBS copolymer. The normalized damping curve peak width for PS block changes a little whereas that for PB block remains almost unaffected by the presence of Pani·DBSA. This result indicates that the Pani·DBSA presents more affinity towards PS phase than PB phase of SBS. The activation energy of the relaxation processes does not change substantially with the addition of Pani·DBSA. On the other hand, the E_a of the PS relaxation increases substantially when EB is added to the SBS matrix, indicating a better affinity of the polyaniline with this phase.

The addition of Pani·DBSA to SBS makes the system more polar and electrically conductive in nature. Both dielectric constant and loss factor increases with increase in Pani·DBSA concentration. Dielectric loss factor (ε'') data of SBS and their blends with Pani·DBSA also revealed a sharp increase at temperatures above the glass transition of the PS phase because of interfacial polarization and ionic conductivity contributions. These phenomena are important at low frequency measurement. Concerning the blend with 15 wt% of Pani·DBSA, the relaxations attributed to both Pani·DBSA blend component and PS phase of the SBS copolymer can be observed only when the measurement are performed at frequencies lower than 10^3 Hz.

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