Reactive Processing and Evaluation of Butadiene–Styrene Copolymer/Polyaniline Conductive Blends

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ABSTRACT: Blending is an important way to obtain materials based on intrinsically conductive polymers and conventional plastics and rubber materials. Much research has been carried out to determine the best performance of materials be used for electrostatic dissipation and electromagnetic interference shielding. Mechanical mixing, codissolution, and *in situ* polymerization have been used to prepare these materials. The method used depends on the host polymer and its thermal stability and acid attack resistance. Homogeneity and miscibility are properties that should be controlled during blend preparation. In this study, we prepared a conductive thermoplastic elastomer material based on butadiene–styrene copolymer (SBR) and polyaniline (PANI) doped with dodecylbenzene sulfonic acid (DBSA) and poly(styrene sulfonic acid) (PSS). PSS also acted as compatibilizer between PANI and SBR. PANI was doped by reactive processing with DBSA and PSS to produce the conductive complex PANI–DBSA–PSS. This complex was mixed with 90, 70, and 50% (w/w) SBR in a counterrotatory internal mixer. Conductivity tests, swelling studies, thermal analysis, and mechanical property and reflectivity testing were done, and the results show a strong dependence on PANI concentration and the ratio between PANI–DBSA and PSS. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 681–685, 2006

Key words: blends; conducting polymers; reactive processing

INTRODUCTION

The goal of combining the mechanical properties and processability characteristics of polymers with the electrical properties of metals has finally been achieved by the preparation of blends of conducting and conventional polymers. In recent years, considerable efforts have been made to improve these properties in conductive polymers. Although polyacetylene and other conducting polymers have, in principle, such potential, they do not exhibit the properties inherent in high-performance polymers,[1] including flexibility, tensile strength, elasticity, and processability. Among the conducting polymers, blends with polyaniline (PANI) have obtained the greatest technological importance due to the remarkable properties of this conductive polymer, namely, its simple synthesis and doping, low cost, environmental stability, solubility, and processability.[2]

The conventional method of doping PANI emeraldine base (EB) is its mixture with a functionalized protonic acid in a liquid medium, such as dodecylbenzene sulfonic acid (DBSA).[3] Additionally, in another doping approach,[4] a PANI–DBSA conductive complex can be prepared in the absence of solvents by heating at an elevated temperature, which results in thermal doping. Nowadays, there are many reports of melt processing as a doping method for preparing blends with elastomeric polymers, which is also called reactive processing.[5,6]

The use of elastomers as insulating polymer matrices is very interesting because of their unique mechanical properties. Conducting blends of PANI with EPDM,[7] nitrile rubber,[8] and polychloroprene[9] have been reported in the literature. The use of butadiene–styrene (SBR) copolymer as insulating matrix is advantageous because of its elastomer–thermoplastic nature; that is, it presents good mechanical properties as an elastomeric material without the need for a vulcanization process and can be processed as a thermoplastic material. It also provides excellent capability for processing, which thus leads to better properties in

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the final artifact and a resulting increase in elasticity. In addition, melt blending with SBR copolymer can be performed at temperatures low enough so as to not cause degradation of PANI.

Conductive elastomers have been extensively studied and have been used as sensors, electromagnetic radiation absorbers, static electricity dissipation fillers, and so on.[10–12] They are usually prepared by the addition of ferrite, carbon black, or other conductive fillers to a polymeric matrix. However, these fillers present the disadvantage of having a higher density than conducting polymers. Conductivity changes with the frequency of the incident radiation has made these kinds of polymers useful in the formulation of radar-absorbing materials applied to military and civil areas.

In this study, our aim was to obtain an electrically conductive rubber material by reactive processing and to evaluate the use of this conductive elastomer as a microwave-absorbing material.

EXPERIMENTAL

Materials

PANI

PANI was prepared on a pilot-plant scale by the chemical oxidation of aniline (Bann Quimica, Paulinia, Brazil) with $(NH_4)_2O_8$ (Synth, 98%, Diadema, Brazil) in a HCl (Solvay, pro analysis (or analytical grade purity), p.a., $1M$; Ribeirão Pires, Brazil) solution.[13] PANI (HCl) was dedoped in a $1M$ NH_4OH (Synth, p.a.) aqueous solution under stirring for 24 h; this produced PANI EB. PANI EB was redoped with DBSA (Chemco, commercial) and poly(styrene sulfonic acid) (PSS). The PSS was prepared according to Martins and De Paoli.[14] The doping process occurred by reactive processing, simultaneously with blend preparation, in an internal mixer and was done by the mixture of PANI EB with DBSA (Hoechst, Guarulhos, Brazil) and PSS (weight ratio = 1 : 2 : 0.25).[15,16]

Matrix polymer

The SBR copolymer (27 wt % styrene and 77 wt % butadiene) was kindly supplied by Nitriflex (Duque de Caxias, Brazil).

Blend preparation

The following sequence was used to prepare the mixtures in a double-screw counterrotating internal mixer coupled to a torque rheometer (Haake, Rheocord 90) with the compositions described in Table I:

1. The mixer was loaded with SBR at 130°C and 60 rpm.

TABLE I
Sf's and Sf$_r$'s for Different SBR/PAni–DBSA–PSS Blends

Blend	SBR (wt %)	PAni–DBSA–PSS (wt %)	Sf (obtained)	Sf_r (calculated)
SBR	100	—	32 ± 1.1	—
SBRPAni	90	10	22 ± 0.1	28.8
SBRPAni	70	30	14 ± 1.6	22.4
SBRPAni	50	50	22 ± 0.9	16.0

2. The PANI–DBSA–PSS complex was loaded 2.0 min after temperature stabilization and was then mixed for 3.0 min under the same conditions. The total mixer time was 5 min.
3. The mixer chamber was discharged and the mixture was laminated in an open-roll mill at 70°C and 19–23 rpm to prepare the homogeneous films. The samples were laminated five times (cyclic processes).

Characterization

Swelling studies

Soluble fraction (Sf) determinations were done by swelling measurements at room temperature in $CHCl_3$ (Ecibra) for 8 days. Sf was calculated from the weight ratio of the dried samples before and after extraction.

Thermal analysis

The thermal behavior of the SBR/PANI blends was studied by differential scanning calorimetry in a TA Instruments 2100 analyzer from −150 to 200°C at 20°C/min under N_2. The glass-transition temperatures (T_g's) were calculated from the second heating cycle.

Conductivity measurements

Electrical conductivity (σ) was measured by an adaptation of the Coleman method with a Keithley 617 programmable electrometer and a four-probe sensor with gold contacts.[17,18]

Mechanical properties

Stress–strain properties were measured for eight test samples in an EMIC DL 2000 instrument, according to the DIN 53504 standard, with a crosshead speed of 200 mm/min and a cell of 500 N.

Reflectivity measurements

Blend reflectivity measurements over a frequency range of 8–12 GHz were done at room temperature with a wave guide coupled to an Agileant Synthesized
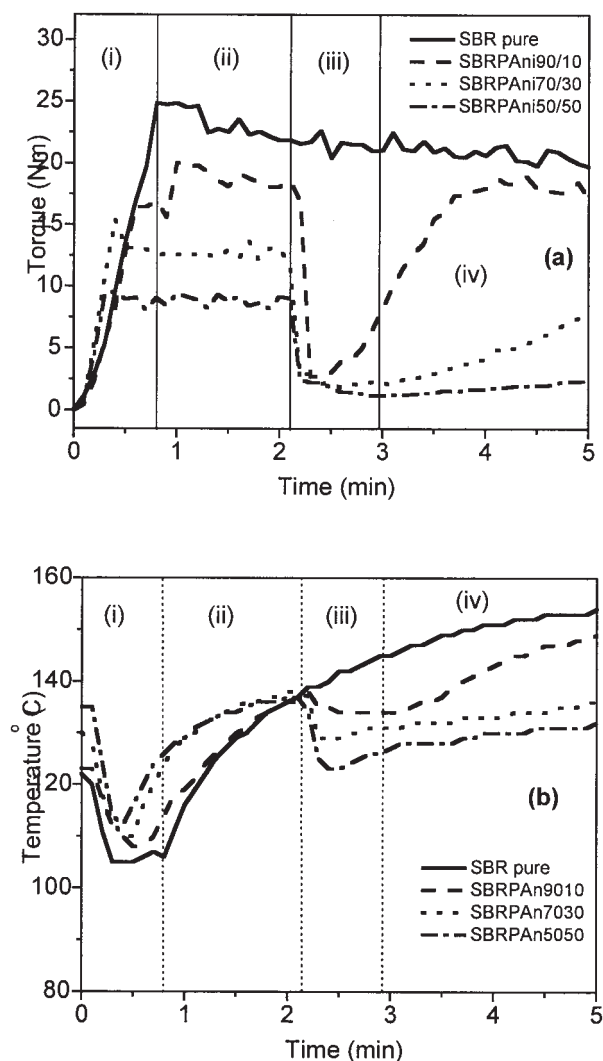
Figure 1 Torque (a) and temperature (b) curves as a function of processing time for pure SBR and its blends.

Sweeper 8375A and a Hewlett-Packard spectrum analyzer 7000.[19] Flat plaques, with dimensions of 20 × 7 × 3.0 mm, were prepared by compression molding at 4.5 MPa and 25°c.

RESULTS AND DISCUSSION

Doping and processing characteristics

Figure 1 shows the torque and temperature curves for SBR and its blends with the PANI–DBSA–PSS complex as a function of processing time. To analyze the behavior of the blends during processing, these curves are divided into four regions, which provide the following information: (i) the initial peak corresponding to the feeding of the elastomeric matrix (SBR), (ii) the mastication process of the SBR matrix, (iii) the opening of the mixing chamber followed by a torque decrease and loading with the PANI–DBSA–PSS complex, and

(iv) the mixing process of the components and PANI doping during 5 min of total processing. The reactive processing corresponded to the doping process, which occurred by mixing, homogenization, and the reaction between the components during processing.[16] This result is confirmed by Figure 1(a), which shows the torque increase during the mixing. The torque curves were modified depending on the conductive polymer content. The blend with 10% (w/w) PANI–DBSA–PSS showed an increase in torque (region 4) that reached similar values to the initial process. This increase was related to the viscosity of the mixture, which was near to that of pure SBR. However, for the blend with 30% (w/w) PANI–DBSA–PSS complex, in the same region, we observed a torque decrease. This was assigned to the difference in the viscosity of the PANI phase in the blend, which resulted in a less viscous system because of the presence of dopant acids and, consequently, favored the increase in the plasticity of the material. This result was confirmed when the PANI–DBSA–PSS complex concentration was increased to 50% (w/w). The preparation of laminated sheets in the open-roll mill was easier for this composition of 50% (w/w). Figure 1(b) shows the temperature versus time curves for these blends during the processing, where regions i and ii are equivalent to the initial temperature imposed on the mixer (130°C) following the melting of the SBR matrix and temperature stabilization and regions iii and iv are equivalent to the opening of the mixing chamber for the addition of the conductive polymer in the form of a powder, closure of the chamber and recording of changes in the temperature during the processing. For the blend with 50% of the PANI–DBSA–PSS complex, the temperature decrease has been shown by the plasticizing effect of the conducting polymer in the SBR elastomer.

Swelling studies

To identify which process was occurring in stage iii, we determined swelling parameters such as Sf and relative soluble fraction (Sf_r; Table I). These results provide information related to the crosslinking degree of the material. The ability of $CHCl_3$ to dissolve SBR associated with the long extraction period (8 days) allowed the total extraction of the elastomeric phase if it was not crosslinked. When the pure SBR (Sf of 32%) was compared with the blends, the influence of PANI was verified. Sf_r showed lower values, which suggested a chemical interaction of SBR with the PANI–DBSA–PSS complex. A crosslinking and/or physical entanglement or chemical reaction is proposed. For the 50% (w/w) SBR/PANI–DBSA–PSS blend, Sf was higher than Sf_r, which indicated that some PANI phase was also dissolved during the extraction (the solution showed a green coloration).
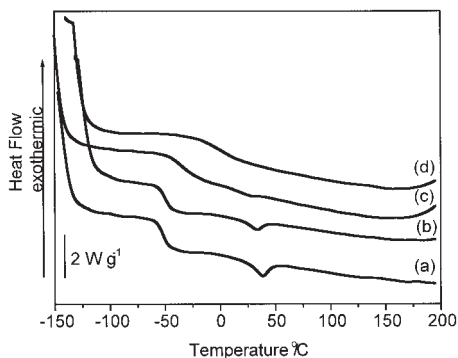
Figure 2 DSC curves for pure SBR (a) and SBR blends with: (b) 10, (c) 30 and (d) 50% (w/w) of PAni-DBSA-PSS.
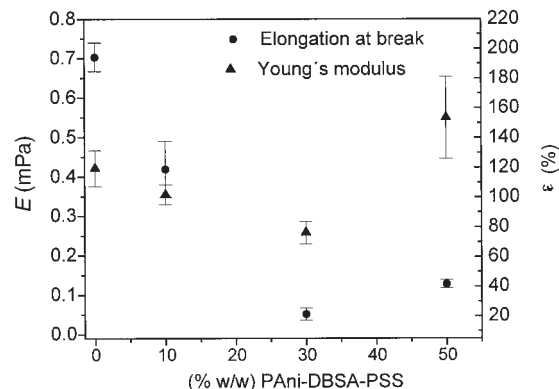
Thermal properties

Studies have shown that PANI can be thermally processed when it is plasticized with functional protonating agents such as sulfonic acids, phosphoric acid esters, and phosphoric acids.[20–23] These surfactants improve the compatibility between the polymeric chains and decrease the T_g and tensile modulus. The differential scanning calorimetry curves for pure SBR and SBR/doped PANI blends are shown in Figure 2. The SBR matrix exhibited T_g's at -50 and $45°C$, corresponding to the butadiene and styrene blocks, respectively. With the increase of doped PANI content, only one T_g was exhibited (between -50 and $45°C$), indicating that the presence of the conducting polymer contributed to a partial plasticization and produced a more homogeneous and compatible material.

σ

The increase in σ of SBR/PANI–DBSA–PSS blends with increasing content of the conducting complex is shown in Figure 3. We believe that the percolation threshold occurred at values lower than 10% (w/w) for the PANI–DBSA–PSS complex because the 90/10
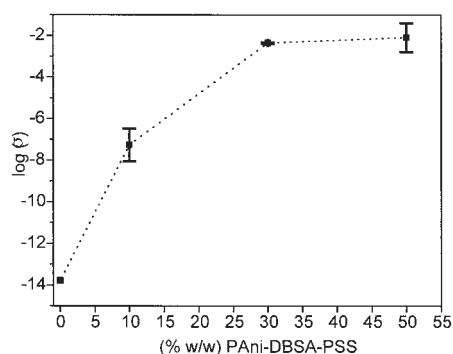
Figure 3 Variation of the logarithm of the electrical conductivity (σ) as a function of PAni-DBSA-PSS complex concentration in SBR blends.

Figure 4 Effect of PAni-DBSA-PSS complex concentration on the mechanical properties of blends, Young's modulus (E) and elongation at break (ε_r).

blend was already conductive (ca. 10^{-7} S/cm). For 50% (w/w) of the conductive component, these values were close to the intrinsic σ of the pure PANI–DBSA–PSS complex sample used in these blends (ca. 10^{-2} S/cm).[16]

Mechanical properties

When two polymers are mechanically or otherwise mixed for blending purposes, they will form domains. If they are totally immiscible (more commonly denoted "incompatible"), they will not stick together, and the blend will have very poor mechanical properties. If they are sufficiently compatible to interpenetrate, at least in the vicinity of the phase boundary, they will form a heterogeneous structure that may have valuable properties.[24] Figure 4 shows the mechanical performance of SBR/PANI–DBSA–PSS blends as a function of the conductive complex concentration. The elongation at break (ε_r) decreased considerably for all of the mixtures, indicating that the conducting complex was incompatible with the SBR matrix, despite the nature of the counteranion used for PANI protonation. Barra et al.[6] also observed this behavior for ethylene–vinyl acetate copolymer/PANI–DBSA blends prepared in a Haake internal mixer and for blends with higher concentrations of a PANI–DBSA complex [>15% (w/w) were too brittle and could not be subjected to tensile testing]. ε_r depends on the interfacial adhesion between the phases. If the adhesion is not perfect, the fissure that induces sample break originates in the interfacial region. The absence of this adhesion makes this region weaker. On the other hand, for the blend with 50% (w/w) PANI–DSSA–PSS, we observed a significant improvement in the mechanical properties, as indicated by an increase in Young's modulus (E; MPa) and a higher ε_r.

Reflectivity measurements

We studied the behavior of SBR/PANI–DBSA–PSS blends related to the preparation of microwave-ab-
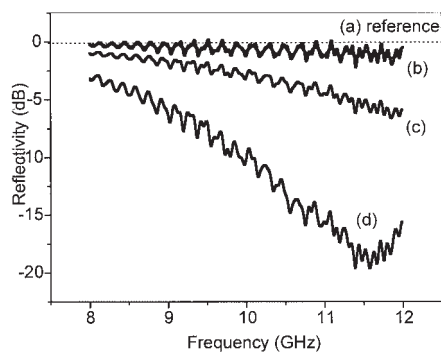
Figure 5 Attenuation of reflectivity for SBR blends with: (b) 10, (c) 30 and (d) 50% (w/w) of PAni-DBSA-PSS. Thickness of blends (3.0 mm). The solid line (a) corresponds to the curve for an A1 plate used as reference.

sorbing materials, evaluating σ of the blends as a function of the PANI–DBSA–PSS complex concentration. Measurements of absorbed energy in the frequency range 8–12 GHz were performed with the wave guide method.[19] A material used as an absorbing material should present σ values in the range 10^{-1} to 10^{-3} S/cm.[25] Figure 5 shows the attenuation of the blends with 10, 30, and 50% (w/w) PANI–DBSA–PSS as a function of frequency. The radiation attenuation was calculated from the difference between the attenuation curves of the blend and an aluminum plate (the reference). For SBR/PANI–DBSA–PSS blends, an increase is observed in the attenuation values with high PANI–DBSA–PSS concentrations. This was assigned to different σ values obtained for blends, where it was known that the radiation absorption in a determined frequency was related to σ of the material. In previous research with elastomeric blends with PANI–DBSA, this behavior was also verified for 3 mm thick samples, where EPDM/PANI–DBSA blends absorbed at a higher frequency and produced high attenuation values at 20 dB (ca. 99.9% of incident radiation was absorbed).[26]

CONCLUSIONS

Conductive thermoplastic elastomer blends of SBR copolymer and PANI doped with DBSA and PSS were prepared by thermal reactive processing and evaluated as radar-absorbing materials. Setter attenuation results were found for the blend with 50% (w/w) PANI–DBSA–PSS, which also presented similar σ to doped PANI ($\sigma = 6.8 \times 10^{-3}$ S/cm), which indicated that it is possible to produce a conductive elastomer with a good shielding effectivity value (ca. 20 dB).

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