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Influence of plasticizers (DOP and CNSL) on mechanical and electrical properties of SBS/polyaniline blends

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Abstract

Electrically conductive blends based on polyaniline–dodecylbenzene sulfonic acid (Pani.DBSA)/styrene–butadiene–styrene (SBS) block copolymer have been prepared in the presence of different plasticizers such as dioctyl phthalate (DOP) and cashew nut shell liquid (CNSL). The products were characterized by ultraviolet–visible (UV–vis) spectrometry, scanning electron microscopy, X-ray diffraction, electron paramagnetic resonance (EPR) and resistivity measurements. The presence of DOP resulted in an increase of the electrical resistivity whereas the increasing concentration of CNSL resulted in a decrease of electrical resistivity. In the latter case, the presence of cardanol, a phenol-type compound in CNSL, may be responsible for the improved electrical performance, probably because of a secondary doping process, which changes the molecular conformation of Pani.DBSA chains from “compact coil” to “expanded coil”. In addition, CNSL contributes to the formation of cocontinuous-type morphology with conducting pathways in larger extension. EPR studies also showed an increase of the polaron mobility as the amount of CNSL in the blend increases.

Keywords: Polyaniline; Conductivity; SBS

1. Introduction

Polyaniline-based conducting blends have been extensively studied with the aim of developing new materials which combine the good electrical properties of polyaniline and the mechanical performance of the host insulating polymer [1]. In the sense, the use of styrene–butadiene–styrene (SBS) triblock copolymer as the insulating matrix is advantageous due to its elastomer–thermoplastic characteristic, that is, it presents good elastomer properties and can be processed as a thermoplastic. Melting blends of SBS with polyaniline doped with dodecylbenzene sulfonic acid (Pani.DBSA) have been recently studied in our laboratory [2,3]. For these studies, Pani.DBSA was prepared by blending the emeraldine base with an excess of DBSA in a mortar, through a redoping process (Pani.DBSA$_{red}$). DBSA was chosen as the protonating agent because of its ability in improving the compatibility between the blend components and also due to its plasticizing character [4,5]. The excess of DBSA also promoted an additional protonation of the polyaniline chain during melt mixing [2]. As a consequence, good electrical conductivity has been achieved. However, the mechanical properties have decreased substantially because of the side reactions between the DBSA and the double bond of the polybutadiene segment of SBS.

Another interesting method for the synthesis of Pani.DBSA consists of one-step emulsion polymerization of aniline in the presence of DBSA and the oxidant (Pani.DBSA$_{emul}$) [6]. Melt blend of SBS with Pani.DBSA synthesized by this method

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presented an outstanding mechanical performance and could be processed at relatively high temperature (around 100 °C) and under shear forces in an internal mixer without significant degradation of the SBS matrix [7]. However, the electrical conductivity was lower than that achieved in blends containing Pani.DBSA$_{red}$. This behavior was attributed to the presence of isolated aggregates of Pani.DBSA$_{emul}$ without the formation of conducting pathway in large excess. The formation of these aggregates was caused by the poor processability of the blend because of the absence of excess DBSA.

In order to improve the processability and dispersion of Pani.DBSA$_{emul}$ in SBS matrix and avoid the deleterious effects of the excess of DBSA on the mechanical performance of the blend, we decided to study the influence of external plasticizers on the electrical and mechanical properties of SBS/Pani.DBSA melt blends. These plasticizers are expected to improve or at least maintain acceptable mechanical performance of the system and also facilitate the formation of the conducting pathway of Pani.DBSA in the matrix. Two different plasticizers were investigated in this study: dioctyl phthalate (DOP) and cashew nut shell liquid (CNSL). The former is a well-known plasticizer for plastic and rubber. The second one is a by-product of the cashew industry, whose main component is cardanol, a phenol derivative containing C15 unsaturated hydrocarbon chain [8–10].

2. Experimental

2.1. Materials

SBS (TR-1061; PBD content = 70 wt%; $\langle M_w \rangle = 120{,}000$ g/mol, density = 0.98 g/cm^3) was kindly supplied by Petroflex S.A. (Rio de Janeiro, Brazil). Aniline (analytical grade from Vetec, Brazil), ammonium peroxydisulfate (APS) (analytical grade from Vetec, Brazil), dodecyl benzenesulfonic acid (DBSA) (commercial grade from Solquim LTDA, Brazil), DOP (Vulcan Ltda, Brazil) and CNSL (USIBRAS Ltda, Brazil) were used without further purification.

2.2. Synthesis of Pani.DBSA

Polyaniline doped with DBSA (Pani.DBSA$_{emul}$) was synthesized by a one-step emulsion polymerization in toluene, according to the literature [6]. In a typical procedure, 4.7 mL (0.051 mol) of aniline and 16.7 g (0.051 mol) of DBSA were dissolved into 250 mL of toluene under constant stirring. The medium was kept at 0 °C and an aqueous solution containing 11.36 g (0.051 mol) of APS in 40 mL of water was slowly added over a period of 20 min. After 6 h, the reaction medium was poured into methanol, filtered, washed several times with methanol and dried. Pani.DBSA prepared by this procedure presented a surface conductivity of 2.1 S/cm. The experimental set up included a Keithley 6517A electrometer; a Minipa ET2907 multimeter and a home-made four-probe device with a medium distance between the probes of 0.17 ± 0.03 cm. The electrical resistivity measurements were performed by the conventional four-point method, on pressed Pani.DBSA powder prepared at room temperature.

2.3. Blend preparation

SBS copolymer was first introduced into a Haake Rheocord 9000 internal mixer operating with Cam rotor at 60 rpm and 100 °C. After 2 min, the mixture containing the conducting filler and the appropriate amount of plasticizer was introduced into the chamber and mixing was carried out for 8 min. The total amount of the used materials never exceeded 60 g.

2.4. Mechanical tests

The samples for tensile tests were compression molded into sheets (80 × 80 × 2 mm) at 100 °C, for 3 min under pressure of 6 MPa. Tensile experiments were performed in an Instron 5569 tensile machine, at room temperature according to ASTM D638.

2.5. Characterization

Volume resistivity of the blends was determined according to ASTM D257, using a Keithley 6517A electrometer. The samples were compression molded as disks with 38 mm diameter, at 100 °C, for 3 min, with pressure 6 MPa.

The UV–vis spectrometry measurements were performed between 300 and 900 nm, on a Varian UV–vis Spectrometer Model CARY 100. The samples were dissolved in toluene at a concentration of 5.5×10^{-5} g/mL.

The morphology of the samples was determined by scanning electron microscopy (SEM) on a JEOL equipment model JSM-LV5300 with 10 kV of voltage acceleration. The micrographs were taken from cryofracturated surfaces after coating with a thin gold layer.

Wide-angle X-ray diffraction (WAXD) scans of SBS/Pani.DBSA blends were obtained using a Phillips X'Pert X-ray diffractometer at room temperature. X-ray patterns were taken from monochromatized Cu Kα radiation source ($\lambda \approx 0.154$ nm). The scan range (2θ) was 5–50° with 0.05° step. The degree of crystallinity was estimated by comparing the integrated intensity of crystalline components, which were determined by subtracting the total scattered intensity from the amorphous halo, according to the typical procedure reported in literature [11,12].

The EPR measurements were performed on a Bruker ESP-380 FT-CW spectrometer operating in X-band (~9.5 GHz) and at a frequency modulation of 100 kHz. The spectra were obtained at room temperature in a cylindrical resonating cavity. The g-factors were determined against diphenylpicrylhydrazyl standard (DPPH) ($g = 2.0023$). In order to avoid saturation of the EPR signal, all spectra were measured in low power (0.5 mW), using modulation amplitude of 0.3 mT. The EPR susceptibilities were estimated by double-integrating the EPR signal, using the Bruker WinEPR® software.

3. Results and discussion

3.1. Melt processing and mechanical properties

Table 1 summarizes the effect of the plasticizer on the totalized torque (TTQ) of the blend containing 30% of Pani.DBSA. The presence of Pani.DBSA resulted in a substantial decrease of totalized torque of the blend because of the plasticizing effect of the counteranion, DBSA. The addition of DOP or CNSL resulted in an additional decrease of torque, as expected due to the plasticizing action of these components.

The effect of plasticizers on the mechanical properties of the blends is presented in Table 2. The hardness decreased continuously as the amount of plasticizer increased and lower values were obtained in blends with DOP. SBS/Pani.DBSA blend displayed lower values of tensile properties than pure SBS but the results are still considered very good, as compared to similar blend containing Pani.DBSA$_{red}$ [2]. The ultimate tensile properties of the blends are also illustrated in Fig. 1, as a function of the plasticizer content. The presence of 5 phr of CNSL resulted in a significant improvement of elongation at break without affecting the other properties, such as tensile strength and hardness. Further increase of CNSL content decreased both the ultimate tensile properties. On comparing both plasticizers, the CNSL displayed the best mechanical performance in all studied compositions. This behavior may be attributed to the good affinity of CNSL for both SBS and Pani.DBSA components. The phenol moiety of CNSL is able to interact with the Pani backbone while the long hydrocarbon chain is compatible with the SBS matrix.

Table 1
The effect of the plasticizer content on melt processability of SBS/Pani.DBSA (70:30) blends

Blend component (wt%)		DOP		CNSL	
SBS	Pani.DBSA	Amount (phr)	TTQ (NMs)	Amount (phr)	TTQ (NMs)
100	0	0	11,372 ± 28	0	11,372 ± 28
70	30	0	7063 ± 18	0	7063 ± 18
70	30	5	6987 ± 16	5	7232 ± 18
70	30	10	6123 ± 15	10	6680 ± 17
70	30	15	5822 ± 15	15	5581 ± 14
70	30	20	5531 ± 14	20	5000 ± 12

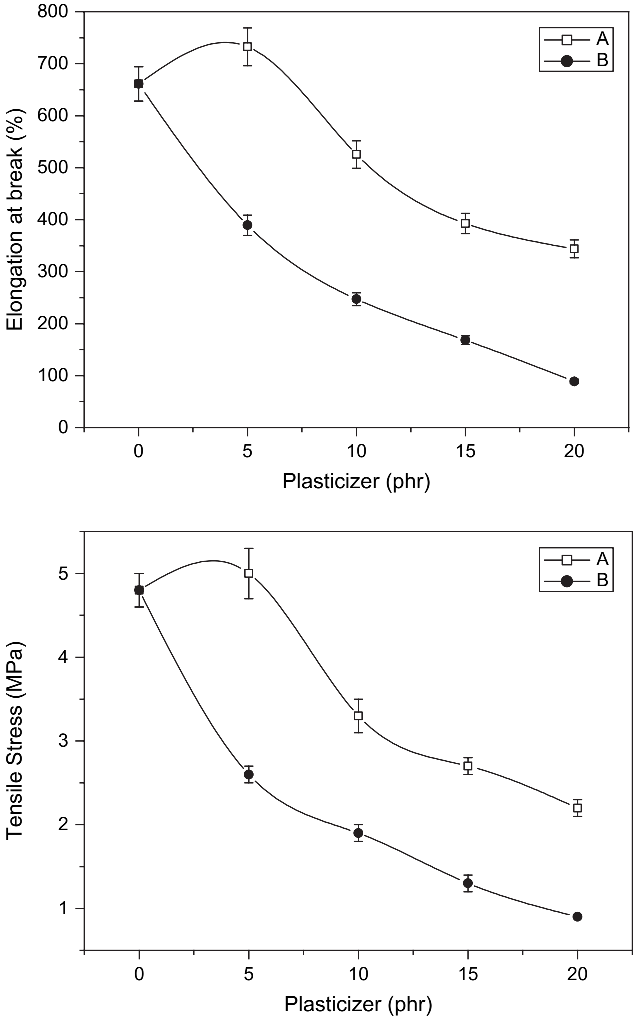

Fig. 1. The ultimate tensile properties of SBS/Pani.DBSA (70:30) blends, as a function of the plasticizer content.

3.2. Volume resistivity

The logarithm of volume resistivity of SBS/Pani.DBSA blends is illustrated in Fig. 2, as a function of the plasticizer content. Pure SBS displayed a very high electrical resistivity (around 3.8×10^{15} Ω cm), as expected for an insulating polymer. The presence of 30% of Pani.DBSA decreased the resistivity around six times, whose value was found to be around 2.6×10^{9} Ω cm, which is still very high to be considered

Table 2
The effect of the plasticizer content on mechanical properties of SBS/Pani.DBSA blends

Sample	Plasticizer (phr)	Hardness shore A		Elongation at break (%)		Ultimate tensile strength (MPa)	
		CNSL	DOP	CNSL	DOP	CNSL	DOP
SBS	0	73 ± 2		720 ± 4		7.7 ± 0.4	
SBS/Pani (70:30)	0	65 ± 2		661 ± 3		4.8 ± 0.2	
	5	63 ± 2	63 ± 2	733 ± 4	389 ± 2	5.0 ± 0.3	2.6 ± 0.2
	10	59 ± 2	56 ± 4	525 ± 3	247 ± 1	3.3 ± 0.2	1.9 ± 0.3
	15	55 ± 2	48 ± 2	393 ± 2	168 ± 1	2.7 ± 0.1	1.3 ± 0.1
	20	48 ± 4	43 ± 2	344 ± 2	89 ± 1	2.2 ± 0.1	0.9 ± 0.2

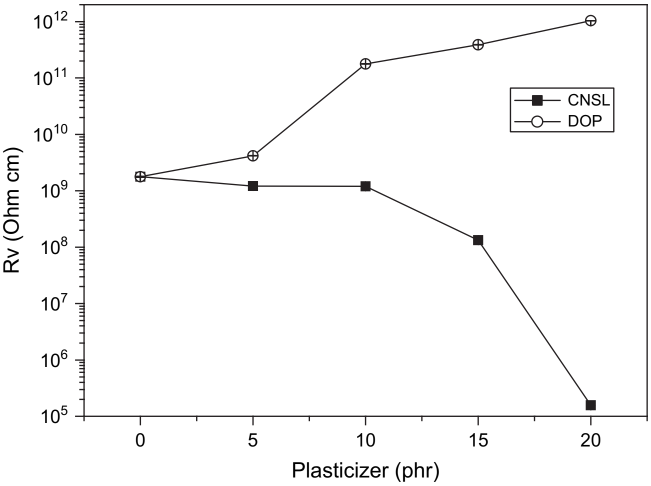

Fig. 2. The logarithm of volume resistivity of SBS/Pani.DBSA (70:30) blends, as a function of the plasticizer content.

a conducting blend. The presence of DOP resulted in a continuous increase of the blend resistivity, indicating that the conducting pathway was destroyed in some extent, probably because of the increased dispersion of Pani.DBSA particles inside the SBS matrix.

A very interesting phenomenon was observed when CNSL was employed as the plasticizing system. The increase of the CNSL content in the blend resulted in a decrease of resistivity and this behavior was significant at a concentration of 20%. This phenomenon may be attributed to a secondary doping effect on Pani.DBSA, promoted by the phenol moiety in the cardanol present in CNSL [9]. The secondary doping was reported in several papers when polyaniline was treated with *m*-cresol [13–16]. The role of the secondary dopant is based on decreasing of the polarization and on the elimination of the structural defects by creating a strong interaction with the polyaniline backbone and/or the primary doping agent [17,18]. As a consequence, an ordered structure is achieved, which contributes for an increase of charge mobility and conductivity [13].

3.3. Morphology

Fig. 3 compares the SEM micrographs of SBS/Pani.DBSA blends containing different amounts of DOP or CNSL. White dispersed particles are related to polyaniline. The blend without plasticizer is characterized by the presence of polyaniline as aggregates with some interconnections between each other, forming some conducting pathways (see Fig. 3a). The addition of DOP resulted in a higher dispersion of polyaniline with lower interconnection between the particles. Higher amount of DOP resulted in the formation of bigger aggregates with poor connection between them. The morphological behavior of the DOP-based systems can be attributed to the high plasticizing effect of DOP, which contributes to a decrease of the matrix viscosity. Consequently, the encapsulation of the Pani.DBSA particles by the SBS is enhanced. These results are in agreement with the resistivity behavior.

Blends containing CNSL presented a peculiar morphology. Both the polyaniline and the SBS phases form cocontinuous morphology and this feature is more pronounced with higher amounts of CNSL. The continuity of the Pani phase is probably one of the main reasons for the improved conductivity of these blends.

3.4. UV–vis spectroscopy

The effect of the plasticizer on the UV–vis absorption spectra of SBS/Pani.DBSA blends is illustrated in Fig. 4. This figure only shows the spectra corresponding to blends containing 20% of plasticizer because all other concentrations displayed similar patterns. In all the systems, three characteristic absorption peaks are observed: at around 350 nm, which is ascribed to π–π^* transition of the benzenoid rings, and at 400–420 and 750–800 nm, attributed to polaron–π^* transition and π–polaron transition, respectively [19–21]. Blend containing 20% of CNSL exhibits the highest absorption at 400–420 nm, which is assigned to the localized polarons, a characteristic of the protonated polyaniline. In addition, a decrease of the absorption peak at around 770 nm is observed, which can be attributed to a conformational change of Pani chains from ‘‘compact coil’’ to ‘‘expanded coil’’, caused by the interaction between cardanol and Pani.

The presence of 20% of DOP did not affect the intensity of the polaronic absorption peak at 770 nm but decreased significantly the absorption at 400–420 nm, indicating a decreasing doping level of Pani.DBSA. These results are in complete agreement with the resistivity results.

3.5. X-ray diffraction

X-ray diffraction patterns of SBS/Pani.DBSA blends are compared with pure SBS in Fig. 5. In all blends containing Pani.DBSA, it is possible to observe a weak and a sharp peak at $2\theta = 25°$ and a very broad peak at around 19°, the last one is related to the amorphous portion of the blend. In addition, blends containing no plasticizer (curve b) or 20% of CNSL (curve c) also display two small peaks at around 36° and 48°, indicating the presence of different molecular arrangements/crystal structures. In blend containing 20% of DOP, these peaks are too small. The peaks related to crystal region of SBS/Pani.DBSA containing 20% of CNSL are higher than the other, indicating a higher crystallinity degree. In fact, the overall crystallinity of CNSL-based blend was found to be around 14%, which is higher than SBS/Pani.DBSA blend without plasticizer (around 10%) and that containing 20% of DOP (9%).

3.6. EPR spectra

Table 3 presents the effect of the amount of different plasticizers on the peak-to-peak linewidth (ΔH_{pp}) obtained from the EPR spectra. In both plasticizer systems, the increase of the DOP or CNSL concentration resulted in a decrease of this EPR parameter. According to the literature [22], the peak-to-peak linewidth in conducting polymer systems is related to

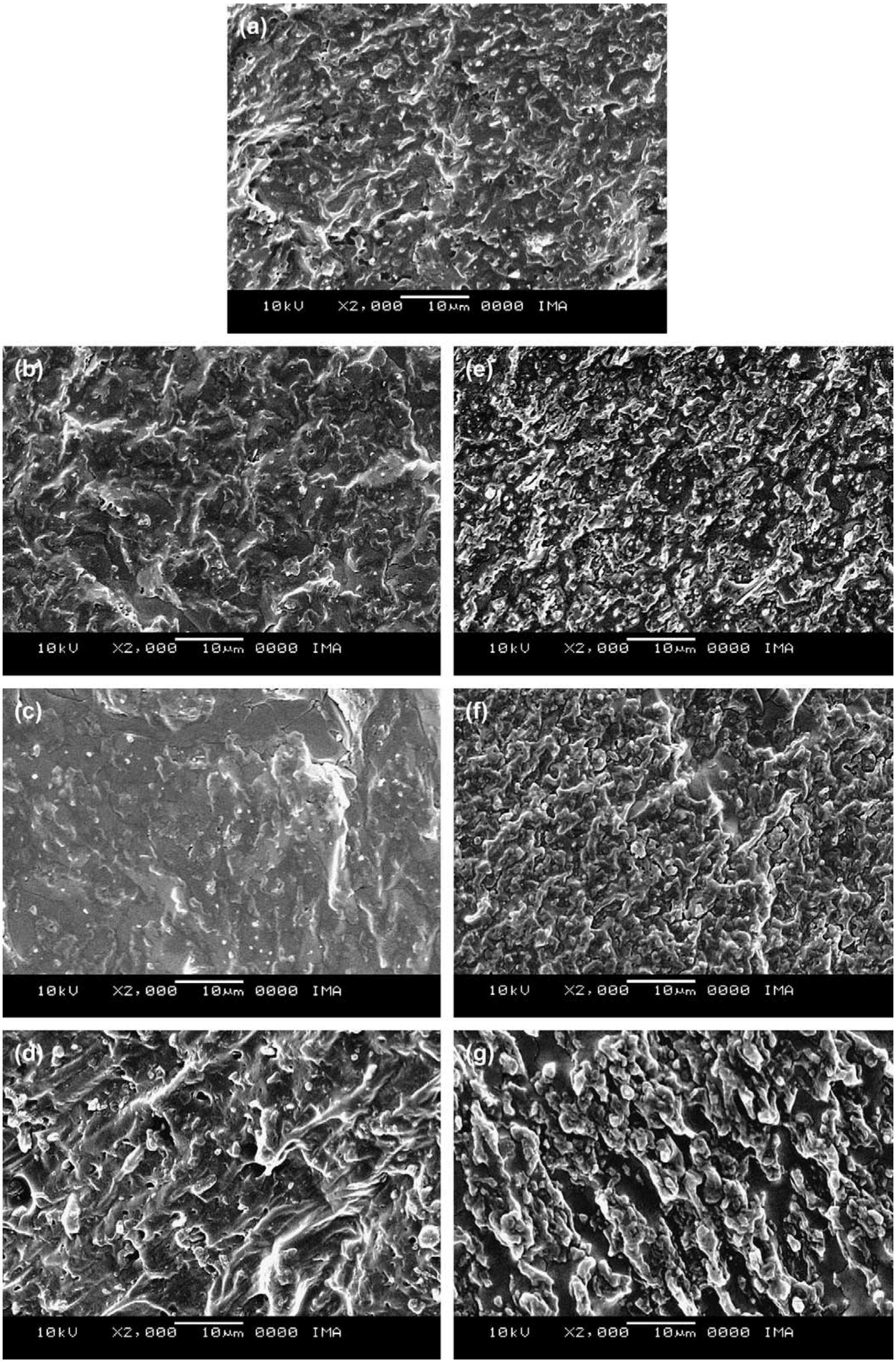

Fig. 3. SEM micrographs of SBS/Pani.DBSA (70:30) blends: (a) without plasticizer; with DOP in a proportion of (b) 5%, (c) 10%, (d) 20%; with CNSL in a proportion of (e) 5%, (f) 10%, (g) 20%.

polaron mobility and a less localized structure of the polarons: the narrower the linewidth, the greater the polaron mobility is. Therefore, from the EPR measurements, both plasticizers contribute to an increase of polaron mobility but this effect is more pronounced by using CNSL.

4. Conclusions

The use of cashew nut shell liquid (CNSL) in polyaniline-based conducting composites was reported for the first time in this paper. This compound improved the processability of

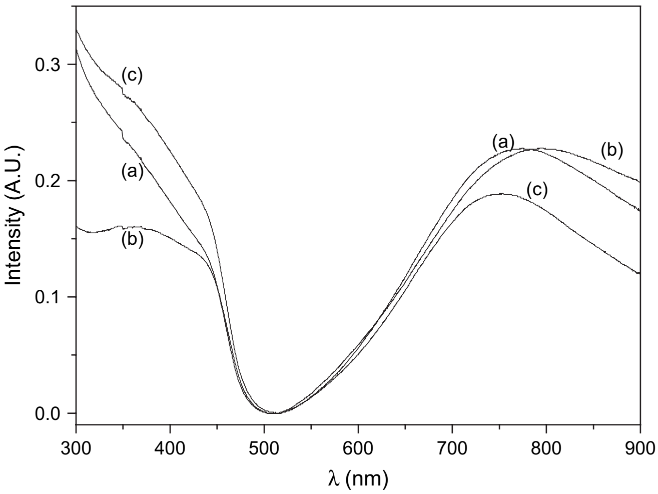

Fig. 4. UV–vis absorption spectra of SBS/Pani.DBSA blends (a) without plasticizer, (b) with 20% of CNSL and (c) with 20% of DOP.

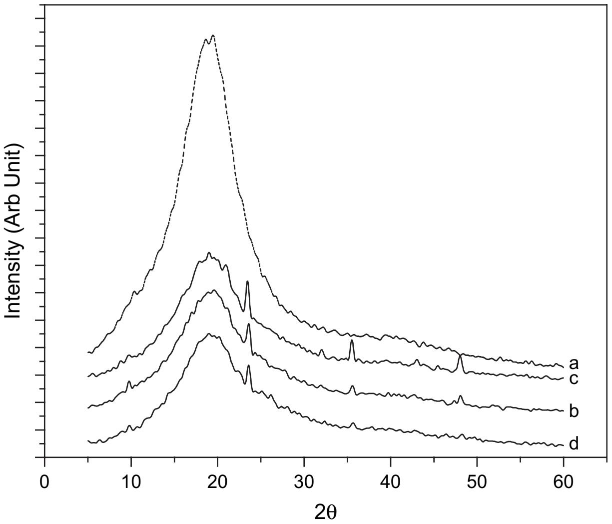

Fig. 5. X-ray diffraction patterns of (a) pure SBS and SBS/Pani.DBSA blends (b) without plasticizer, (c) with 20% of CNSL and (d) with 20% of DOP.

Table 3
The effect of the plasticizer content on the peak-to-peak linewidth (ΔH_{pp}) parameter, obtained from the EPR spectra, for SBS/Pani.DBSA (70:30 wt%) blends

Plasticizer (phr)	DOP	CNSL
0	2.95 ± 0.03	2.95 ± 0.03
5	2.75 ± 0.03	2.42 ± 0.02
10	2.53 ± 0.03	2.31 ± 0.02
15	2.39 ± 0.02	2.35 ± 0.02
20	2.26 ± 0.02	2.23 ± 0.02

SBS/Pani.DBSA blends and also promoted an additional increase of the electrical conductivity. This phenomenon is known as secondary doping, and was achieved without additional protonation of polyaniline. In this case, the conductivity is enhanced by conformational changes of the polyaniline chains from compact coil to expanded coil, imparted by the phenol moiety of cardanol present in CNSL. This arrangement resulted in an increase of polaron mobility as evidenced by UV–vis and EPR spectroscopies and an increase of crystallinity degree and turns easier the charge transport, which is responsible for the additional conductivity. Similar phenomenon has been observed in several other systems when polyaniline was exposed to vapor of *m*-cresol [13–18]. The CNSL used in our system contains 85% of cardanol, a phenol-type compound with long hydrocarbon chain, similar to *m*-cresol, the phenol moiety of cardanol is able to interact with the polyaniline chains, giving rise to more orientated chains. The great advantage of our system is that the secondary doping is achieved during the processing the CNSL with the blend components (SBS and Pani.DBSA) in a two-roll mill, in an internal mixer or in an extruder, without the dangerous and toxic step of exposing the material to vapor of *m*-cresol as performed in other systems. In addition, CNSL is a by-product from the cashew industry and its use in conducting composites constitutes a new and interesting approach to develop polyaniline-based blends with an outstanding electrical behavior in addition to better processability.

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