

MECHANICALLY AND THERMALLY STABLE BLENDS OF POLY(STYRENE-BUTADIENE-STYRENE) WITH CONDUCTING POLY(THIOUREA-AZO-NAPHTHYL)

Ayesha Kausar* and Syed Tajammul Hussain

*Nanosciences and Catalysis Division, National Centre for Physics, Quaid-i-Azam University Campus,
Islamabad 44000, Pakistan*

Abstract A new aromatic azo-polymer, poly(thiourea-azo-naphthyl) (PTAN), has been synthesized using 1-(5-thiocarbamoylaminonaphthyl)thiourea and diazonium salt solution of 2,6-diaminopyridine. PTAN was easily processable using polar solvents and had high molar mass 57×10^3 g/mol. Electrically conducting, mechanically and thermally stable rubbery blends of poly(styrene-butadiene-styrene) (SBS) triblock copolymer and PTAN were produced by solution blending technique. FESEM of SBS/PTAN blends revealed nano-scale dispersion of the conducting filler showing good adhesion between the matrix and PTAN. Remarkable effects of azo-content on the conductivity of SBS-based blends have been observed. Accordingly, PTAN loading from 10 to 60 wt% increased the conductivity from 1.24 to 1.66 S/cm. Relationship between PTAN loading and thermal stability of the materials was also investigated. With increasing the PTAN content, 10% gravimetric loss was increased from 484 to 500 °C, while glass transition was enhanced from 119 to 126 °C. Thermal and conducting data of the blend showed better results relative to pure elastomer but were lower than those of the conducting filler. Similarly, the tensile strength (57.35–62.33 MPa) of SBS/PTAN was improved relative to there of SBS. Fine balance of properties renders new materials fairly better than the existing elastomeric blends used in a number of applications.

Keywords: Poly(thiourea-azo-naphthyl); SBS; Electrical conduction; Thermal stability; Tensile strength.

INTRODUCTION

Recently, conducting polymer systems have been established by the conducting filler dispersed inside an insulating polymer matrix as a method to fabricate polymeric blends. These high performance materials possess good mechanical properties, thermal stability and processability of the matrix together with the electrical properties of the conducting component^[1–3]. Consequently, electro-conductive polymer-based materials with tailored conductivity for a number of applications can be developed by mixing conductive polymers or fillers into conventional polymer matrices. Usually, filler is located within one phase or at the interface of a heterogeneous blend signifying a co-continuous morphology, the conducting particles interact with each other resulting in the formation of conducting pathway even with low filler contents^[4, 5]. Various research efforts involve carbon black as conductive filler in the polymer matrix^[6–8]. However, the exercise of intrinsically conducting polymers such as polyaniline (PANI) is not so frequent owing to stability of these polymers at temperatures required for melt-blend processing. In solution blending, polyaniline is also not ideal because of low solubility in common solvents. This behavior can be improved by the nature of protonating agent used to impart conducting properties to PANI. The protonation with dodecylbenzenesulfonic acid is quite significant incidentally^[9].

* Corresponding author: Ayesha Kausar, E-mail: asheesgreat@yahoo.com

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Elastomer blends have been repeatedly exploited in various industries to obtain best compromise physical properties including processability, cost, *etc.* In this regard, styrene-butadiene block copolymers form an imperative class of thermoplastic elastomers. In particular poly(styrene-butadiene-styrene) (SBS) triblock copolymer has been exploited as matrix for conductive materials. Among several heterogeneous systems, the one constituted by SBS as the insulating matrix is quite advantageous due to its thermoplastic-elastomeric nature. Thus, it is the unique combination of mechanical properties and processability^[10]. Attributable to the thermodynamic incompatibility of polystyrene and polybutadiene blocks, SBS may present a morphology segregated into different phases with a typical micro domain structure^[11]. Reports on SBS block copolymer melt-blended with PANI have been found in literature. Several results have also been reported concerning the conducting SBS/polyaniline blends prepared by solution process^[11–14]. Moreover, SBS-based conducting blends were developed by exploiting both polyaniline and polypyrrole as the conducting polymer filler^[15–18]. In this article we reported on a soluble, thermally stable and electrically conductive polymer, poly(thiourea-azonaphthyl) (PTAN). Accordingly, this effort involved the solution blending of SBS with PTAN instead of traditional methods using conducting polymeric fillers. The electrical conductivity, heat stability and mechanical properties of SBS/PTAN blends have been studied as a function of the increasing PTAN content. Structure-property relationship and comparison of the physical properties of SBS/PTAN blends with those of the neat polymers have also been investigated.

EXPERIMENTAL

Materials

Poly(styrene-butadiene-styrene) (styrene 45 wt%), 2,6-diaminopyridine (97%) and 1,5-diaminonaphthalene (97%) were provided by Aldrich (St. Louis, Missouri, USA). Ammonium thiocyanate (98%) and tetrahydrofuran (THF) (99.5%) were procured from Merck (Nottingham, UK).

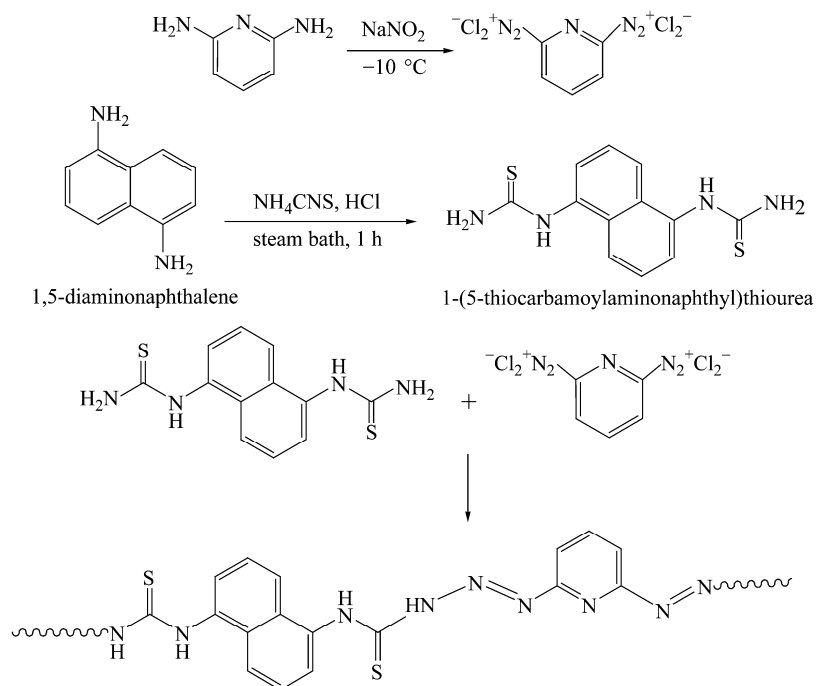
Synthesis of Monomer

Synthesis of 1-(5-thiocarbamoylaminonaphthyl)thiourea (TCANT)

1,5-diaminonaphthalene (0.2 mol), concentrated HCl (16 mL), ammonium thiocyanate (0.2 mol) and deaerated water (120 mL) were heated in a porcelain dish (2 h) with a steam bath. The mixture was allowed to cool to room temperature. The mixture was then gradually evaporated to dryness for 6–7 h. The product was boiled with charcoal in ethanol, filtered and cooled. 1-(5-thiocarbamoylaminonaphthyl)thiourea was recrystallized from ethanol and dried under vacuum at 90 °C (36 h)^[19]. Elemental analysis for C₁₂H₁₂N₄S₂: Calculated (%) = C 52.15, H 4.38, N 20.27; Found (%) = C 51.07, H 4.19, N 19.41. FTIR (KBr): 3319 cm⁻¹, 3276 cm⁻¹ (N–H stretch), 3036 cm⁻¹ (aromatic C–H stretch), 2934 cm⁻¹ (aliphatic C–H stretch), 1598 cm⁻¹ (N–H bend), 1411 cm⁻¹ (C–N stretch), 1153 cm⁻¹ (C=S stretch). ¹H-NMR (300.13 MHz, DMSO-d₆), δ : 4.14 (s, 4H, H_a), 9.26 (s, 2H, H_b), 6.45 (d, 2H, H_c), 7.01 (t, 2H, H_d), 7.22 (d, 2H, H_e). ¹³C-NMR (75.47 MHz, DMSO-d₆), δ : thiocarbonyl C=S 177.2 (C₁), 141.4 (C₂), 107.3 (C₃), 125.1 (C₄), 110.2 (C₅).

Diazotization

2,6-diaminopyridine (0.04 mol) was first added to concentrated hydrochloric acid (10 mL) and then dissolved in distilled water (50 mL). The mixture was placed in a freezing-bath to cool to –10 °C, ensuing brown-colored precipitate. To the above suspension, 0.04 mol sodium nitrite solution (20 mL) was added vigilantly with constant stirring. After complete addition, the mixture was allowed to stir for 1 h at –10 °C, to avoid the decomposition of diazonium salt. At the end, excess of nitrite was removed by the addition of urea (2 g) with stirring of 20 min, resulting in a brown colored diazonium salt solution. The route leading to intermediates is outlined in Scheme 1.



Scheme 1 Scheme for the synthesis of monomer and poly(thiourea-azo-naphthyl)

Synthesis of PTAN

TCANT (0.04 mol) was dissolved in sodium hydroxide (10%) and the diazonium salt solution obtained was added drop wise keeping the temperature below $-10\text{ }^\circ\text{C}$. The mixture was stirred for 3 h and acidified with dilute HCl (10%). The resulting precipitate was filtered, washed with hot water and then with hydrochloric acid (3%). The precipitate was again dissolved in sodium hydroxide (3%) followed by re-precipitation in HCl^[20]. The polymer was dried under vacuum at $80\text{ }^\circ\text{C}$. FTIR (KBr, cm^{-1}) (Fig. 1): 3332 and 1597 cm^{-1} (sec. amine N—H stretch and bend), 3082 cm^{-1} (aromatic C—H stretch), 1413 cm^{-1} (—N=N— stretch), 1126 cm^{-1} (C=S stretch), 829 cm^{-1} (C—S stretching). $^1\text{H-NMR}$ (300.13 MHz, DMSO- d_6), δ : 8.82 (s), 9.93 (s) (N—Hs chemical shifts), 7.44 (d), 7.53 (d), 7.88 (t) (pyridine unit), 6.55 (d), 7.15 (t), 7.21 (d) (naphthalene unit).

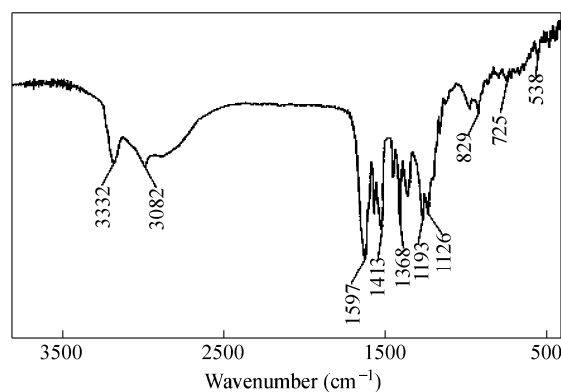


Fig. 1 FTIR spectrum of PTAN

SBS/PTAN Blends

Solutions of SBS and poly(thiourea-azo-naphthyl)s in THF were prepared separately. PTAN solution was added to the solution of SBS at desired proportions. The mixed solutions were ultrasonicated (30 W and 50 Hz) for 5 h.

Thin films (61 ± 5 μm thickness) were cast by pouring the blend solution on glass Petri's, and solvent was evaporated at 80°C for 24 h.

Measurements

Nuclear magnetic resonance (NMR) spectra were scanned at room temperature using a BRUKER (Karlsruhe, Germany) Spectrometer (300.13 MHz for ^1H -NMR) in deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$). Infrared (IR) spectra were recorded using a Fourier transform infrared (FTIR) Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD (California., USA) with 4 cm^{-1} resolution. The number and weight-average molecular weight (M_n & M_w) was calculated through gel-permeation chromatography using THF and refractive index (RI) detector. Field emission scanning electron microscopy (FE-SEM) of freeze fractured samples was performed using an instrument of JSM5910, JEOL Japan. Thermogravimetric analysis (TGA) was performed by a METTLER TOLEDO TGA/SDTA 851 $^\circ$ thermo-gravimetric analyzer using 1–5 mg of the sample in Al_2O_3 crucibles at a heating rate of 10 K/min. Differential scanning calorimetry (DSC) was performed by a METTLER TOLEDO DSC 822 $^\circ$ differential scanning calorimeter taking 5–10 mg of samples in aluminum pans and heated at a rate of 10 K/min. Electrical conductivity of thin films was measured using a Keithley 614 electrometer and the four-probe method. Stress-strain response of the samples was obtained on a Universal Testing Machine INSTRON 4206 according to the ASTM 638 method. A crosshead speed of 100 mm/min was used during the test.

RESULTS AND DISCUSSION

Preparation of PTAN and SBS/PTAN Blends

Scheme 1 shows the preparation of PTAN having the sole combination of azo, thiourea and naphthalene linkages via a simple and straightforward route. High molar mass PTAN showed good solubility in THF. 0.5 g/dL polymer solution was prepared in THF for molar mass measurement. The M_n was found to be 32×10^3 g/mol, while M_w was measured as 57×10^3 g/mol at 30°C . Solubility behavior of the azo-polymer and new blends in polar aprotic solvents as *N,N*-dimethylacetamide (DMAc), dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), THF and chloroform is presented in Table 1. The system showed good solubility, so representing good affinity between the two blend components. Fine electrical conductivity and heat stability owing to the structural architecture of PTAN were attained. Later on, the conducting polymer was exploited as a filler in SBS matrix to improve mechanical, conducting and thermal properties of new materials. The increase in PTAN content was, therefore, found to enhance the physical characteristics of the SBS/PTAN system.

Table 1. Solubility behavior of PTAN and blends

Sample	Solvent					
	NMP	DMAc	DMF	DMSO	THF	Chloroform
PTAN	++	++	++	++	++	+ h
SBS/PTAN 1 (90:10)	++	++	++	++	++	+ h
SBS/PTAN 2 (70:30)	++	++	++	++	++	+ h
SBS/PTAN 3 (40:60)	++	++	++	++	++	+ h

Solubility: ++ Soluble at room temperature; + h Soluble on heating

Mechanical Properties

The pristine PTAN polymer exhibited tensile strength 24.22 MPa, elongation at break 0.45% and toughness 19.65 MPa. The presence of as low as 10 wt% of PTAN in the blend resulted in a significant increase of both ultimate tensile strength (57.35 MPa) and elongation at break (0.69) as compared to the pure SBS sample (Table 2 and Fig. 2). This behavior was more accentuated for blends containing a higher amount of azo-filler. With rising filler content SBS/PTAN 2 (30 wt%) exhibited strength of 61.01 MPa and SBS/PTAN 3 (60 wt%)–62.33 MPa. Because of the good compatibility between the blend components, the mechanical performance was excellent. The initial modulus of SBS/PTAN 1 sample at room temperature was found to be

6670 MPa, 8340 MPa for SBS/PTAN 2 and increased up to 9230 MPa for the blend with 60 wt% PTAN. Higher value of elongation at break was also observed for SBS/PTAN 3 (0.72) relative to other blends. However, the elongation at break for pure SBS elastomer was 3.34, which decreased upon the addition of the filler/azopolymer in the matrix (0.45–0.72). Nevertheless, within the system the strain slightly increased by only 0.1% *i.e.*, obviously a negligible ascend. Therefore, we can say that the SBS elasticity decreased with the inclusion of rigid PTAN. Toughness of the materials, evaluated by integrating area under the stress-strain curve, was in the range 21.16–25.72 J/m³. Similarly, toughness of the material was increased due to the stiffness and inflexibility effect of the azo- and naphthalene-based filler addition. In comparison with the reported SBS-based blends, these values seemed to be pretty high^[21]. This type of tensile behavior is well in agreement with the nano-level compatibility of the blends showing superb interaction between the two components *i.e.* SBS and PTAN, so increasing the overall strength of the system.

Table 2. Mechanical properties of SBS/PTAN blends

Sample	Strength (MPa)	Elongation at break	Initial modulus (MPa)	Toughness (J/m ³)
PTAN	24.22 ± 0.1	0.45 ± 0.05	1330 ± 0.1	19.65 ± 0.3
SBS/PTAN 1 (90:10)	57.35 ± 0.1	0.69 ± 0.05	6670 ± 0.1	21.16 ± 0.3
SBS/PTAN 2 (70:30)	61.01 ± 0.1	0.70 ± 0.05	8340 ± 0.1	22.51 ± 0.3
SBS/PTAN 3 (40:60)	62.33 ± 0.1	0.72 ± 0.05	9230 ± 0.1	25.72 ± 0.3
Neat SBS	20.31 ± 0.1	3.34 ± 0.05	99 ± 0.1	3.02 ± 0.3

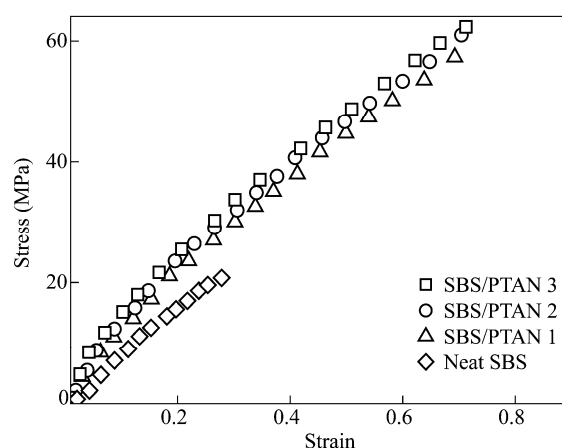


Fig. 2 Stress-strain curves of SBS/PTAN blends

Morphological Aspect

Figure 3 illustrates the micrographs of SBS/PTAN blends containing 10 to 60 wt% of the conducting component. A fine compatible morphology is obvious from Figs. 3(a)–3(d) showing improved adhesion of the dispersed polymer with the elastomer. The addition of PTAN to SBS changed the morphology to some extent, as size of the dispersed phase was found to slightly increase with the addition of conducting polymer. The effect was more pronounced in SBS/PTAN 3 (Figs. 3c & 3d) at 60% addition of conducting filler. Overall FESEM investigation depicted a morphology constituted of fine molecular distribution of PTAN into SBS matrix. Due to the affinity of hydrophobic chains of PTAN with the SBS, the matrix and azo-polymer were compatible with nano-level phase separation. The benzene ring in the styrene block of SBS was capable of forming π - π stacking interaction with the aromatic structure of azopolymer. In all the micrographs, no conducting polymer aggregates were perceived. A somewhat uniform network at nano-level can be observed, indicating that this system achieved a high level of dispersion. Higher level of molecular mixing and formation of uniform network restricted the conformation mobility of azo-chain and can explain the improved conductivity performance. Due to good solvent miscibility of PTAN, these blends contain finely dispersed SBS and PTAN phases forming a

very fine continuous structure that acted as bridges interconnecting the fine molecular dispersion of PTAN phase, thus, promoting the conductivity of the material. This structural hierarchy composed of excellent dispersion of filler was responsible for fine conducting new blends as compared to known SBS/PANI blends^[14].

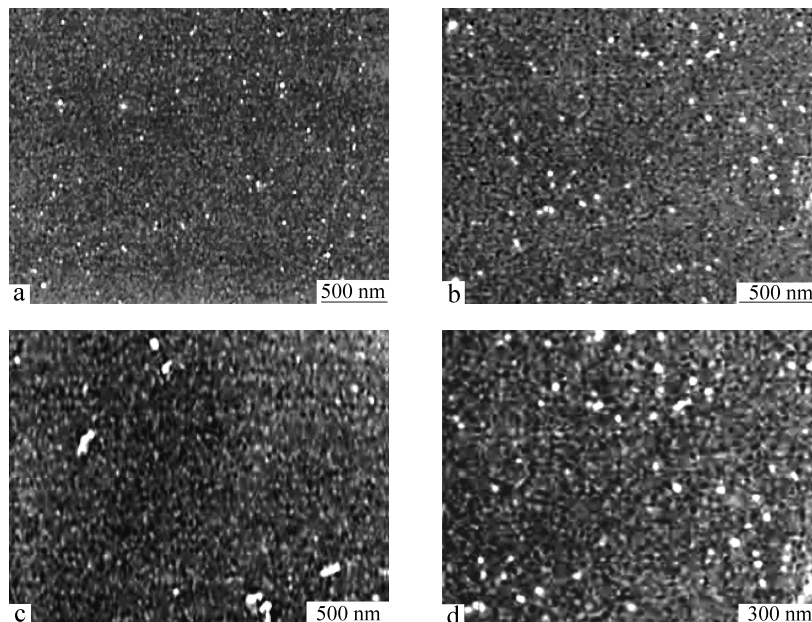


Fig. 3 FESEM images of (a) SBS/PTAN 1, (b) SBS/PTAN 2, (c) and (d) SBS/PTAN 3 of different magnification

Thermal Stability

Thermal stability of SBS/PTAN blends and pure resin and filler was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA thermograms of neat PTAN and SBS/PTAN blends are given in Fig. 4 and data are presented in Table 3. Pure azo-polymer showed single-stage decomposition starting at 471 °C and the major weight loss occurred between 470 and 570 °C. For SBS/PTAN 1 (10 wt%), the thermogravimetric analysis curve owned initial decomposition temperature T_0 at 456 °C, 10% gravimetric loss temperature T_{10} at 484 °C and the decomposition continued up to 525 °C. In contrast, at higher content of filler blended (30 and 60 wt%) the thermal degradation occurred at higher temperatures. SBS/PTAN 2 exhibited T_0 of 461 °C, T_{10} of 494 °C and T_{max} up to 533 °C. SBS/PTAN 3 had higher heat stability among the blends prepared with $T_0 = 465$ °C, $T_{10} = 500$ °C and T_{max} was up to 547 °C. Single-step thermal decomposition above 450 °C was found in all the thermograms due to the decomposition of PTAN backbone; mainly the azo and naphthalene-based architecture is fairly stable at high temperatures. In addition the heteroaromatic structure (pyridine) in the main chain of a polymer would impart excellent stability derived from aromaticity, polarizability and molecular symmetry resulting from electronegative atom. Thus, the dipole-dipole interaction of pyridine groups offered stability and increased the thermal properties. Consequently, the addition of rigid-rod polymer with azo-naphthalene architecture significantly increased the heat stability of the elastomer. In other words as the proportion of rigid polymer decreased in the blends the heat resistance decreased. This is also an evidence to support the observation that the heat stability is dependent on the structure of the new polymer. Therefore, the decrease in rigid rod architecture reduced the thermal properties of the blends. Similarly, the blends also possessed suitably higher char yield 46%–51% at 600 °C compared with SBS. However, the heat stability values of blends was lower relative to those of pure poly(thiourea-azo-naphthyl). Figure 5 represents DSC thermograms of SBS/PTAN blends containing 30-60 wt% filler and filler without SBS. Neat PTAN demonstrated high glass transition temperature T_g (212 °C) relative to the blended materials (Table 3). Thermal transition of SBS/PTAN 1-3 was recorded in the range 119–126 °C. An obvious shift of T_g to higher temperatures occurred, as obvious

from the thermograms, with increasing filler content. When comparing the glass transition of new blends, following order was observed:

$$T_g(\text{SBS/PTAN 3}) > T_g(\text{SBS/PTAN 2}) > T_g(\text{SBS/PTAN 1}) > T_g(\text{SBS})$$

The lower T_g value at 90:10 ratio of SBS:PTAN indicated the flexibility of blend structure due to higher weight percent of elastomer, consequently the effect of PTAN was almost negligible. Moreover an interesting observation was that the low T_g value (-58°C) for the styrene blocks could not be observed in the new blends. In the blend system, SBS chains were not alone in fact they were merged with the chains of azo-polymer forming a new stable/rigid structure. It seems that the rigid poly(thiourea-azo-naphthyl) chains when incorporated into the elastomer, restricted the SBS chain mobility. The azo and bulky naphthyl groups, thus, lowered the SBS chain flexibility, and caused the increase in glass transition of new blended structure. Thermal data, so, revealed that the addition of azo-polymer to SBS has positive effect on the thermal properties. T_g values of new blends were intermediate between that of the pure matrix (-58°C) and the filler. On the whole, new materials were thermally more stable relative to reported SBS blends with polyaniline^[22, 23].

Table 3. Thermal analyses data of PTAN and blends

Polymer	T_g ($^\circ\text{C}$)	T_0 ($^\circ\text{C}$)	T_{10} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	Y_c at 600°C (%)
Neat SBS	-58	414	434	476	21
SBS/PTAN 1	119	456	484	525	46
SBS/PTAN 2	122	461	494	533	50
SBS/PTAN 3	126	465	500	547	51
PTAN	212	471	516	566	53

T_g : Glass transition temperature; T_0 : Initial decomposition temperature; T_{10} : Temperature for 10% weight loss;

T_{max} : Maximum decomposition temperature; Y_c : Char yield; weight of polymer remained

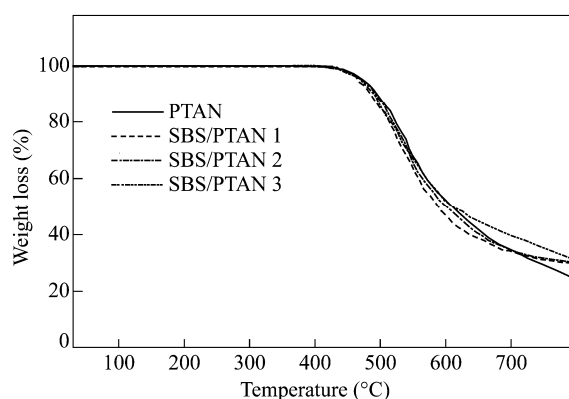


Fig. 4 TGA curves of PTAN and SBS/PTAN blends at a heating rate of 10 K/min in N_2

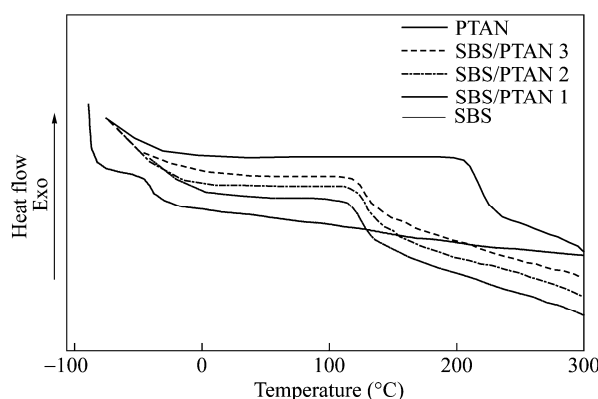


Fig. 5 DSC thermograms of PTAN, SBS and SBS/PTAN blends at heating rate of 10 K/min in N_2

Electrical Conductivity

The dependence of conductivity on the amount of poly(thiourea-azo-naphthyl) was the same as normally found for insulating polymer matrices loaded with conducting fillers. Table 4 compares the electrical conductivity of blends with different compositions and pure azo-polymer. Azo-moieties were found to evidently increase the

Table 4. Conductivity measurements of SBS/PTAN blends

Blend	Conductivity (S/cm)
SBS/PTAN 1	1.24
SBS/PTAN 2	1.39
SBS/PTAN 3	1.66
Neat PTAN	2.12

conductivity of the SBS-based material. The conductivity value of the blend containing 60 wt% of this conducting polymer was the highest (1.66 S/cm) among the samples prepared. However, the conductivity of blends was lower than that of pure PTAN (2.12 S/cm). Overall fine electrical conductivity of the system indicated the existence of a conductive SBS/PTAN network in these nano-blends. The conducting network was so fine and somewhat visible in nano-level compatible blends. Presence of azo moieties in SBS/PTAN system fashioned better conductive network, so denoted higher conductivity. In the blend systems, the conductivity increased gradually with the increase in PTAN content. These values were pretty higher than the intrinsic conductivity of the PANI-based elastomeric blends^[23–25].

CONCLUSIONS

The results presented in this article demonstrated that solution blends of poly(thiourea-azo-naphthyl) in SBS matrix presented good electrical conductivity, reaching values as high as 1.66 S/cm with around 60 wt% of the conductive additive in the blend. The conductivity values were fairly enhanced with the addition of filler from 1.24 S/cm to 1.66 S/cm. Solution blending technique improved the dispersion level of azo-polymer in the SBS matrix. Mechanical performance of the conductive blends was also good when compared to pure SBS. Both tensile strength and elongation at break increased with the addition of the conductive component. Thermal stability investigation suggested that blending SBS up to 60 wt% PTAN could produce materials with 10% gravimetric loss round 434–500 °C. However, the heteroaromatic filler exhibited higher T_g , thermal and electrically conducting properties relative to neat SBS and all the blends prepared in literature owing to rigid backbone aromatic azo and naphthalene-based structure.

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