Design, synthesis and physical properties of poly(styrene–butadiene–styrene)/poly(thiourea-azo-sulfone) blends

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Abstract. A new aromatic azo-polymer, poly(thiourea-azo-sulfone), has been synthesized using 1-(4-thiocarbamoylaminophenylsulfonylphenyl)thiourea and diazonium salt solution. Conducting and thermally stable rubbery blends of poly(styrene-block-butadiene-block-styrene) (SBS) triblock copolymer and poly(thiourea-azo-sulfone) (PTAS) were produced by solution blending technique. PTAS possessed fine solubility in polar solvents and high molar mass $63 \times 10^3 \text{ g mol}^{-1}$. Microscopic analysis on SBS/PTAS blends revealed good adhesion between the two polymers without macro phase separation. Electrical conductivity measurement recommended that blending of SBS with 60% PTAS was sufficiently conducting 1.43 S cm^{-1} . A relationship between PTAS loading and thermal stability of blends was observed. With the increasing PTAS content, 10% gravimetric loss was increased from 481 to 497 °C, while glass transition improved from 123 to 136 °C (better than neat SBS but lower than PTAS). The blends also established higher tensile strength (52.40–59.96 MPa) relative to SBS. Fine balance of properties renders new SBS/PTAS, potential engineering plastics for a number of aerospace relevance.

Keywords. Poly(thiourea-azo-sulfone); SBS; electrical conductivity; thermal stability; tensile strength.

1. Introduction

Elastomer blends have been recurrently exploited in various industries to obtain best compromised physical properties including processability. In this regard, styrene–butadiene block copolymers form an imperative class of thermoplastic elastomers (Dechant 1986; Leyva *et al* 2002; Lodge 2003). Synthetic rubber has made a great contribution to many industries, almost all are combustible in air (McManus and Rempel 1995; Zhou and Cho 2003; Xu and Xino 2011). A blend can offer a set of properties that can confer the potential of inflowing relevance not possible with either of the polymers comprising the blend. Generally, styrenic polymer blends find acceptance in the commodity plastics field because of their advantages as balanced properties and cost-effectiveness. Among the blends of commercial use, those composed of a poly(styrene-block-butadiene-block-styrene) (SBS) triblock copolymer are the most important. Many researchers have found that mechanical properties of styrene butadiene block copolymers rely heavily on their phase-separated morphology (Li *et al* 2000; Yao *et al* 2000). Mechanical properties of the copolymer also depend on orientation of the microdomain structure (Sathe *et al* 1996). However, it has strength and resistance against

thermo-oxidative degradation. Many attempts have been made to increase the strength of elastomers and also to improve its oxidative resistance. One attempt to increase the strength is by the introduction of rigid rod polymers (Zhou *et al* 2000).

Polymers and polymer-based materials with electro-conductive properties are materials with potential applications in antistatic packaging (Anand *et al* 1998), energy storage (Gulakhmedova *et al* 1996), electro-optical devices (Cao *et al* 1993; Wu and Benatar 1997; Lin *et al* 2012), etc New materials are being offered in every area and novel products are constantly being introduced. Among these new materials, those made of electro-conductive filler in insulating polymer matrix are being used for electrostatic discharge protection, packaging industries, etc (Virtanen *et al* 1997). One promising approach for the manufacture of this kind of material is to generate the electrically conductive fibres *in situ*, i.e. during the actual forming of the component. Polyaniline has been one of the most promising conductive polymers due to its excellent chemical stability combined with relatively high levels of conductivity (Shacklette *et al* 1993; Lux 1994; Jousseume *et al* 1998; Zilberman *et al* 1998a; MacDiarmid 2001). There has been an extensive investigation regarding the physical properties and microstructure of such two-component blend systems. It has been shown that under appropriate conditions, the dispersed phase can produce different structures such as ellipsoids, spheres,

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short fibres, etc. Studies concerning the microstructure of SBS-based blends revealed that the homopolymer polystyrene formed a separate phase, which in some cases was in the form of well-developed fibrils (Folkes and Reip 1986; Ehtaiatkar *et al* 1989). Preparation of conducting materials that use poly(styrene-block-butadiene-block-styrene) triblock copolymer as insulating matrix may be very interesting because these materials consent to the development of conducting and/or semiconducting resins with good flexibility and elasticity without vulcanization (Leyva *et al* 2001; Souza *et al* 2006a,b). Although, polyaniline has attracted the interest of many researchers due to its high conductivity, heat stability, low production costs, etc, the main disadvantage of this conducting polymer is its poor processibility both in the melt and in solutions of common organic solvents, because of the stiffness of its backbone (Souza *et al* 2005). Consequently, our main objective was to establish the feasibility of producing soluble, thermally stable and electrically conductive azo-polymer compatible with SBS matrix. Accordingly, this effort involved the solution blending of SBS with PTAS instead of traditional conducting polymeric fillers. The electrical conductivity, heat stability and mechanical properties of SBS/PTAS blends have been studied as a function of increasing PTAS content.

2. Experimental

2.1 Materials

Poly(styrene-co-butadiene) (styrene 45 wt%), 2,6-diaminopyridine (97%), 4-(4-aminophenylsulfonyl)benzenamine (APSBA) (97%) were provided by Aldrich. Ammonium thiocyanate (98%) and tetrahydrofuran (THF) (99.5%) were procured from Merck.

2.2 Measurements

NMR spectra were scanned at room temperature using BRUKER spectrometer (300.13 MHz for ^1H NMR) in deuterated DMSO. IR spectra were recorded using FT-IR spectrometer, Model no. FTSW 300 MX, manufactured by BIO-RAD (4 cm^{-1} resolution). The number and weight-average molecular weight (M_n and M_w) were calculated through GPC using THF as an eluent and refractive index (RI) detector. Field emission scanning electron microscope (FE-SEM) of freeze fractured samples was performed using JSM5910, JEOL, Japan. Thermal stability was verified by METTLER TOLEDO TGA/SDTA 851° thermogravimetric analyser using 1–5 mg of the sample in Al_2O_3 crucible at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed by METTLER TOLEDO DSC 822° differential scanning calorimeter taking 5–10 mg of samples in aluminum pans

and heated at a rate of 10 °C/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 Universal Testing Machine INSTRON 4206 according to ASTM 638 method. A cross-head speed of 100 mm/min was used during the test.

2.3 Synthesis of monomer

2.3a Synthesis of 1-(4-thiocarbamoylaminophenylsulfonylphenyl)thiourea (TCAPST): 4-(4'-aminophenylsulfonyl)benzenamine (0.2 mol), conc. HCl (16 mL), ammonium thiocyanate (0.2 mol) and deaerated water (120 mL) were mixed and heated in a porcelain dish (2 h) on a steam bath. The mixture was cooled to room temperature and later gradually evaporated to dryness for 6–7 h. The product obtained was boiled with charcoal in ethanol, filtered and cooled. 1-(4-thiocarbamoylaminophenyl-sulfonylphenyl)thiourea was recrystallized from ethanol and dried under vacuum at 90 °C (36 h) (Vasanthi and Ravikumar 2007; Kausar *et al* 2011). Elemental analysis for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2\text{S}_3$: Calculated = %C 45.88, %H 3.85, %N 15.29; Found = %C 43.32, %H 3.69, %N 14.49. FT-IR (KBr): 3365 cm^{-1} , 3234 cm^{-1} (N–H stretch), 3019 cm^{-1} (aromatic C–H stretch), 2945 (aliphatic C–H stretch), 1599 cm^{-1} (N–H bend), 1413 cm^{-1} (C–N stretch), 1301 and 1157 cm^{-1} (S=O stretch), 1123 cm^{-1} (C=S stretch). ^1H NMR (300.13 MHz, $\text{DMSO}-d_6$, δ ppm): 4.38 (s, 4H, H_a), 9.32 (s, 2H, H_b), 6.65 (d, 4H, H_c), 7.71 (d, 4H, H_d). ^{13}C NMR (75.47 MHz, $\text{DMSO}-d_6$, δ ppm): thiocarbonyl C=S 175.1 (C_1), 142.4 (C_2), 125.3 (C_3), 128.1 (C_4), 139.9 (C_5).

2.3b Diazotization: 0.04 mol 2,6-diaminopyridine 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-coloured precipitate. To the above suspension, 0.04 mol/L sodium nitrite solution (20 mL) was added with constant agitation. After the complete addition, mixture was allowed to stir for 1 h at -10 °C, to avoid the decomposition of diazonium salt. The excess of nitrite was finally removed by the addition of urea (2 g), resulting in diazonium salt solution.

2.4 Synthesis of poly(thiourea-azo-sulfone)

0.02 mol TCAPST was dissolved in 10% sodium hydroxide solution and then the diazonium salt solution obtained (§2.3b) was added drop-wise (at -10 °C). The mixture was further stirred for 3 h and acidified with dilute HCl (10%). The resulting precipitate was filtered, washed with hot water and then with 3% hydrochloric acid solution. The precipitate was again dissolved in sodium hydroxide and reprecipitated in HCl (Sivadhyanithy

et al 2007). The polymer obtained was dried under vacuum at 70 °C for several hours. FT-IR (KBr, cm^{-1}) (figure 1): 3264 and 1596 (sec. amine N-H stretch and bend), 3066 (aromatic C-H stretch), 1413 ($-\text{N}=\text{N}-$ stretch), 1302 and 1151 (S=O stretch), 1121 (C=S stretch), 823 (C-S stretching). ^1H NMR (300.13 MHz, $\text{DMSO}-d_6$, δ ppm) (figure 2): 8.99 (s), 9.64 (s) (N-Hs chemical shifts), 7.97 (d), 8.63 (d), 8.26 (t) (pyridine unit), 6.63 (d), 7.52 (d) (phenylene ring protons).

3. Results and discussion

3.1 Preparation of poly(thiourea-azo-sulfone) and its blends

A new polymer with the unique combination of azo, thiourea and sulfone linkages has been developed (scheme 1). PTAS obtained showed good solubility in THF and high molar mass 63×10^3 . Structural architecture of poly(thiourea-azo-sulfone) suggested good electrical conductivity and fine thermal properties. Later, this azo-polymer was used as a filler in SBS matrix to improve

Figure 1. FT-IR spectrum of PTAS.

Figure 2. ^1H -NMR spectrum of PTAS.

thermal, mechanical and conducting properties of novel blends. Solutions of SBS and poly(thiourea-azo-sulfone) in THF were first prepared separately. PTAS and SBS solutions were then mixed at required proportions. The mixed solutions were ultrasonicated for 5 h. Thin films were solution-casted on Petri glass, and solvent was evaporated at 80 °C for 24 h. Blending of PTAS with SBS unlocked an interesting route to compatible, thermally and mechanically constant and electrically conducting blends. The increase in PTAS content was, thus, found to increase the physical properties of SBS/PTAS blend system.

3.2 Tensile strength

Tensile strength measurement of neat SBR and SBS/PTAS with varying amounts of PTAS are given in table 1 and figure 3. Results demonstrated that the tensile strength and maximum elongation of the samples increased progressively as the quantity of poly(thiourea-azo-sulfone) increased. The tensile strength of SBS/PTAS 1 with 10% PTAS content was found to be 52.40 MPa. Whereas, it gradually increased with rising amount of azo-polymer as SBS/PTAS 2 with 30% PTAS exhibited maximum stress 56.67 MPa and SBS/PTAS 3 with 60% PTAS had 59.96 MPa. It also revealed that the tensile strength of SBS blended with poly(thiourea-azo-sulfone) was much more times greater relative to pure SBS. The excellent tensile strength of SBS-blends was in fact due to the presence of rigid rod azo-polymer. The initial modulus of SBS/PTAS 1 sample at room temperature was found to be 567, 768 MPa for SBS/PTAS 2 and increased up to 888 MPa for the blend with 60% PTAS. Higher value of the elongation at break was also observed for SBS/PTAS 3 0.68 relative to that of SBS/PTAS 1 0.65. Toughness of the materials, evaluated by integrating area under the stress-strain curve was in the range 19.41–23.28 J/m^3 . In comparison with the reported SBS-based blends, these values initially seemed to be pretty high (Kim *et al* 2001).

3.3 Morphology

Figure 4 illustrates SEM images of new blends prepared. One can see a single-phase morphology showing PTAS chains agglomerated along with the chains of SBS matrix. Figure 4(a–d) presents better adhesion of the dispersed polymer with the elastomer as both the phases could not be recognized in these micrographs. The addition of PTAS to SBS also changed the morphology to some extent. Size of the coagulated SBS/PTAS chains was found to increase with the addition of conducting polymer. The effect was more pronounced in SBS/PTAS 3 (figures 4d and e) at 60% addition of PTAS. In 10% PTAS loaded blend (figures 4a and b), chains of azo-polymer seemed

Scheme 1. Scheme for synthesis of monomer and poly(thiourea-azo-sulfone).

Table 1. Mechanical properties of SBS/PTAS blends.

Samples	Maximum stress (MPa) ± 0.1	Maximum strain ± 0.05	Initial modulus (MPa) ± 0.1	Toughness (J/m ³) ± 0.3
SBS/PTAS 1 (90 : 10)	52.40	0.65	567	19.41
SBS/PTAS 2 (70 : 30)	56.67	0.66	768	21.51
SBS/PTAS 3 (40 : 60)	59.96	0.68	888	23.28
Neat SBS	20.31	0.27	123	3.12

to be less coalesced together with that of SBS. Whereas, 30 and 60% PTAS loaded blends (figures 4c–e) displayed a more banded together structure, consequently there was shorter distance between adjacent chains. Besides, gaps between SBS/PTAS chains can be observed in all micrographs which might be depicting the development of some conducting path ways.

3.4 Thermal analysis

TGA thermograms of neat PTAS and SBS/PTAS blends are given in figure 5 and table 2. Pure PTAS showed

single-stage decomposition at a temperature of initiation, 465 °C and the major weight loss was between 460 and 550 °C. At low level of blending (SBS/PTAS 1), the thermogravimetric analysis curve presented lower values of initial decomposition (T_0) at 442 °C, 10% gravimetric loss (T_{10}) of 481 °C and the decomposition extends up to 524 °C. On the contrary, at higher level of blending (30 and 60% PTAS), the thermal degradation occurred at higher temperature. For SBS/PTAS 2, T_0 of 447 °C, T_{10} 488 °C and T_{max} up to 537 °C were observed. Further better heat stability was perceived for SBS/PTAS 3, where T_0 was 461 °C, T_{10} was 497 °C and T_{max} was 543 °C. With the

Table 2. Thermal analyses data of PTAS and blends.

Samples	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Y_c at 600°C (%)
Neat SBS	-58	414	434	476	21
SBS/PTAS 1 (90 : 10)	123	442	481	524	45
SBS/PTAS 2 (70 : 30)	131	447	488	537	51
SBS/PTAS 3 (40 : 60)	136	461	497	543	53
PTAS	227	465	500	551	56

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.

Figure 3. Stress-strain curves of SBS and SBS/PTAS blends.**Table 3.** Conductivity measurement of SBS/PTAS blends.

Sample	Conductivity ($S\ cm^{-1}$)
SBS/PTAS 1	0.65×10^{-1}
SBS/PTAS 2	0.91×10^{-1}
SBS/PTAS 3	1.43
Neat PTAS	2.42

addition of rigid rod polymer, the heat stability of SBS elastomer was found to increase considerably. The blends also had sufficiently higher char yield of 45–53% (600 °C) as compared to SBS. However, thermal stability of the blends was lower relative to pure poly(thiourea-azo-sulfone). Figure 6 demonstrated thermal data by DSC for PTAS and SBS/PTAS blends (table 2). Thermal transition at 227 °C was recorded as the glass transition temperature (T_g) of PTAS. Overall appearance of the blend thermograms was similar to that of azo-polymer. The blends exhibited glass transition around 123–136 °C, however, there was a shift in T_g occurring to the right as the level of PTAS increased. SBS/PTAS 1 showed a clear thermal transition at 123 °C, whereas 60% PTAS containing blend revealed thermal transition at 136 °C. This observation exposed that as the level of azo polymer increases T_g also increased. The lower T_g value at 90% SBS loading indicated the flexibility of azo-chain due to

replacement of rigid bonds in the backbone by freely rotating bonds (elastomer). T_g values of new blends were in consequence, intermediate between pure PTAS and neat SBS (–58 °C). These materials own better thermal stability relative to the previous polyaniline-SBS blends (Cruz-Estrada and Folkes 2000).

3.5 Conductivity measurement

Table 3 indicated conductivity data for the blends and azo filler. Pure PTAS depicted good electrical conductivity around $2.42\ S\ cm^{-1}$. Azo-moieties were found to noticeably increase the conductivity of SBS-based blends. The conductivity measurement of SBS/PTAS 3 revealed that the blend with 60 wt% of PTAS showed higher conductivity of the order $1.43\ S\ cm^{-1}$. However, the conductivity of SBS/PTAS 2 with 30% azo filler was a bit lower, $0.91 \times 10^{-1}\ S\ cm^{-1}$. Lowest conductivity was depicted by SBS/PTAS 1, i.e. 0.65×10^{-1} due to lower azo content. Recently, polyaniline has been employed to improve the conducting properties of a wide range of polymers via blending (Subrahmanyam *et al* 2012). However, the conductivity and thermal properties of our SBS/PTAS blends are much higher than the reported systems such as polyaniline-*p*-toluene sulfonic acid blend with thermoplastic polymers, polyvinyl chloride/polyaniline blends, etc

Figure 4. FESEM images of (a) SBS/PTAS 1 (1 μm); (b) SBS/PTAS 1 (500 nm); (c) SBS/PTAS 2 (500 nm); (d) SBS/PTAS 3 (500 nm) and (e) SBS/PTAS 3 (300 nm).

Figure 5. TGA curves of PTAS and blends at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 .

Figure 6. DSC thermograms of PTAS and blends at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 .

(Zilberman *et al* 1998b; Hosseini and Entezami 2005). The tensile modulus and electrical conductivity of SBS/PTAS blends have also found to be significantly higher compared with poly(vinylidene fluoride)/polyaniline system (Subrahmanyam *et al* 2012; Martins *et al* 2013). Similarly, addition of new conducting polymer enhanced the conductivity of insulating SBS matrix, relative to other reported polyaniline-based blends (Cruz-Estrada and Folkes 2000; Leyva *et al* 2001).

4. Conclusions

Blending of electro-conductive polymer with traditional insulating materials has been a promising approach for the production of materials for various applications. Accordingly, we have reported a favourable method for manufacturing these kind of materials which involved generating the processable azo-polymer having high molar mass. Electrically conductive (2.42 S cm^{-1}) and thermally stable (T_g : 227°C , T_{10} : 500°C , $T_{\max}$: 551°C) poly(thiourea-azo-sulfone) was solution blended with polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) at different weight compositions. Physical property investigation suggested that blending SBS up to 60 wt% of PTAS could produce an electrically conductive blend with a reasonably good level of conductivity (1.43 S cm^{-1}). PTAS loading also considerably increased the thermal properties of new SBS/PTAS system as SBS/PTAS 3 (60% PTAS) having T_g 136°C and T_{10} 497°C . However, the heteroaromatic PTAS exhibited higher T_g , thermal and electrically conducting properties compared with neat SBS and all SBS/PTAS blends owing to rigid aromatic structure (Tsvetkov 1983; Feast *et al* 1996).

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