

Synthesis and Properties of Melt Processed Poly(thiourea-azo-sulfone)/Carbon Nanotubes Nanocomposites

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Abstract An aromatic azo-polymer, poly(thiourea-azo-sulfone) (PTAS), has been prepared using 4-(4-aminophenylsulfonyl)benzenamine and diazonium salt solution of 2,6-diaminopyridine. PTAS was easily processable using polar solvents and had high molar mass $63 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ according to GPC. Mechanically and thermally stable and electrically conducting polymer/CNTs nano-composites were obtained *via* melt processing technique. Fine distribution of CNTs in a polymer matrix performed an essential role in the preparation of polymer/CNTs nano-composites based on interfacial interaction between CNTs and polymer matrix. Scanning electron micrographs showed good dispersion of filler and adhesion of matrix on the surface of nanotubes. Accordingly, increasing the amount of CNTs from 0.1 wt% to 5 wt% increased the electrical conductivity from $2.99 \text{ S}\cdot\text{cm}^{-1}$ to $3.56 \text{ S}\cdot\text{cm}^{-1}$. Mechanical strength of functional nanotubes-based hybrids was enhanced from 43.22 MPa to 65.02 MPa compared with that of hybrids with non-functional filler in matrix 37.21 MPa. A rapport between nanotube loading and thermal stability of the materials was also observed. 10% gravimetric loss temperature was increased from 528 °C to 578 °C, while glass transition was improved from 241 °C to 271 °C. Adding up of small quantity of functional CNTs strongly affected the tensile, electrical and thermal properties of materials. Improvement of the physical properties of CNT-reinforced polymer nano-composites was ascribed to the melt processing technique.

Keywords: Poly(thiourea-azo-sulfone); Melt processing; Tensile strength; Thermal stability; Electrical conductivity.

INTRODUCTION

Recent advances and scale-up potentials in the technology of producing carbon nanotubes (CNTs) have given motivation towards emergent applications to exploit the exceptional material properties. One of the potential relevance of carbon nanotubes has been the development of nanotube-based nanocomposites^[1–3]. Introduction of high aspect ratio fibers in a polymer matrix has been known to increase the strength and modulus of a composite through stress transfer mechanism from matrix to the fiber during external loading^[4–7]. With good strength, CNTs have tremendous potential for applications in many scientific and technological fields, especially for use as composite fillers in polymers to improve the mechanical, thermal and electrical properties of the resulting composites^[8–10]. However, most important challenge has been identified as the technical difficulty because of poor dispersion and weak interfacial bonding, which are essential for realizing the full potential of nanotubes as reinforcing agents. One of the efficient ways of increasing the dispersibility is the chemical functionalization of CNTs, which intern enhances the interfacial bonding between the nanotube and polymer interface^[11, 12]. The properties of polymer/CNT nano-composites have, thus, been strongly dependent on the extent of nanotube dispersion which can be improved *via* enhancing the interaction between the polymer and CNTs components

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instigating wrapping of filler with the polymer matrix^[13, 14]. Non-covalent modification of CNTs included the physical adsorption and/or packaging of polymers to the surface of the CNTs^[15–18]. Whereas, covalent modification of CNTs generally involves the chemical bonding/grafting of polymer chains to CNTs, which considerably develops interfacial interactions between nanotubes and polymer matrix. Furthermore, research has exposed that unfunctionalized CNTs produce poor adhesion between the nanotubes and the polymer matrix. Currently, different processing techniques (solution mixing, coagulation, melt compounding, *in situ* polymerization, latex technology, solid-state shear pulverization, *etc.*) have been used to prepare polymer/CNT nanocomposites^[19–24]. In general, major interaction between the polymer backbone and nanotube surface occurs through π - π interaction. Although, π - π interaction is a weak bond compared with covalent bonds, the sum of π - π interactions creates a large net-stabilizing energy that results in superior and stable systems. Consequently, the electrical and mechanical properties of polymer/CNTs nano-composites can be altered due to their dependency on CNTs dispersion in the polymer matrix^[25, 26]. It should be noted that the insufficient dispersion has been cited as a process limitation and key diminishing factor on composite mechanical properties. Efforts to improve CNTs dispersion include the use of surfactants and the oxidation or chemical functionalization of nanotube surface. The employment of azo-polymer in polymer/carbon nanotube composites is still a derelict area of research, which motivated us to develop novel conducting high performance azo-polymer/carbon nanotube materials. In the current effort, initially we have prepared a new polymer poly(thiourea-azo-sulfone) (PTAS). Afterwards, we have reported the fabrication of new nanocomposites using melt blending technique. By physical linking of carbon nanotubes with the matrix, mechanically and heat stable materials with good electrical properties were attained. Melt procedure was a feasible approach to fabricate low cost high performance nanocomposites which would in sequence facilitate commercial scale-up. Understanding the rapport between processing, morphology and composite properties was the major objective of this research, which may lead to favorable reinforcement of polymer matrices with CNTs. Major confront at the moment, was to accomplish superior performance through the homogeneous dispersion of nanotubes in the polymer matrix and also the interfacial interaction between nanotube and azo-polymer. The probable contact between the polymer backbone and nanotube surface was through π - π interaction and hydrogen bonding. Even though these are bonds weaker than covalent bonding, but the computation of π - π interactions may cause a large net-stabilized structure. These types of polymer/nanotube composites may proffer momentous advantages in many applications including microelectronics, sensors, energy systems, *etc.*

EXPERIMENTAL

Materials

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.

Measurements

NMR spectra were scanned at room temperature by using a BRUKER Spectrometer (300.13 MHz for ¹H-NMR) in deuterated DMSO. IR spectra were recorded with an FTIR Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD (4 cm⁻¹ resolution). Number average and weight average molecular weight was calculated through gel permeation chromatography (GPC) using THF eluent and refractive index (RI) detector. Field emission scanning electron microscopy (FE-SEM) of freeze fractured samples was performed using JSM5910, JEOL Japan. Thermal stability was verified by a Mettler Toledo TGA/SDTA 851° thermo gravimetric analyzer using 1–5 mg of the sample in Al₂O₃ crucible at a heating rate of 10 K/min. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822° differential scanning calorimeter taking 5–10 mg of samples at 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.

Synthesis of CNTs

CNTs were prepared by the patented technology (Patent number: US2009208403). The HRTEM and XPS analysis were performed for the nano-tubes produced^[27].

Functionalization of CNTs

Raw multi-walled carbon nano-tubes were initially annealed at 400 °C for 0.5 h to remove any amorphous carbon content. In order to eradicate metal catalyst, which was incorporated inside the nano-tubes during synthesis, CNTs were refluxed in HCl for 3 h at ambient temperature. First, the purified CNTs were refluxed and sonicated at 70 °C (2 h, 6 h, 8 h and 24 h) in a mixture of 8 mol/L sulphuric and 5 mol/L nitric acid (3:1 respectively). After that, 300 mL of deionized water was added to the above mixture, which was filtered (using cellular membrane filter paper, pore size 0.2 µm) and washed several times with deionized water to pH *ca.* 6 to obtain functionalized CNTs^[28].

Synthesis of Monomer

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)^[28, 29]. Elemental analysis for C₁₄H₁₄N₄O₂S₃: Calculated = C% 45.88, H% 3.85, N% 15.29; Found = C% 43.32, H% 3.69, N% 14.49. FTIR (KBr, cm⁻¹): 3365, 3234 (N–H stretch), 3019 (aromatic C–H stretch), 2945 (aliphatic C–H stretch), 1599 (N–H bend), 1413 (C–N stretch), 1301 and 1157 (S=O stretch), 1123 (C=S stretch). ¹H-NMR (300.13 MHz, DMSO-d₆, δ): 4.38 (s, 4H, H_a), 9.32 (s, 2H, H_b), 6.65 (d, 4H, H_c), 7.71 (d, 4H, H_d). ¹³C-NMR (75.47 MHz, DMSO-d₆, δ): thiocarbonyl C=S 175.1 (C₁), 142.4 (C₂), 125.3 (C₃), 128.1 (C₄), 139.9 (C₅).

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-colored precipitate. To the above suspension, 0.04 mol 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.

Synthesis of Poly(thiourea-azo-sulfone)

To a solution of 0.02 mol TCAPST and 10% sodium hydroxide, diazonium salt solution obtained was slowly added (at –10 °C). The mixture was further stirred for 3 h and acidified with dil. 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 re-precipitated in HCl^[30]. The polymer obtained was dried under vacuum at 70 °C for several hours. FTIR (KBr, cm⁻¹) (Fig. 1): 3264 and 1596 (sec. amine N–H stretch and bend), 3066 (aromatic C–H stretch), 1413 (–N=N– stretch), 1302 and 1151 (S=O stretch), 1121 (C=S stretch), 823 (C–S stretching). ¹H-NMR (300.13 MHz, DMSO-d₆, δ) (Fig. 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).

Poly(thiourea-azo-sulfone)/CNTs Nanocomposites

Former to the preparation of PTAS/CNTs nanocomposites, acid functionalized CNTs were dried in a vacuum oven at 70 °C for 24 h. A Brabender Plastograph 200 Nm W50EHT mixer with a blade type rotor (Duisburg, Germany) was used to blend poly(thiourea-azo-sulfone) and CNTs with a rotor speed of 50 r/min and a temperature of 200 °C for 0.5 h. After blending, the nano-composites were pressed into 1 mm thick films using a hydrolytic press. The standard specimens for further characterization were finally prepared.

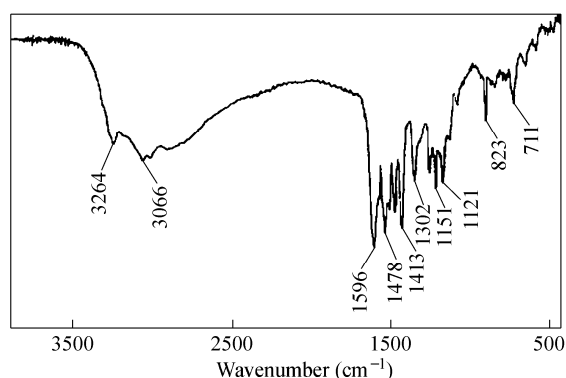
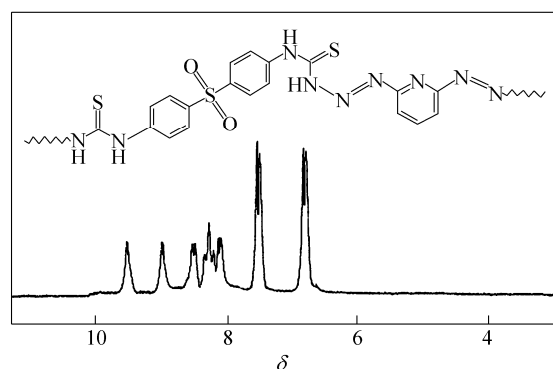


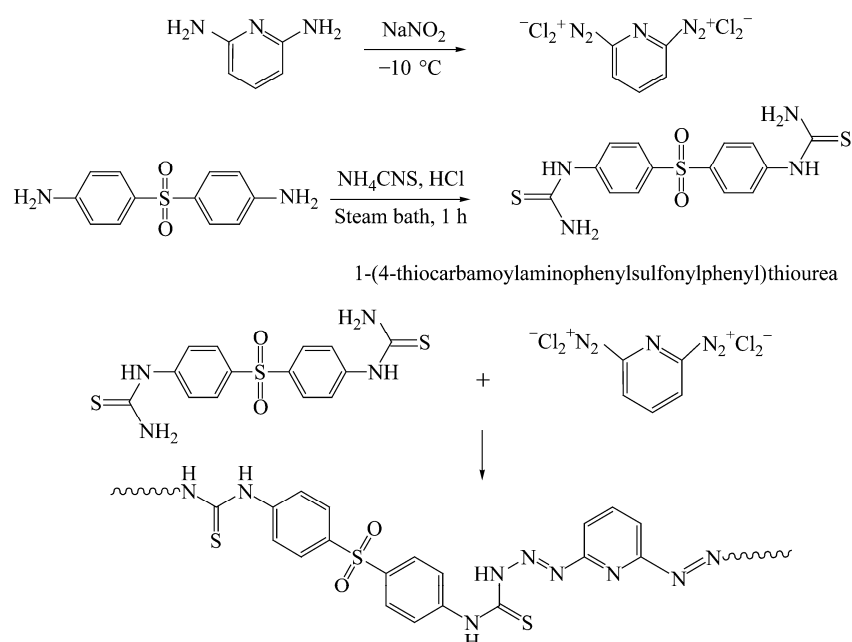
Fig. 1 FTIR spectrum of PTAS

Fig. 2 ¹H-NMR spectrum of PTAS

RESULTS AND DISCUSSION

Preparation of Poly(thiourea-azo-sulfone) (PTAS)/CNTs Nanocomposites

Scheme 1 shows the preparation of poly(thiourea-azo-sulfone) having the sole combination of azo, thiourea and sulfone linkages *via* simple route. Molar mass of PTAS was studied using gel permeation chromatography. The number average molecular weight was 45×10^3 g/mol while weight average molecular weight was found to be 63×10^3 g/mol. The polymer also exhibited good solubility in THF. Fine electrical conductivity and heat stability owing to the structural architecture of poly(thiourea-azo-sulfone) was achieved. Later on, the conducting polymer was exploited as a matrix with CNTs filler to improve mechanical, conducting and thermal properties of new materials. Azo-polymer was melt blended with functional and non-functional carbon nanotubes in desired proportions. Physical characteristics of PTAS/CNTs system were enhanced considerably with an increase in CNTs content and melt compounding technique adopted. Improved mechanical, thermal and conducting properties of new materials well justified the triumph of the methodology employed.



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

Mechanical Properties

Figure 3 and Table 1 demonstrate the tensile strength of PTAS/CNTs nanocomposites at different CNTs loading contents. Mechanical strength was improved with carbon nanotubes content increasing from 1 wt% to 5 wt%. Tensile modulus calculated from the initial slopes of stress-strain curves was realistically high, and presented an increase up to 5 wt% CNTs in the matrix. PTAS/CNTs 0.1 had initial modulus 991 MPa which improved upto 1003 MPa for PTAS/CNTs 0.5. Further increase in the filler content enhanced the property significantly. Initial modulus for PTAS/CNTs 1 was 1098 MPa which increased upto 1187 MPa for PTAS/CNTs 2 and 1324 MPa for PTAS/CNTs 3. However, the modulus was lower for PTAS/CNTs NF 987 MPa. The ultimate stress at break for PTAS/CNTs hybrids was also enhanced with increase in filler content. Tensile strength observed for PTAS/CNTs 3 was 65.02 MPa, whereas with 1 wt% filler tensile strength was rather low 60.61 MPa.

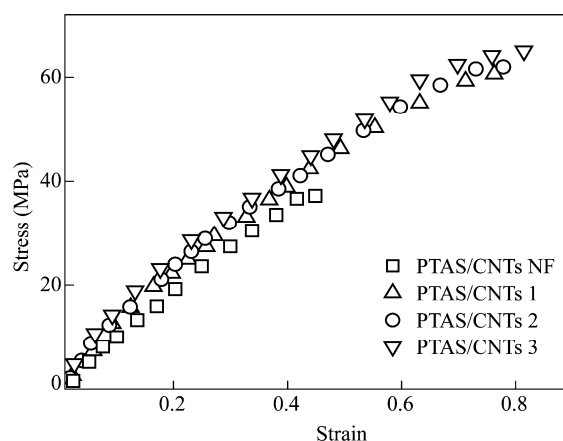


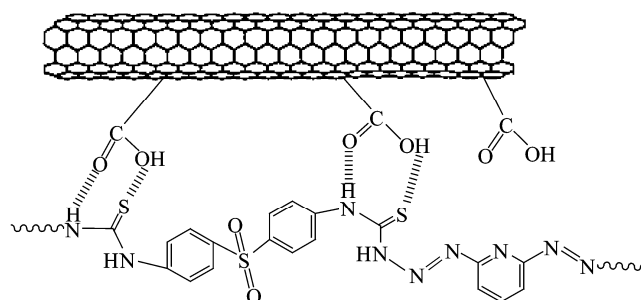
Fig. 3 Stress-strain curves of PTAS/CNTs nanocomposites

Table 1. Mechanical properties of PTAS/CNTs nanocomposites

Sample	Maximum stress (MPa) ± 0.1	Maximum strain ± 0.05	Initial modulus (MPa) ± 0.1	Toughness (J/m ³) ± 0.3
PTAS	33.54	0.37	888	10.32
PTAS/CNTs NF (CNTs 1 wt%)	37.21	0.45	987	11.23
PTAS/CNTs 0.1 (CNTs 0.1 wt%)	43.22	0.54	991	17.22
PTAS/CNTs 0.5 (CNTs 0.5 wt%)	52.11	0.61	1003	22.31
PTAS/CNTs 1 (CNTs 1 wt%)	60.61	0.76	1098	27.27
PTAS/CNTs 2 (CNTs 3 wt%)	61.98	0.79	1187	28.93
PTAS/CNTs 3 (CNTs 5 wt%)	65.02	0.82	1324	32.85
PTAS/CNTs 4 (CNTs 7 wt%)	44.44	0.33	666	22.21

PTAS/CNTs 0.1 possessed the lowest tensile strength and elongation at break in the functional system *i.e.* 43.22 MPa and 0.54 respectively. 1 wt% nanotubes-based hybrid had maximum strain value of 0.76 that was improved up to 0.82 with 5 wt% CNTs. Toughness, calculated by integrating the area under stress-strain curve, of PTAS/CNTs 0.1 was 17.22 J/m³ while PTAS/CNTs 0.5 had the higher value 22.31 J/m³. Furthermore, PTAS/CNTs 1 with 1 wt% CNTs showed a value of 27.27 J/m³ that increased with adding reinforcement and was maximum 32.85 J/m³ for 5 wt% content. The affirmative effect on tensile strength was possibly owing to the stiffness of CNTs layers contributing to the presence of immobilized polymer phases and fine nanoscale dispersion of nano-filler layers in the matrix^[31]. Additionally, nano-tube layer and macro-molecular orientation added to the experiential reinforcement effect. Nevertheless, filler may tend to bundle together because of built-in van der Waals attraction between the individual tubes together with high aspect ratio and surface area of the nanotubes, leading to some agglomeration on the polymer matrix^[32]. Certainly, the decrease in tensile strength at filler content above 7 wt% (PTAS/CNTs 4) could be attributed to predictable aggregation of the

nanotubes. Experimental increase in tensile strength revealed strong interfacial interaction because of free carboxylic acid groups of nano-tubes hydrogen bonded to the chains of PTAS matrix (Scheme 2). This effect was not observed in the case of PTAS/CNTs NF showing lower tensile strength where the matrix was reinforced with non-functional filler. These results demonstrated that the stress transfer or strength of polymer/nanotube nanocomposites can be effectively increased by the interactions^[33]. This was most likely attributable to some void defects symptomatic of more scope for property improvement.



Scheme 2 Physical interactions in PTAS/CNTs nanocomposites

Morphological Aspect

Morphology investigation of PTAS/CNTs nanocomposites was crucial as it influences the mechanical properties of the hybrid system. Usually, fine dispersion of CNTs in the matrix and well-built interfacial adhesion between the two phases are necessary to achieve a composite material with rational mechanical properties. Scanning electron microscopy was used to study the fracture surface of PTAS/CNTs nanocomposites, in which the major component (PTAS) formed the matrix and the minor component (nanotubes) constituted the dispersed phase. In Fig. 4(a) (PTAS/CNTs NF), bulk matrix and non-functional CNTs can be seen separately without any linking.

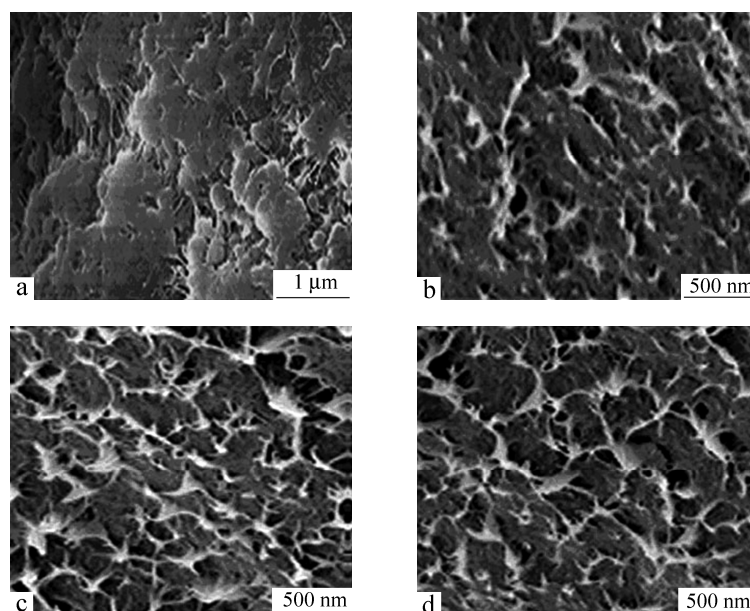


Fig. 4 FESEM images of (a) PTAS/CNTs NF, (b) PTAS/CNTs 1, (c) PTAS/CNTs 2 and (d) PTAS/CNTs 3

Whereas, in the case of PTAS/CNTs 1, functional nanotubes were pragmatic embedded in the matrix, and smooth interfaces between CNTs and PTAS can be perceived. Accordingly, CNTs were considered to have good wettability for matrix so encompassing several physical contacts. There was, consequently, a sufficient

dispersion and homogeneity of functional CNTs in the matrix. With the increase in nanotube loading upto 5 wt% (Figs. 4c & 4d), there was adequate dispersion and good interfacial adhesion between filler and matrix. The probable physical contact between the filler and matrix is outlined in Scheme 2.

Thermal Stability

Thermal stability of PTAS/CNTs nanocomposites and pure resin was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA thermograms, obtained by thermogravimetric analysis, of functional as well as non-functional PTAS/CNTs nanocomposites are shown in Fig. 5 and data are presented in Table 2. PTAS/CNTs showed single-stage decomposition with major weight loss between 500 °C and 600 °C. Thermogravimetric curve showed initial decomposition temperature T_0 at 466 °C, 10% gravimetric loss temperature T_{10} at 478 °C and decomposition continued up to 577 °C, for PTAS/CNTs NF with 1 wt% filler. In contrast, raising functional CNTs filler content from 0.1 wt% to 5 wt%, the degradation occurred at higher temperatures. PTAS/CNTs 0.1 revealed T_0 and T_{10} at 488 and 528 °C respectively, while PTAS/CNTs 0.5 had values of T_0 497 and T_{10} 533 °C. PTAS/CNTs 1 exhibited T_0 of 515 °C, T_{10} 547 °C and T_{max} up to 586 °C. PTAS/CNTs 2 also showed good heat stability among these PTAS/CNTs nano-composites *i.e.*, T_0 was 527 °C, T_{10} was 561 °C and T_{max} was up to 611 °C. Furthermore, PTAS/CNTs 3 with 5 wt% filler had the highest heat stability among these hybrid materials T_0 of 534 °C, T_{10} 578 °C and T_{max} up to 623 °C. The inclusion of functional reinforcement, hence, extensively enhanced the heat stability of the new polymer. Char yield of functional CNTs hybrids was also sufficiently high 65%–71% at 700 °C relative to non-functional filler-based material (57%). Nevertheless, these thermal stability values were higher compared with those of the pure polymer used. On the whole, thermal stability data showed better results compared with those of the reported polyamide/CNTs material^[34, 35]. Differential scanning calorimeter was used to resolve T_g 's of nano-composites *via* measurement of heat flow versus change in temperature. Figure 6 shows the variation of glass transition

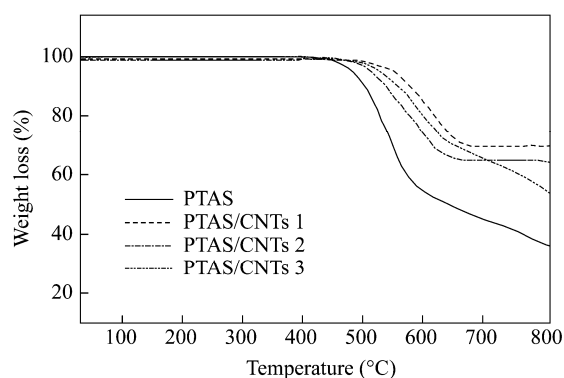


Fig. 5 TGA curves of PTAS and PTAS/CNTs nanocomposites at a heating rate of 10 K/min in N_2

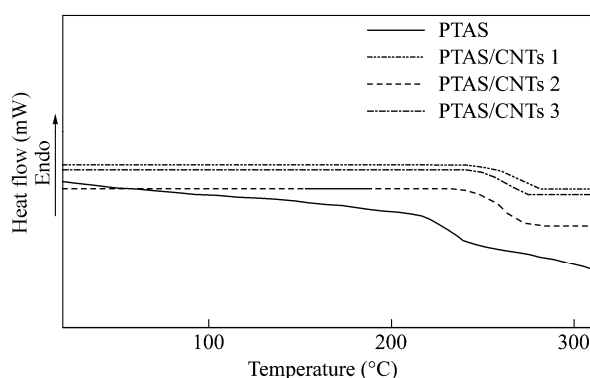


Fig. 6 DSC thermograms of PTAS and PTAS/CNTs nanocomposites at a heating rate of 10 K/min in N_2

Table 2. Thermal analysis data of PTAS and PTAS/CNTs nanocomposites

Sample	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Y_c at 700 °C (%)
PTAS/CNTs NF	237	478	511	577	57
PTAS/CNTs 0.1	241	488	528	579	59
PTAS/CNTs 0.5	252	497	533	580	61
PTAS/CNTs 1	258	515	547	586	65
PTAS/CNTs 2	262	527	561	611	68
PTAS/CNTs 3	271	534	578	623	71
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

temperature of PTAS/CNTs with adding functional CNTs (PTAS/CNTs 1–3). Inclusion of functional nano-filler enhanced the thermostability of nano-composites (T_g from 258 °C to 271 °C), which may be due to decrease in the mobility of polymer chains around the nano-filler by strong interfacial interaction. The glass transition, however, was lower in the case of non-functional CNTs loading in PTAS/CNTs NF (237 °C).

Electrical Conductivity

Dependence of conductivity on the CNTs content in poly(thiourea-azo-sulfone) matrix was similar to that of typical polymer matrices loaded with conducting fillers^[36, 37]. Tables 3 represents the electrical conductivity of pure heteroaromatic azo-polymer and nano-composites with different compositions. Carbon nano-tubes along with azo and heteroaromatic pyridine moieties were found to evidently increase the electrical conductivity of new materials. The conductivity of poly(thiourea-azo-sulfone) was consequently improved with CNTs loading; PTAS/CNTs 1 had 3.17 S·cm⁻¹, PTAS/CNTs 2 owned 3.32 S·cm⁻¹ and 3.56 S·cm⁻¹ for PTAS/CNTs 3. These values were found superior than the intrinsic conductivity of reported nano-composites^[38]. The conductivity was also sufficiently higher than that of pure PTAS 2.42 S·cm⁻¹.

Table 3. Conductivity measurements of PTAS/CNTs nanocomposites

Sample	Conductivity (S·cm ⁻¹)
PTAS/CNTs NF	2.51
PTAS/CNTs 0.1	2.99
PTAS/CNTs 0.5	3.03
PTAS/CNTs 1	3.17
PTAS/CNTs 2	3.32
PTAS/CNTs 3	3.56
Neat PTAS	2.42

CONCLUSIONS

Melt processing technique was used to fabricate new polymer/multiple-walled carbon nanotube hybrid materials, in this endeavor. Novel conducting matrix material was designed and prepared *i.e.* poly(thiourea-azo-sulfone). Non-functional and acid-functionalized carbon nanotubes, having excellent electrical conductivity, high tensile modulus and thermal properties were proved to be ideal fillers for new polymer nano-composites. Reactive functional groups were competent of appending physically to the azo-polymer, thus, fully integrated nanotubes and poly(thiourea-azo-sulfone) nano-composites by functionalization have been achieved. TGA and DSC examination showed that the CNTs inclusion in matrix raised the heat resistant to a significant extent. Values of tensile strength increased up to 65.02 MPa with 5 wt% filler loading, and excess of nanotubes exceeding this weight percent may set off the aggregation of nanotubes phase and consequently reduce the compatibility between the acid-treated CNTs and poly(thiourea-azo-sulfone). Moreover, the electrical conductivity of azo-polymer was increased from 2.42 S·cm⁻¹ to 3.56 S·cm⁻¹ with the nanotube addition. To conclude, PTAS/CNTs hybrids demonstrated noticeably improved thermal, electrical and mechanical properties, since the interfacial forces were the stronger hydrogen bonds.

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