

Enhancing Dielectric and Mechanical Behaviors of Hybrid Polymer Nanocomposites Based on Polystyrene, Polyaniline and Carbon Nanotubes Coated with Polyaniline*

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Abstract The dielectric and mechanical properties of hybrid polymer nanocomposites of polystyrene/polyaniline/carbon nanotubes coated with polyaniline (pCNTs) have been investigated using impedance analyzer and extensometer. The blends of PS/PANI formed the heterogeneous phase separated morphology in which pCNTs are dispersed uniformly. The incorporation of a small amount of pCNTs into the blend of PS/PANI has remarkably increased the dielectric properties. Similarly, the AC conductivity of PS/PANI is also increased five orders of magnitude from 1.6×10^{-10} to $2.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ in the hybrid nanocomposites. Such behavior of hybrid nanocomposites is owing to the interfacial polarization occurring due to the presence of multicomponent domains with varying conductivity character of the phases from insulative PS to poor conductor PANI to highly conductive CNTs. Meanwhile, the tensile modulus and tensile strength are also enhanced significantly up to 55% and 160%, respectively, without much loss of ductility for three phase hybrid nanocomposites as compared to the neat PS. Thereby, the hybrid nanocomposites of PS/PANI/pCNTs become stiffer, stronger and tougher as compared to the neat systems.

Keywords: Nanocomposites; Carbon nanotubes; Dielectric behavior; Mechanical properties; Polystyrene.

INTRODUCTION

Hybrid organic-inorganic nanocomposites are becoming the prominent materials owing to their unique characteristics of superior dielectric, mechanical and physical properties^[1, 2]. Particularly, blending the combination of insulative and conductive polymer matrices with or without the inclusion of nanofiller for designing the functional materials containing high dielectric properties are becoming the potential candidates for the miniaturization of the electronic gadgets. The heterogeneous or phase separated nature of polymer blend systems with well dispersion of inclusions into the matrix would eventually give remarkable synergistic properties^[3]. Various types of nanofillers of conductive nature like carbon nanotubes (CNTs)/graphene or non-conductive like layered silicates/ferroelectric ceramics were employed in various kinds of polymer matrices to investigate the improvement in their dielectric properties^[4–6]. However, limitation arises owing to the increase in one set of properties at the expense of other set of properties; higher dielectric constant originated at the expense of high loss tangents and conductivity as well as overall low mechanical performance because higher values for nanocomposites with ceramic fillers are obtained at higher loading^[7, 8].

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Polyaniline (PANI) is commonly used as conductive polymer in combination with various conventional polymers to form intrinsically conductive polymer blends^[9, 10]. Depending on the type of dopant and processing route for the synthesis of PANI, the conductivity ranges from 10^{-10} S·cm⁻¹ to 10 S·cm⁻¹^[11]. Moreover, conventional insulating polymer matrices usually have low dielectric constant as well as dielectric losses along with good processability and strength. To tailor their properties, three phase systems are designed by incorporation of nanofillers into the blends of conductive and insulative matrices. Owing to the large surface area of interaction of nanofillers with the polymer matrix, there arises the possibility of higher polarization as well as enhancement of mechanical properties of the system. Nanofillers like multiwall carbon nanotubes (MWCNTs) not only offer outstanding electrical characteristics but also have exceptional mechanical properties *i.e.* elastic modulus and tensile strength of 1.2 TPa and 50–200 GPa, respectively^[12]. Recently, Zhou *et al.*^[13] reported significant increase in the dielectric properties of PVDF/PANI coated MWCNTs in which the PANI layer was non-conductive and increased the dielectric permittivity at lower loss tangent. Similarly, hybrid composites of polysiloxane with PANI (EHSiPA)/MWCNTs/Epoxy showed higher dielectric constant with low dielectric loss at much lower percolation threshold^[14]. Moreover, Huang *et al.*^[15] reported core-shell strategies for achieving the suitable balance between the dielectric constant, dielectric loss and breakdown strength of high-*k* composites. Therefore, obtaining the polymer system with balanced electrical and mechanical properties is still under investigation.

In this work, the dielectric and mechanical properties of three phase polymer nanocomposites of polystyrene (PS)/polyaniline (PANI)/PANI coated MWCNTs (pCNTs) are investigated using impedance analyzer and extensometer, respectively. PS is an insulating amorphous thermoplastic polymer which has high dielectric strength but has a weak dipole moment resulting in low values of dielectric constant as well as dielectric loss with respect to the frequency^[16, 17]. The blends of PS/PANI formed the heterogeneous structure in which PANI coated MWCNTs (pCNTs) are dispersed to investigate the dielectric and mechanical properties. Although some reports are found for the two phase systems of either PS/PANI^[18] or PS/CNTs^[12, 19], to the best of our knowledge, this is the first report for the three phase blend system of PS/PANI/pCNTs. The concentration of pCNTs is varied from 0.1 wt% to 1.0 wt% in the blend of PS containing 10 wt% of PANI. The incorporation of small amounts of pCNTs into the blend network of PS/PANI has significantly increased the dielectric constant from 4 to 1899 at 100 Hz whereas, enhanced the tensile strength and modulus up to 160% and 55%, respectively. Overall the three phase hybrid nanocomposites of PS/PANI/pCNTs have become stiffer, stronger and tougher along with remarkable improvement in the dielectric properties.

EXPERIMENTAL

Materials

Polystyrene granules of 143E CC were provided by the courtesy of BASF, Germany. Aniline was purchased from Uni CHEM chemical reagents and purified through distillation. Ammonium peroxydisulfate (APS, 99% pure) was purchased from Daejung chemicals, Korea. Dodecylbenzenesulphonic acid (DBSA), toluene of analytical grade and commercially available MWCNTs (inner and outer diameter in range of 2–6 nm and 10–15 nm, respectively, with an average length of 0.1–10 μ m) were bought from Sigma Aldrich.

Sample Preparation

Polyaniline was prepared using emulsion polymerization method^[20] in which an emulsion of 50 mL of toluene in 200 mL of deionized (DI) water was prepared by adding 0.1 mol DBSA followed by addition of 0.06 mol (2.79 g) aniline monomer. The polymerization was initiated by drop wise addition of 0.04 mol (4.56 g) APS aqueous solution into the emulsion at 0 °C in an inert atmosphere followed by overnight stirring. After completion of reaction, 200 mL of toluene was added to reaction mixture and left for 2 h in a separating funnel. Finally two separate layers appeared with PANI in emeraldine salt form dissolved in upper organic toluene layer and unreacted reactants in the lower watery milky emulsion. The upper layer of toluene with dissolved PANI was washed with DI water until a clear lower layer of water is obtained indicating the removal of excess reagents and

side products.

For coating the PANI layer onto the MWCNTs, 0.1 g of CNTs was added to the polyaniline emulsion prepared by mixing 50 mL of toluene in 200 mL of DI water. This mixture was probe sonicated for 1 h and stirred for 2 h for allowing surfactant to completely adsorb on CNTs. Polymerization was initiated by adding APS to this reaction mixture drop wise at aforementioned conditions. The reaction mixture was poured in separating funnel to get separate layers of PANI coated CNTs in toluene and unreacted reactants in aqueous milky emulsion. The washing was carried out as reported earlier. The PANI coated CNTs were dried in an oven at 50 °C. The samples of PANI coated onto MWCNTs will be referred as pCNTs in the rest of the paper.

For the preparation of nanocomposites, PS was dissolved in toluene at a concentration of 0.06 g·mL⁻¹ by stirring for 6 h. For preparing the polymer blend of PS/PANI while keeping the concentration of PANI up till 10 wt%, 1 mL of PANI solution with 0.06 g·mL⁻¹ concentration was added to 9 mL of PS solution. After mixing, the blend was ultrasonicated for 3 h followed by stirring for 6 h. Then, the blend was poured in a petri dish for drying in fume hood overnight at ambient temperature. Polymer blend films were then dried in vacuum oven at 40 °C for 6 h. Similar procedure was followed for making nanocomposite with 0.1 wt%, 0.5 wt% and 1.0 wt% of pCNTs by preparing its 0.06 g·mL⁻¹ concentration in toluene. The samples were cut from the casted films of PS/PANI blends as well as PS/PANI/pCNTs systems for their characterization.

Characterization Techniques

Impedance analyzer

Dielectric behavior was studied using precision impedance analyzer (Wayne Kerr 6500B) at room temperature. The capacitance C and dissipation D were measured through impedance analyzer in the frequency range of 100 Hz to 1 MHz. The discs with thickness of 0.1 mm and diameter of 13 mm were cut from cast films.

Scanning electron microscope

The morphology of the samples was examined using a scanning electron microscope (SEM) (JEOL-instrument JSM-6490A). The samples were frozen in liquid nitrogen where it became fragile and broken to generate the fresh surface. The samples were mounted on aluminium stubs and coated the surfaces with gold.

X-ray diffractometer

The X-ray diffractometer (XRD) pattern was recorded by using powder X-ray diffractometer (STOE, Theta/Theta diffractometer) having Cu K α λ = 0.15406 nm as a source of radiation at 40 mA, 40 kV at room temperature with 2θ in the range of 10° to 40°.

Extensometer

The tensile parameters of the samples were determined using universal tensile testing machine (AG-20KNXD Plus, Shimadzu) at strain rate of 1 mm/min. The rectangular shaped samples conforming to the ASTM standard D882-95A were cut from the cast films. The dimensions of the samples were 50 mm × 10 mm × 0.1 mm (length × width × thickness) and gauge length of 10 mm. All the samples were tested at room temperature and the values represent the average of the five samples for each system.

Analysis of Dielectric Data

Dielectric relaxations present in the dielectric spectra of polymer systems arise from the polymer matrix, interfacial phenomena and conductivity effects. In this study, dielectric data is first expressed in terms of real (ϵ') and imaginary part of dielectric permittivity (ϵ'') which is obtained from the complex permittivity as follows^[21]:

$$\epsilon = \epsilon' - i\epsilon'' \quad (1)$$

Dielectric constant is the ability of a substance to store electrical energy in an electric field, which can be calculated by using the following expression:

$$\epsilon' = \frac{Cd}{A\epsilon_0} \quad (2)$$

where C is the observed capacitance of the sample, d is the thickness (meters), A is the area (meters) and ϵ_0 is the permittivity of free space. Dielectric loss can be calculated from dielectric tangent loss ($\tan\delta$) which is observed directly from the instrument having the expression:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (3)$$

Tangent loss is the dissipation factor D which is a measure of the energy dissipated by the dielectric material under an oscillating field. The AC conductivity for the dielectric polymer nanocomposites is calculated using the expression:

$$\sigma_{AC} = \omega\epsilon_0\epsilon'\tan\delta \quad (4)$$

All the above mentioned parameters are obtained as a function of frequency at room temperature.

RESULTS AND DISCUSSION

PANI Coated MWCNTs

Figure 1 shows the X-ray diffraction pattern of neat CNTs and PANI coated CNTs (referred as p CNTs from here after). The X-ray pattern of neat CNTs has a sharp peak around $2\theta = 26.1^\circ$ indicating the arrangement of concentric cylinders of the graphitic carbon atoms in the nanotubes. In case of neat PANI, the characteristic peaks at $2\theta = 15.3^\circ$, 20.4° and 25.3° correspond to the (011), (020) and (200) crystal planes in its emeraldine salt form, respectively, as reported elsewhere^[22]. For p CNTs, two peaks are observed: the first one appears at $2\theta = 20^\circ$ pertaining to the PANI structure and the second peak at $2\theta = 26.1^\circ$ belongs to the graphitic carbon atoms in nanotubes. The intensity of the second peak in p CNTs is reduced as compared to the intensity of neat CNTs. Moreover, the characteristic peak of PANI at $2\theta = 15.3^\circ$ disappears while the peak around $2\theta = 20.4^\circ$ shifts to lower angle inferring the presence of PANI layer coated onto the CNTs through the π - π interaction^[23–25].

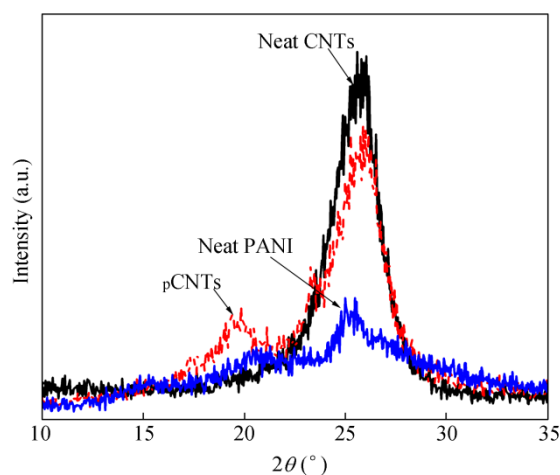


Fig. 1 X-ray diffraction patterns of neat CNTs and PANI coated CNTs also referred as p CNTs

Morphology of PANI Coated CNTs and Composite Films

Figure 2(a) shows the SEM images of p CNTs that are arranged in the form of network of nanotubes. The nanotubes are present in the form of small bundles rather than large aggregated bundles owing to the coated layer of PANI onto the CNTs which prevents the agglomeration of nanotubes. The average size of the p CNTs bundles lie in the range of (35 ± 5) nm. The incorporation of PANI up to 10 wt% concentration in the PS matrix is shown in Fig. 2(b) indicating that the heterogeneous morphology of the blend system contains the separate phases (droplet type of PANI phase is seen in the PS matrix phase). Figure 2(c) shows the morphology of PS/PANI/ p CNTs hybrid nanocomposites in which the p CNTs are embedded uniformly in the heterogeneous

phase of the blend system, thus forming well dispersed network in the PS/PANI blend without any traces of agglomeration. Notably, the size of the pCNTs bundles did not vary after dispersion into the PS/PANI blend. The effect of such hybrid nanocomposite on the dielectric and mechanical properties is further investigated and discussed.

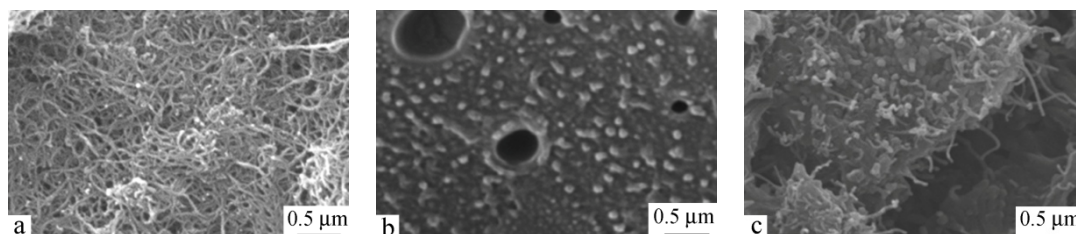


Fig. 2 SEM images of (a) PANI coated CNTs (pCNTs), (b) PS/PANI polymer blend at 10 wt% concentration of PANI and (c) PS/PANI/pCNTs hybrid nanocomposites at 0.5 wt% concentration of pCNTs

Dielectric Behavior

Figure 3 shows the dielectric constant (ϵ') behavior of PS, PS/PANI blend and various concentrations of pCNTs in PS/PANI blend with respect to the frequency at room temperature. The addition of PANI at concentration of 10 wt% into PS increased the ϵ' slightly in the lower frequency region, while at higher frequency region, ϵ' remains intact as compared to PS showing its good stability over wide frequency range. The influence of the second phase of PANI along with the presence of nanofiller pCNTs in PS is quite evident from the significant enhancement of ϵ' of PS. By incorporation of pCNTs up to 0.5 wt% into the blend of PS/PANI, ϵ' is significantly enhanced in the lower frequency region. However, at 1.0 wt% of pCNTs, ϵ' is relatively decreased yet remains extremely higher than neat PS as well as PS/PANI blends system. At the frequency of 100 Hz, ϵ' of PS, PS/PANI blend, PS/PANI/0.5 wt% pCNTs and PS/PANI/1.0 wt% pCNTs is 4, 35, 1899 and 931, respectively. Notably, the influence of pCNTs on the ϵ' behavior of PS/PANI blend is pronounced in the lower frequency region while at higher frequency region, ϵ' is close to each other for all the systems.

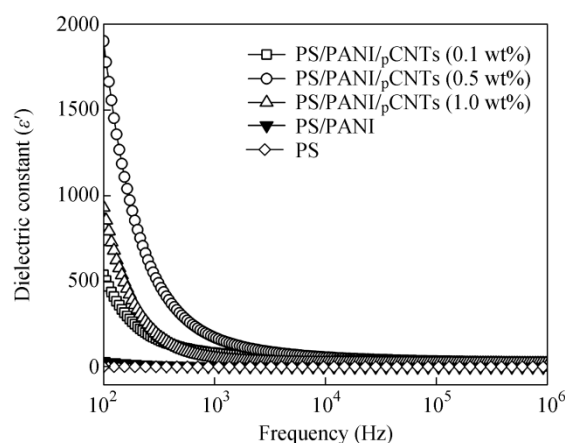


Fig. 3 Dielectric permittivity constant response as a function of frequency at room temperature for neat PS, PS/PANI polymer blends and hybrid nanocomposites of PS/PANI/pCNTs with varying concentrations

Such remarkable increase in ϵ' at lower frequency region of PS/PANI/pCNTs is pertaining to the interfacial polarization also known as Maxwell-Wagner-Sillars effect due to their heterogeneous multi component structure. As a result, the charges are accumulated at the interfaces of the multi component system. Thereby, in the lower frequency region, the accumulated charge carriers at interface (induced dipoles) acquire sufficient time to align and orient themselves parallel to the applied field and ultimately increased the dielectric constant values. Seemingly, the significant increase of the dielectric values up to 0.5 wt% pCNTs is related to the percolation

threshold network formation in PS/PANI system. Beyond the percolation threshold, conductive path networks are started to form and therefore the dielectric values are relatively decreased at concentration of 1.0 wt% pCNTs as discussed by various researchers^[26–31].

Figure 4(a) shows the dielectric loss (ϵ'') behavior of PS, PS/PANI blend and various concentrations of pCNTs in PS/PANI blend with respect to the frequency. ϵ'' is decreased with increasing frequency and in the higher frequency region, the ϵ'' is close to each other for all the samples, however, the response in the lower frequency region is varied. The ϵ'' is increased by the incorporation of PANI as well as pCNTs into the PS matrix but overall the increase in ϵ'' is less as compared to the epoxy/CNTs/PANI hybrid system^[32]. In the meantime, ϵ' of PS/PANI/pCNTs is significantly higher than the previously reported values of other hybrid polymer nanocomposites^[13–15, 26, 32]. Moreover, behavior of dielectric loss tangent ($\tan\delta$) with increasing frequency (Fig. 4b) shows similar trend as observed for ϵ'' .

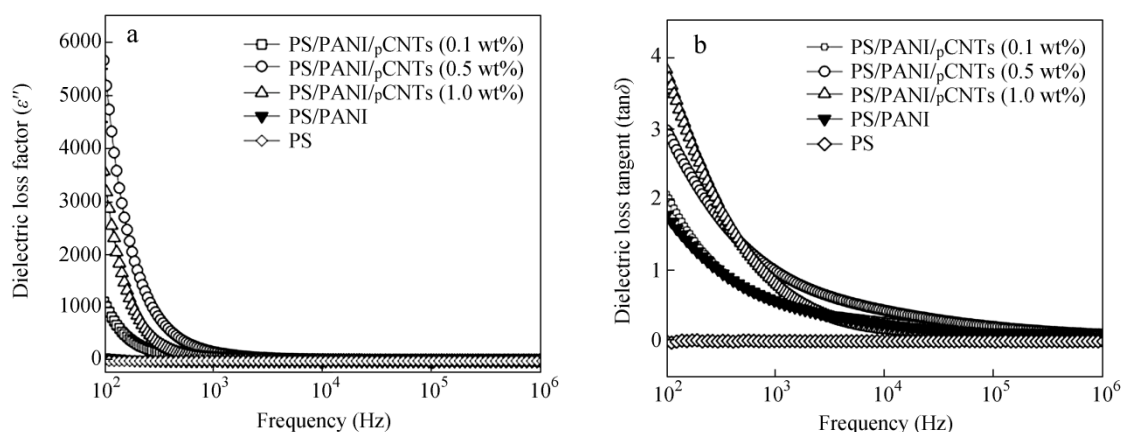


Fig. 4 (a) Dielectric loss and (b) dielectric tangent loss as a function of frequency at room temperature for neat PS, PS/PANI polymer blends and hybrid nanocomposites of PS/PANI/pCNTs with varying concentrations

It is worth noting that the significant increase in the dielectric constant is achieved for 0.5 wt% of pCNTs in PS/PANI blend system. Such unique behavior is attributed to the good dispersion of pCNTs in the PS/PANI blend system. According to microcapacitor model, large numbers of domains (multilayered microcapacitors) are formed in which the layers are distributed in such a manner that the inner layer is more conductive whereas the outer layer is a poor conductor. In our case of heterogeneous network of PS/PANI/pCNTs as shown in Fig. 5, the system consists of three layers: the most inner layer consists of CNTs which are highly conductive, PANI which is relatively less conductive as compared to CNTs and PS which is insulative layer. The advantage of PANI coated onto CNTs is that it hampers the direct contact of CNTs among each other and therefore decreases the formation of direct conductive paths, responsible for electron tunneling current in the lower frequency region. As a result, the polarization takes place at the junctions of the layers where charges are piled up and therefore contributes to the huge increase in the dielectric constant of our system.

Electrical Conductivity

Figure 6 shows the AC conductivity (σ_{ac}) with increasing frequency for all the samples. σ_{ac} is increased in the lower frequency region as well as in the higher frequency region for PS/PANI/pCNTs systems. The maximum increase in σ_{ac} is of five orders of magnitude from 1.6×10^{-10} to 2.0×10^{-5} S·cm⁻¹ for PS/PANI/0.5 wt% pCNTs. Interestingly, σ_{ac} of hybrid nanocomposites is reduced up to 1 kHz and then showed an increasing trend with further increase in frequency. The reduction in σ_{ac} near 1 kHz indicating the contribution of interfacial polarization to induce the conductivity that started to disappear with the increase in frequency. Moreover, above 1 kHz, the σ_{ac} of all the samples shows upward trend as in this region hopping mechanism play the role to enhance the conductivity within the system.

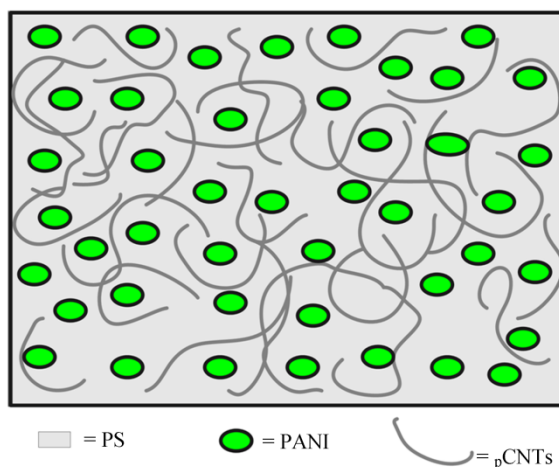


Fig. 5 Schematic illustration for the dispersion of pCNTs in the PS/PANI polymer blend

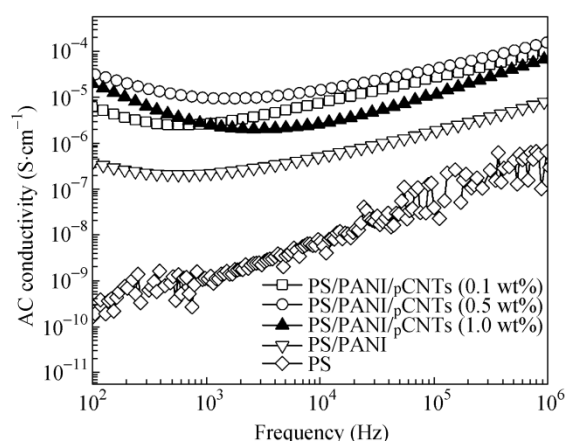


Fig. 6 Frequency dependence of AC conductivity at room temperature for neat PS, PS/PANI polymer blends and hybrid nanocomposites of PS/PANI/pCNTs with varying concentrations

Mechanical Characteristics

Figure 7 shows the stress-strain graph of pure PS, blend of PS with PANI at 10 wt% and hybrid nanocomposites of PS/PANI blend with varying concentration of pCNTs from 0.1 wt% to 1.0 wt%. By the incorporation of PANI up to 10 wt% into the PS matrix, the tensile properties of PS are slightly improved owing to the formation of heterogeneous network of PS and PANI. However, by the addition of CNTs at varying concentration into the blend system of PS/PANI, the tensile properties are significantly improved as shown in Fig. 8. The addition of 1.0 wt% of CNTs induces the maximum improvement in the tensile properties of matrix; for instance, the increase in modulus and tensile strength is up to 55% from 726 MPa to 1128 MPa (Fig. 8b) and 160% from 5.3 MPa to 13.8 MPa (Fig. 8b), respectively. Notably, such increase in the tensile strength and modulus is achieved without much loss of strain at break (Fig. 8c). Thereby, the hybrid nanocomposites of PS/PANI/pCNTs become stiffer, stronger and tougher as compared to the neat blend system.

The factors contribute to affect the overall mechanical properties of polymer nanocomposites include: (1) the reinforcement effect of filler in the polymer matrix and (2) predominance of the type of structural phase present in the polymer matrix^[33]. The latter effect is neglected for PS/PANI system because it occurs in the semi-crystalline polymer matrices, particularly for the matrices containing polymorphism^[34, 35]. The former effect is imparted owing to the dispersion and compatibility of the filler in the matrix. As reflected from the SEM morphology (Fig. 2), pCNTs are well dispersed in the PS/PANI blend system, giving rise to the reinforcement effect by constraining the polymer chains network owing to their strong interfacial interactions.

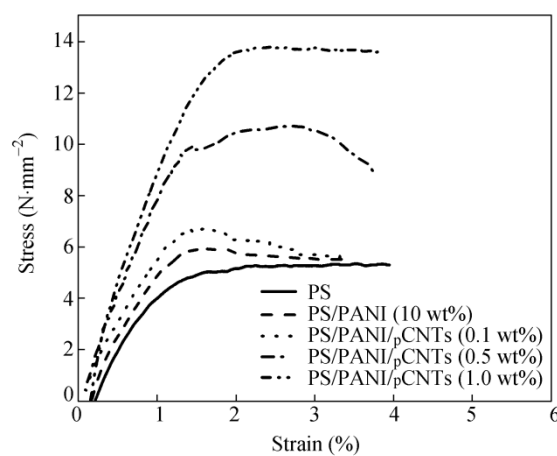


Fig. 7 Stress-strain curves of PS, PA/PANI blends and hybrid nanocomposites of PS/PANI/pCNTs with varying concentrations

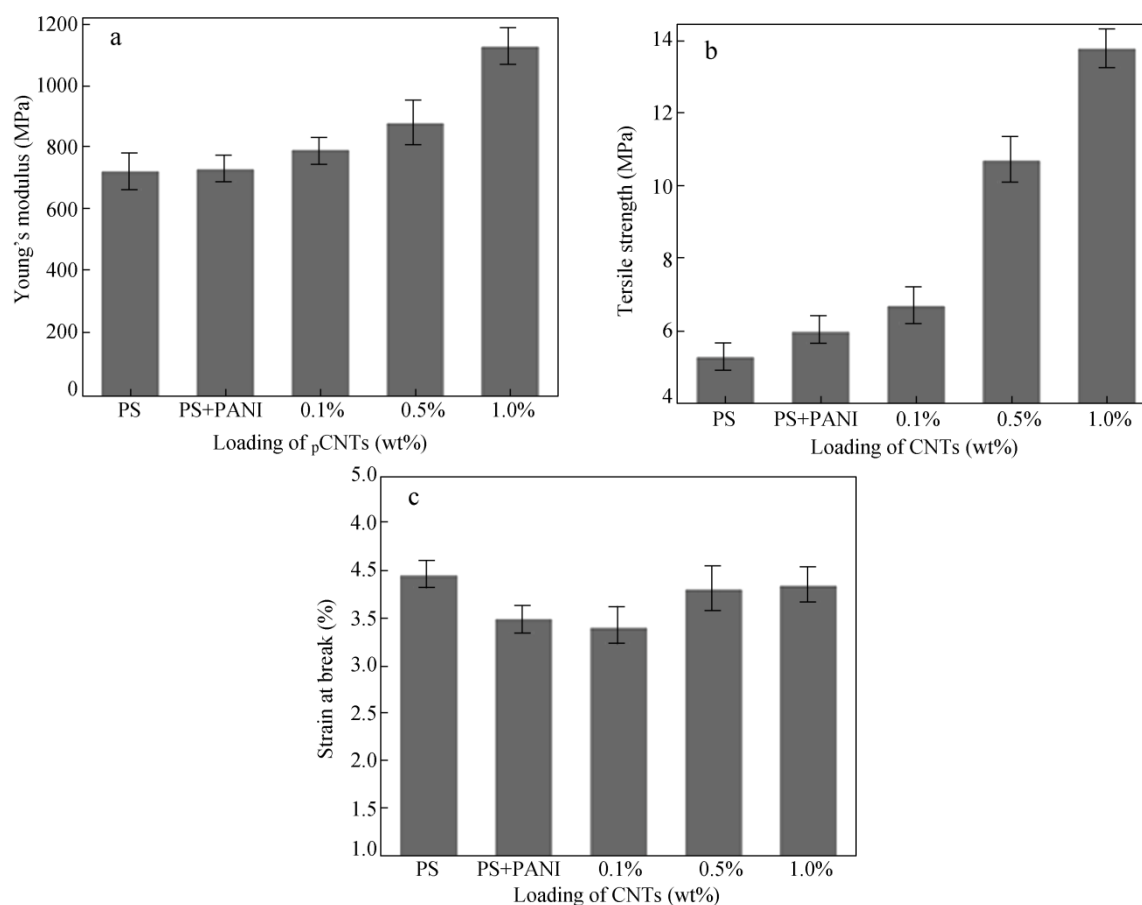


Fig. 8 (a) Young's modulus, (b) tensile strength and (c) strain at break for neat PS, PS/PANI polymer blend and hybrid nanocomposites of PS/PANI/pCNTs with varying concentrations

CONCLUSIONS

In this work, three phase hybrid nanocomposites of polystyrene/polyaniline/CNTs coated with polyaniline are prepared by solution casting method and their dielectric and mechanical properties are investigated using impedance analyzer and extensometer. The blending of 10 wt% concentration of PANI into the matrix of PS showed the heterogeneous phase separated morphology. The concentration of CNTs coated with PANI (pCNTs) was varied from 0.1 wt% to 1.0 wt% in the blend system of PS/PANI. pCNTs were dispersed in the form of small bundles rather than aggregated bundles in the PS/PANI blend owing to the coated layer of PANI onto the CNTs which prevented the agglomeration of nanotubes. The average size of the pCNTs bundles was in the range of (35 ± 5) nm. The dielectric properties of hybrid nanocomposites were remarkably enhanced. The dielectric permittivity constant value of PS increased from 4 to 35 by blending with PANI at 10 wt% concentration which was significantly enhanced to 1899 at a frequency of 100 Hz by the incorporation of pCNTs up to 0.5 wt% in the PS/PANI blend along with the slight increase in dielectric loss and $\tan\delta$. Such remarkable increase in ϵ' of PS/PANI/pCNTs is pertaining to the interfacial polarization also known as Maxwell-Wagner-Sillars effect due to their heterogeneous structure. The interfacial polarization occurs in the hybrid nanocomposites due to the presence of large number of domains with varying conductivity character of the phases from insulative (PS) to poor conductor PANI to highly conductive CNTs. Similarly, the tensile modulus and tensile strength are also enhanced significantly up to 55% and 160%, respectively, without much loss of ductility for three phase hybrid nanocomposites as compared to the neat PS and PS/PANI blends. PS/PANI/pCNTs systems showed very promising dielectric and mechanical results which enable them to use for energy storage applications.

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