Polypyrrole Decorated Mechanically Robust Conductive Nanocomposites via Solution Blending and in Situ Polymerization Techniques

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ABSTRACT: Polypyrrole grafted polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polystyrene (SEBS-*g*-PPy)/multiwall carbon nanotubes (MWCNTs) conductive nanocomposites were fabricated using two different approaches. The approach of system-I involved primarily the grafting of PPy on SEBS and its subsequent composites with nanotubes. In system-II in situ polymerization/grafting of PPy on SEBS was carried out along with MWCNTs yielding nanomaterials. Presynthesized SEBS-*g*-PPy and nanocomposites were characterized by Fourier transform infrared spectroscopy, NMR, field emission scanning electron microscopy, transmission electron microscopy, and electrical, mechanical, and thermal properties. The π−π stacking interactions between PPy of SEBS-*g*-PPy and MWCNTs rendered ample dispersion of the nanotubes in system-II relative to system-I. The electrical conductivity and tensile data showed improvement in these properties of nanocomposites and that system-II nanocomposites can sustain higher stresses, is stiffer, and can absorb more energy before breaking. Thermal stability of both the systems was improved relative to the matrices, and decomposition temperatures were found to increase from 437 to 568 °C. Relative improvement in electrical, thermal and tensile properties were observed for system-II nanocomposites rather than for system-I nanocomposites.
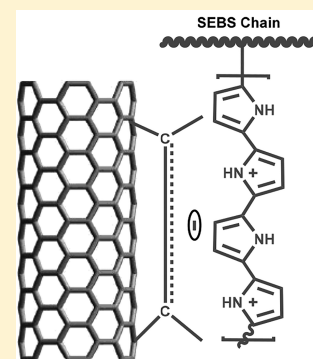
1. INTRODUCTION

The outstanding properties of carbon nanotubes make them attractive fillers for the fabrication of advanced composite materials for a broad range of applications. They are not compatible with any solvent; for this reason efficient chemical functionalization is necessary rendering their homogeneous dispersion in solvents and supporting media, and ample interconnectivity with the matrix. Functionalization techniques may involve covalent (grafting-to and grafting-from)[1−3] and noncovalent (polymer wrapping, π−π stacking interaction), adsorption of surfactants and coupling of surfactants.[4−6] Because of attractive van der Waals interactions, nanotubes tend to aggregate forming bundles, ropes with highly entangled network structures. This type of attraction is well-known for colloids dispersed in polymers.[1] In such a suspension, an attractive force is established between the fillers due to entropic effects.[2] Intensive research on the exfoliation of nanotubes is being carried out for the production of uniform and well-defined structures of composites with improved properties. The dispersion of the nanotubes can be carried out by physical/mechanical or chemical methods. The mechanical route involves physical separation of nanotubes from each other, while in the chemical technique, surfactant or some type of chemical treatment is required. Such nanocomposites find

applications in various fields as they are highly in demand for structural uses because of their lighter, stronger, and tough nature.[7−10] Their conductive nature allows them to be used to develop materials such as electromagnetic interference (EMI) shielding, conductive polymers, or antistatic coatings.[11] Using the efficient thermal conduction of carbon nanotubes, polymers can be well adapted for high temperature use by preventing the thermal degradation of the surrounding polymer.[12] Nanotube-aligned nanocomposites are in use due to anisotropic properties and improved mechanical properties.[8,13] The effective performance of carbon nanotubes in the composites strongly depends on the ability to disperse homogeneously, good interfacial bonding, and interactions between the phases.[14]

Various approaches for the fabrication of these composites have been devised with different functionalization and dispersion methods for the nanotubes.[15] Solution processing of the composites is the most common method and involves the mixing of both nanotubes and a polymer in a suitable
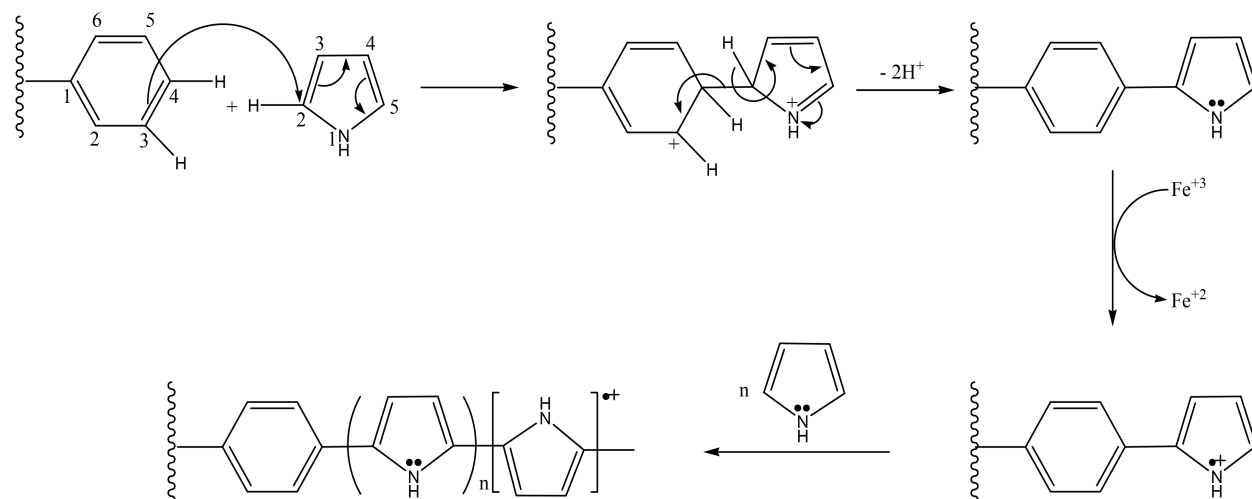
Scheme 1. Mechanism of SEBS-g-PPy Formation

solvent. The dispersion of the components in a solvent, mixing, and evaporation are often supported by mechanical agitation, for example, ultrasonication, magnetic stirring, or shear mixing.[15,16] Insoluble polymers are processed by melt processing techniques[12] while those which cannot be melt-processed, insoluble, and thermally unstable are often in situ polymerized directly and grafted on to the walls of the nanotubes.[17,18] Potential applications of these materials are as energy storage devices (fuel cells), advanced aerospace composites, coaxial cable, field emitters,[19] nanoprobes and sensors,[17,20] conducting polymer composites,[21] heat dissipation coatings,[12] energy storage materials,[19] high strength composites,[16] and EMI shielding materials.[20] Aligned CNT systems are used for data storage, optical transmitters, and detector sensory systems.[21−27]

SEBS nanocomposites fabricated by a high-shear processing technique showed uniform distribution of nanotubes even at high proportions up to 15 wt %.[23] Modulus increased from 16.3 to 186.8 MPa while tensile strength increased from 4.22 to 13.83 MPa at 15 wt % loading of nanotubes. Elasticity decreased while conductivity increased with optimum value (5.16 S cm^{-1}) up to 15 wt % filler loading.[23] Polyisoprene nanocomposites have been produced using SWCNTs under high pressure and room temperature. Thermal conductivity and glass transition temperature increased with 5 wt % addition of SWCNTs due to high cross-linking in the nanocomposites.[24] Sulfonated poly(styrene-b-(ethylene-alt-propylene)/PPy conducting nanocomposites have been prepared by in situ polymerization of pyrrole using FeCl$_3$. The conductivity values obtained ranged from 10^{-3} to 10^{-1} S cm^{-1}.[26] A conductive poly(vinylidene fluoride) (PVDF)/polyamide 6 (PA6)/nanotube composite was produced by a melt blend process with variable contents. Conductivity was significantly enhanced with the increase in the weight ratio of filler with improved physical properties.[27] Polypyrrole/PVA blends have been produced electrochemically as thin conducting layers on the electrode surface.[28] Similarly, polythiophene/PPy conducting blends have been generated on insulating polystyrene and polycarbonate resin electrochemically.[29] Poly(butylene terephthalate) (PBT)/SWCNTs composites have been synthesized using an in situ poly-condensation reaction. Various properties were enhanced with an increase in nanotube loading.[30] Highly conductive core−

shell nanocomposites have been produced using poly(N-vinylcarbazole)/polypyrrole(PNVC/PPy) with MWCNTs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the coating of copolymer on the surface of the nanotubes. The conductivity of the resulting nanocomposites was increased relative to that for the neat PNVC matrix.[31]

In the current endeavor, SEBS-g-PPy/MWCNTs nano-composites were prepared using two strategies. System-I involved the grafting of PPy on SEBS in chloroform and then their subsequent nanocomposites with nanotubes. System-II nanocomposites were produced with in situ polymerization of PPy on SEBS carried out in the presence of MWCNTs. The main objective of this work was to synthesize nanocomposites with improved electrical conductivity and enhanced mechanical properties for various practical applications. A charge transfer complex between the PPy moiety of grafted copolymer and nanotubes may be formed in both the systems investigated. This complex formed between the matrix and filler resulted in resonance due to a delocalized electronic cloud on the MWCNTs surface. The resulting grafted copolymer and nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), NMR, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses along with electrical, mechanical, and thermal properties. These elastomer-based nanocomposites have many practical applications, for example, such nanomaterials can be added to plastering materials for lightening protection of buildings where a high value of electrical conductivity is desirable.

2. EXPERIMENTAL SECTION

2.1. Materials. Triblock copolymer SEBS with molar mass 118 000 g/mol and styrene content 28% procured from Aldrich was used in the present work. Pyrrole monomer (96%) was supplied by Fluka while anhydrous ferric chloride (98%) and acetone were obtained by Reidel-de Haen. Carbon nanotubes, synthesized through CVD had a purity of 85−90% with dimensions (D × L: 8−14 nm × 0.8−5.0 μm), provided by the courtesy of National Center for Physics (NCP), Quaid-i-Azam University, Islamabad. Methanol (99.5%) and chloroform (99%) were purchased from Merck, and the latter was dried by anhydrous calcium chloride before

distillation at constant boiling temperature. The filtrate obtained was refluxed and then collected at 60 °C for use in the formation of nanocomposites.

2.2. Fabrication of Nanocomposites. Two strategies were employed to prepare nanocomposites using MWCNTs as described below.

a. Solution Blending Method (System-I). Initially SEBS was dissolved in chloroform with constant stirring for 24 h, followed by the addition of $FeCl_3$ as an oxidant to polymerize the freshly distilled pyrrole poured dropwise to the above solution. The details of synthesis and characterization of SEBS-*g*-PPy have been described elsewhere.[32] The mechanism for formation of PPy grafted copolymer is given in Scheme 1. For the preparation of nanocomposites, SEBS-*g*-PPy (10 g) was dissolved in chloroform (60 g). Various compositions of SEBS-*g*-PPy and MWCNTs were taken in geometric ratios and agitated for 24 h at ambient temperature for uniform dispersion of the nanotubes. The composite films were cast by evaporation of the solvent and then dried in a vacuum oven to a constant weight.

b. In-Situ Polymerization Method (System-II). This method involved the synthesis of SEBS-*g*-PPy in the presence of filler. For a particular concentration, a measured amount of MWCNTs (0.12 g) was taken in a reaction flask along with $CHCl_3$ (30 mL), and then was ultrasonicated for 2 h to ensure homogeneous dispersion and/or disruption of their entanglement in the solvent. SEBS (0.6 g) solution in chloroform was added in to the nanotube dispersion. The mixture was agitated at 60 °C and then was sonicated. Anhydrous ferric chloride (0.163g) was added with continuous stirring for 30 min, followed by dropwise addition of freshly distilled pyrrole (0.72 mL). The mixture was refluxed for 3 h at 60 °C. The black mass was separated by methanol followed by the repeated washings with methanol, with distilled water, and finally with acetone. Similarly, other concentrations were prepared and then dried under vacuum for 72 h.

2.3. Characterization. The presence of various functional groups in SEBS-*g*-PPy and their nanocomposites was identified using a Thermo Nicolet 6700 FTIR spectrophotometer. The DC electrical conductivity of the films was measured by a four-point probe technique using 50 or 100 voltage. A high resistance meter ($1000-10^{17}$ Ω), model 6517A, Keithley, was used to record the resistivity, which was then converted to conductivity values. The surface morphology of cryogenically fractured samples was monitored by FEI Nova 230 FESEM. The internal morphology of the nanomaterials was observed under FEI Tecnai G2 Spirit Twin transmission electron microscope, operated at an accelerating voltage of 120 kV. To record the images, films were microtomed into 30 nm ultrathin sections with the help of a diamond knife using a Leica Ultracut UCT ultramicrotome. Tensile measurements of the rectangular strips with dimensions (ca. 14 mm × (6.4−7.3) mm × (0.12−0.23) mm) were taken according to DIN procedure 53455 using Testometric Universal Testing machine, model M500-30CT, which had a crosshead speed of 5 mm min^{-1} at 25 °C. The films being casted were vacuum-dried overnight before analysis. The pneumatic gripping system was exploited to prevent the slipping of the strips and the average value of 3−4 measurements was taken. Thermal stability of the nanocomposites was determined using NETZSCH TG 209 F3 thermogravimetric analyzer. The analysis required 1−5 mg of the sample in the Al_2O_3 crucible which was heated from 50 to 800 °C at a heating rate of 10 °C

min^{-1} under nitrogen atmosphere with a gas flow rate of 20 mL min^{-1}.

3. RESULTS AND DISCUSSION

Pristine SEBS has notorious film forming property and did not yield well textured film. The grafting of PPy on SEBS produced smooth films for the SEBS-*g*-PPy matrix as well as for their nanocomposites. The hybrid films were opaque and dark black in color. The presence of various functional groups, characteristic protons of SEBS-*g*-PPy and the molar mass data obtained have been reported somewhere else.[32] The polymerization of pyrrole at the para position of the benzene ring of polystyrene was confirmed by the band that appeared at 841 cm^{-1} (Figure 1).
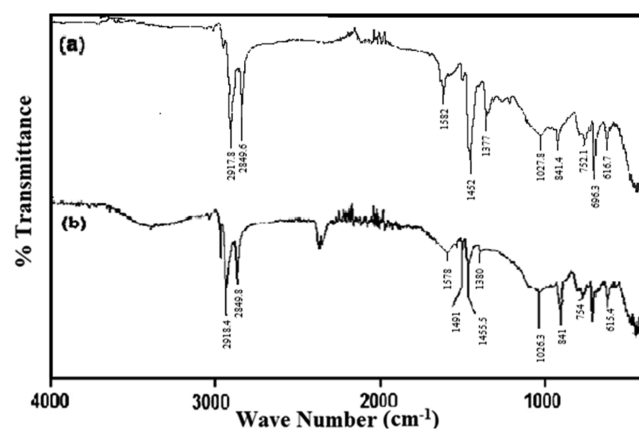

Figure 1. FTIR spectra of SEBS-*g*-PPy/MWCNTs nanocomposites prepared using (a) in situ polymerization; (b) solution blending.

In the nanocomposites, a charge transfer complex was formed and the partial double bond character of carbon increased. This occurred because the extended resonance of the nanotubes in the solution blending technique produced a band at 1380 cm^{-1}, while for the in situ polymerized nanocomposites, the same band appeared at 1377 cm^{-1}. The band at 1566 cm^{-1} in SEBS-*g*-PPy[32] shifted to 1578 cm^{-1} due to a decrease of the double-bond character in solution blended nanocomposites (Figure 1). In situ polymerized nanocomposites showed a more pronounced decrease in the stretching frequency up to 1582 cm^{-1} which might be attributed to a greater attachment of the polymer matrix with the nanotubes.

3.1. Microscopic Analyses. The dispersion of nanotubes in SEBS-*g*-PPy was scrutinized by both SEM and TEM. FTIR frequencies clearly showed the interaction of nanotubes with the matrix, yet it was further confirmed by monitoring their morphology. The surface morphology of the nanocomposites was analyzed by recording field emission scanning electron microscopy (FESEM) images to determine distribution of the nanotubes into the polymer matrix. Micrographs of SEBS-*g*-PPy/MWCNTs prepared using both solution blending and in situ polymerization techniques are given in Figure 2. The micrographs indicated ample interaction between the polymer matrix and the nanotubes with homogeneous dispersion resulting in improved mechanical properties.

A comparison of both fabrication techniques shows that solution blending gave good filler dispersion in the matrix whereas the in situ polymerized sample presented more
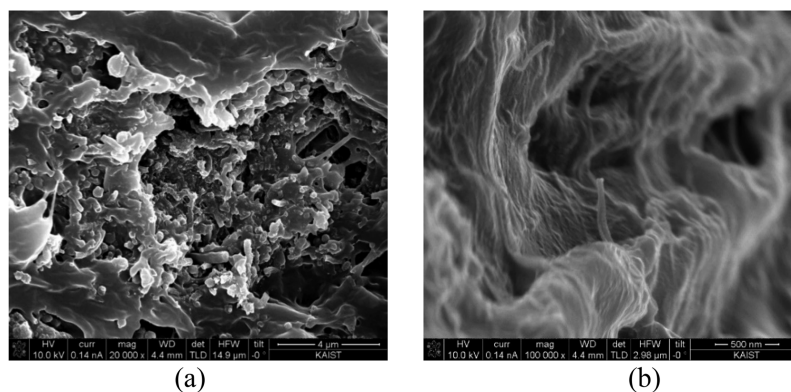
Figure 2. FESEM micrographs of 5% MWCNTs/SEBS-*g*-PPy nanocomposites (a) solution blending (b) in situ polymerized.

compatibilized system with nanotubes fully embedded in the polymer matrix representing a fine network as shown in Figure 2b. SEM images which are in good agreement with IR results indicated a better charge transfer complex in the nanocomposites.

Transmission electron microscopy actually illustrates the internal morphology of the nanocomposites. TEM micrographs of the nanocomposites prepared by solution blending revealed that nanotubes are distributed in the polymer matrix with a good degree of dispersion (Figure 3a). Nanocomposites
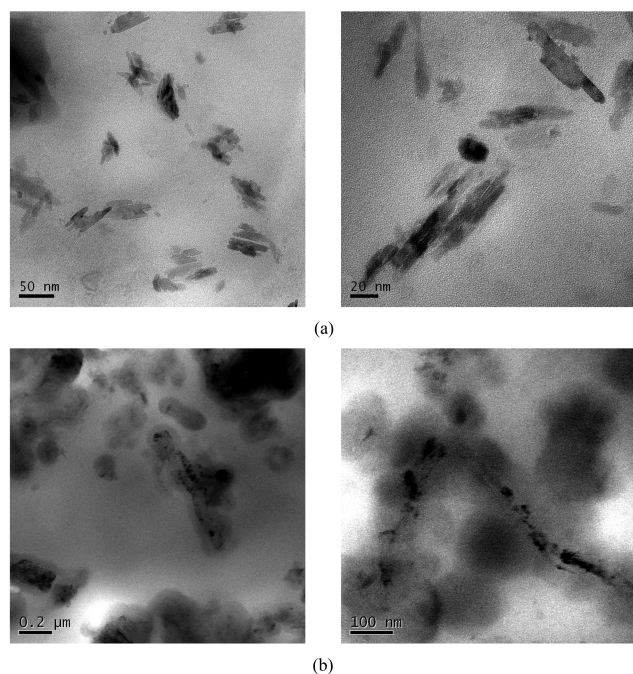

Figure 3. TEM micrographs of 5% MWCNTs/SEBS-*g*-PPy nanocomposites: (a) solution blending; (b) in situ polymerized.

fabricated by in situ polymerization demonstrated that the nanofiller particles are disseminated in the polymer with a high degree of individual dispersed nanotubes (Figure 3b). In-situ polymerized composites again proved to be better candidates on the basis of interaction of polymer matrix with the nanotubes relative to solution blending ones with some agglomeration observed while in situ polymerized showed better dispersion of filler. This may be attributed to the mixing technique used along with the fabrication method which was

mechanical stirring in the former while ultrasonication in the latter.

3.2. Conductivity Measurements. Pure SEBS copolymer is a nonconductor, whereas PPy has excellent electrical conductivity (100 S/cm). The grafting of PPy on elastomer improved both texture and conductivity of resulting SEBS-*g*-PPy materials. The log conductivity value of SEBS-*g*-PPy was found to be −13.69, which was similar to our previous findings.[32] When nanotubes were incorporated into the SEBS-*g*-PPy matrix, the resulting nanocomposites gave enhanced conductivity values as a function of nanotube loading. Nanocomposites made by solution blending (system-I) containing different proportions of MWCNTs (1 to 10-wt %) showed higher conductivity values with an increase in nanotube concentration (Figure 4). Actually, the resistivity of
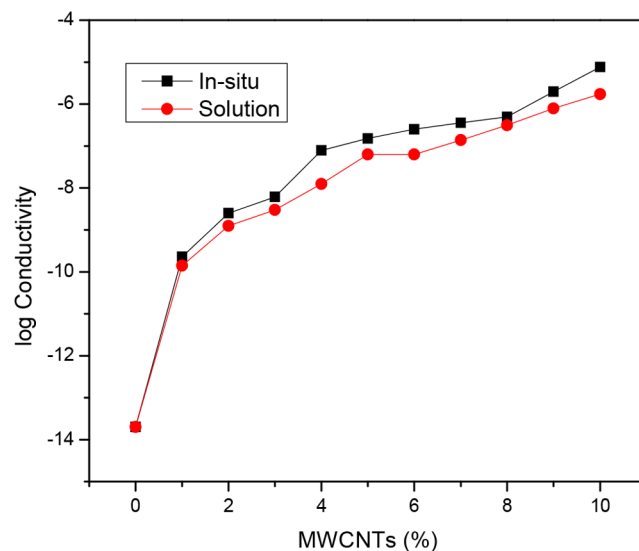

Figure 4. Comparison of conductivity values of in situ polymerized and solution blending SEBS-*g*-PPy/MWCNTs nanocomposites.

three samples was determined using the four-probe method at ambient conditions, and their corresponding average conductivity values were drawn as a function of MWCNTs percentages.

The log conductivity of SEBS-*g*-PPy/MWCNTs displayed a gradual increase upon the addition of nanotubes. Upon 10 wt % of MWCNTs loading; the log conductivity value increased to −5.764 and a continuous increase would be expected upon

further addition of MWCNTs content. SEBS-*g*-PPy/MWCNTs nanocomposites prepared by in situ polymerization technique (system-II) showed an increase in conductivity relative to the matrix and system-I. The log conductivity value was found to be −5.113 with 10 wt % MWCNTs. As nanotubes are conductive fillers and were used to enhance the conductivity of the composite materials, significant improvement in electrical conductivity values were observed relative to the matrix. The increase in electrical conductivity in both systems is attributed to the formation of a charge transfer complex between the polymer matrix and the nanotubes resulting increase in resonance due to delocalized electronic cloud on the nanotube surface (Figure 5).
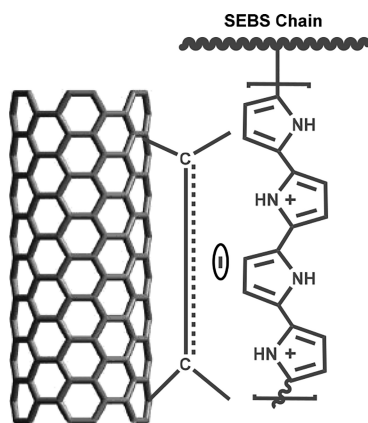

Figure 5. Formation of a charge transfer complex between copolymer chains and the MWCNTs surface.

This complex formed also facilitates the flow of electric current. On comparing both the systems, an appreciable increase in conductivity values of system-II is observed due to better dispersion and network structure as evident from SEM micrographs (Figure 2b). So, in situ polymerized nanocomposites were quite good in terms of filler dispersion and were more conductive than those from the solution blending technique.

3.3. Mechanical Properties. Pure SEBS elastomer has a low stress bearing potential (4.22 MPa),[23] while the grafting of PPy on SEBS yielded uniform and smooth film with an improved stress value (13.48 MPa). Mechanically robust carbon nanotubes when added into a polymer matrix impart strength to the materials. The tensile behavior of both the systems is presented in Figures 6 and 7. The improvement in mechanical properties was observed for SEBS-*g*-PPy/MWCNTs nanocomposites. SEBS-*g*-PPy is itself very flexible in nature, and upon the addition of MWCNTs, the tensile strength of the matrix increased. Also, the mechanical profile of the materials improved upon the formation of nanocomposites in both the systems as given in Figure 8. The ultimate stress at break showed a continuous increasing trend with 13.48 MPa for SEBS-*g*-PPy[32] to 18.31 and 17.64 MPa for in situ polymerization and solution blending nanocomposites with 10 wt % loading of nanotubes respectively (Figure 8a). Maximum strain data showed that in situ polymerized composites were more flexible than solution blending samples.

A sharp decreasing trend in strain values was observed with the addition of nanotubes in both the systems (Figure 8b). The tensile modulus of the composites, which is the measure
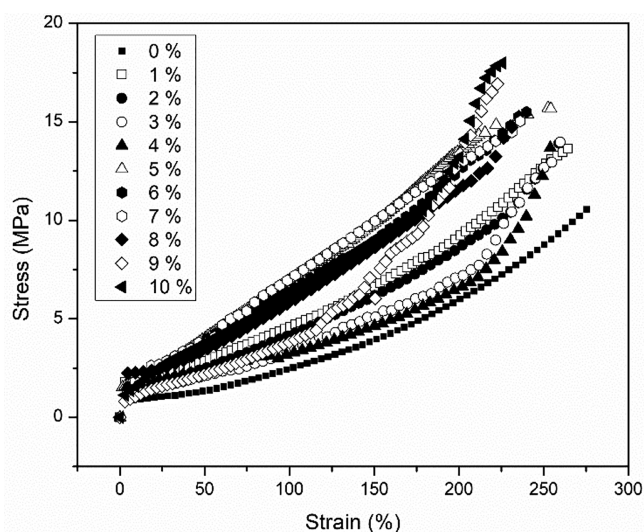

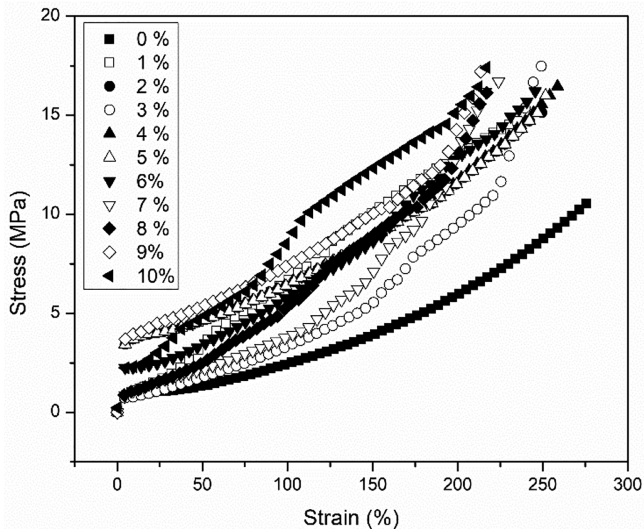**Figure 6.** Stress−strain curves for solution blending SEBS-*g*-PPy/MWCNTs nanocomposites.

Figure 7. Stress−strain curves for in situ polymerized SEBS-*g*-PPy/MWCNTs nanocomposites.

of the stiffness of the system, showed a sharp increase as nanotubes were introduced in SEBS-*g*-PPy matrix (Figure 8c).

The maximum values of moduli were 209 and 196 MPa for in situ polymerized and solution blending nanocomposites, respectively, relative to the matrix (71.3 MPa).[32] These properties are improved relative to the previously mentioned SEBS/MWCNTs composites prepared by high-shearing processing.[23] Toughness is the ability of a material to absorb energy before rupturing and is usually calculated by measuring the area under the stress−strain curve.

Toughness increased as a function of nanotubes loading and keeps on increasing with MWCNTs content rather than with the polymer matrix (Figure 8d). However, beyond 10 wt % addition of MWCNTs, the film forming properties of the materials were lost and cracks were developed in the films that adversely affected the mechanical properties of these materials. Therefore, nanocomposites with higher concentrations of nanotubes were purposely not prepared and analyzed. While comparing the tensile data of both the systems, almost similar
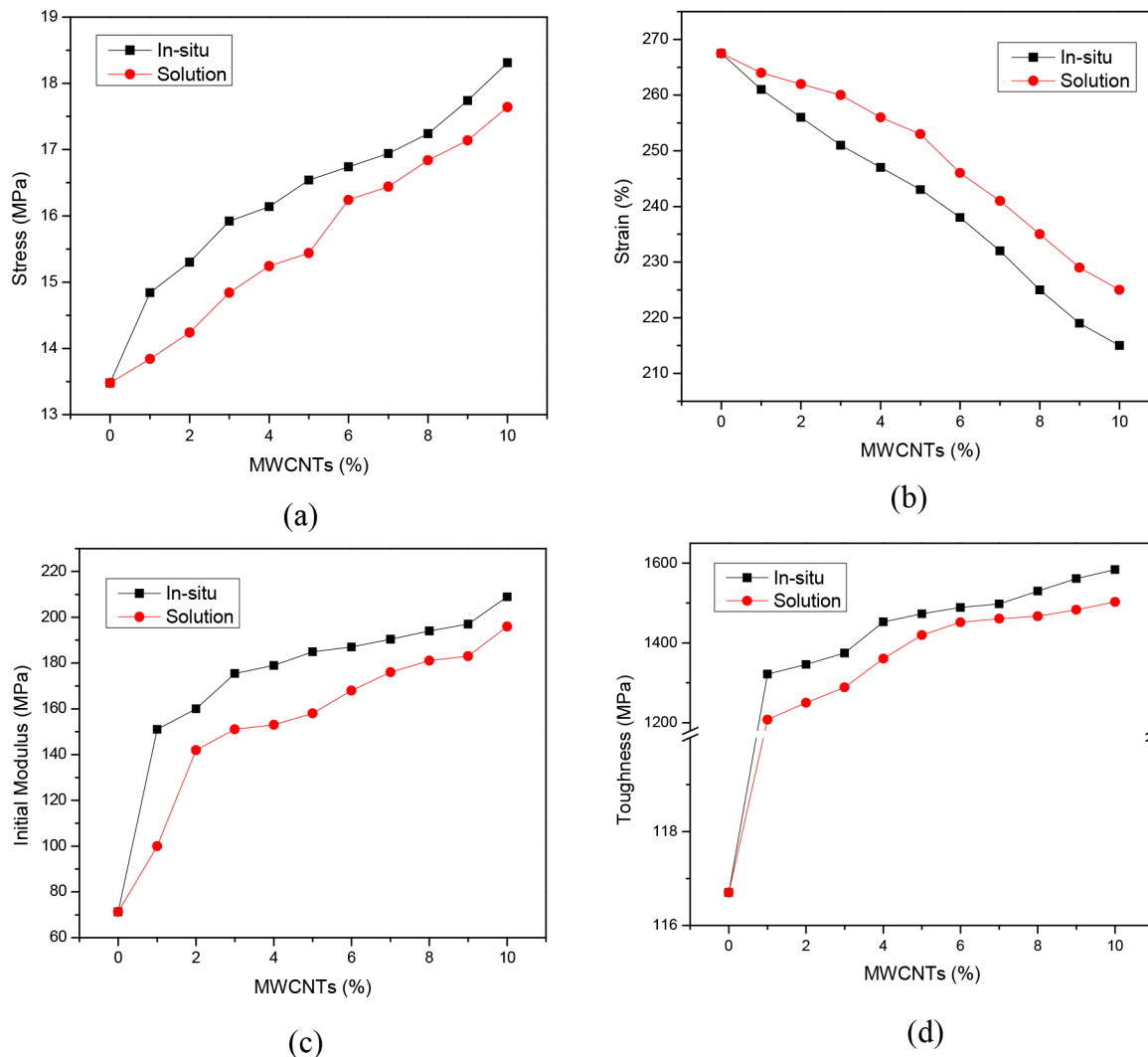
Figure 8. Variation of tensile data vs nanotubes loading for in situ polymerized and solution blending SEBS-*g*-PPy/MWCNTs nanocomposites: (a) stress; (b) strain; (c) initial modulus; (d) toughness.
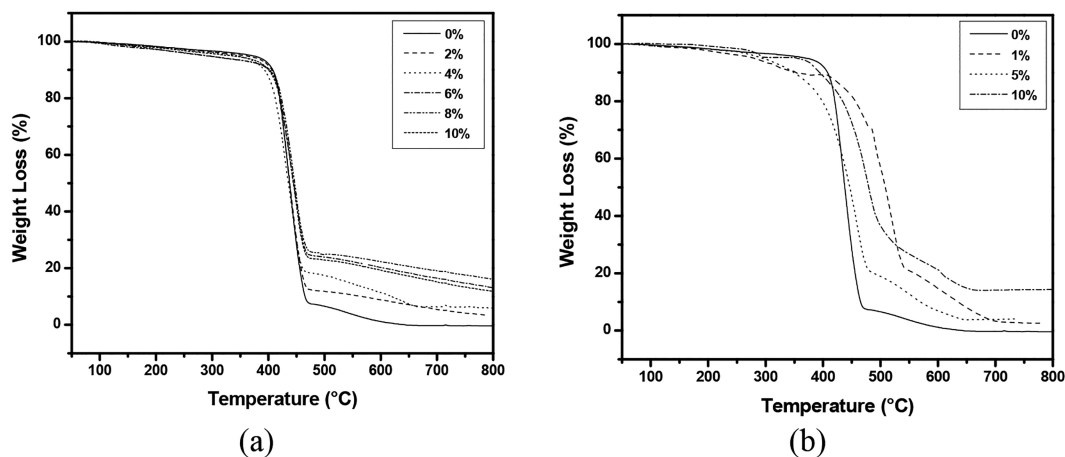

Figure 9. TGA curves of solution blending (a) and in situ polymerized (b) SEBS-*g*-PPy/MWCNTs nanocomposites.

trends are observed in mechanical properties. The mechanical profile of system-II was improved relative to that of system-I. Maximum stress is increased whenever reinforcement is added to the polymer matrix, while brittle and hard filler reduces the value for maximum strain of the system as elasticity of the system is reduced. Similar behavior is observed for both systems.

Improvement in mechanical properties was only found when there was a good dispersion of MWCNTs in the matrix, good interfacial adhesion, and mechanical anchoring between the filler and polymer chains as depicted by FESEM and TEM micrographs. Owing to the formation of a charge transfer complex, there is good interaction between the polymer matrix and the reinforcement, providing better mechanical properties. The resulting composites are strong as compared to the pure polymer matrix but a compromise has to be made on the flexibility or the maximum elongation of the samples, as the nanotubes make the material brittle.[33] At higher concentration of the MWCNTs, the entangled nanotubes as a result of cohesive forces cannot disperse homogeneously into the matrix and so result in the loss of film forming features and mechanical properties.

3.4. Thermogravimetric Analysis. Thermal behavior of the polymer matrix and its nanocomposites derived from both the systems is given in Figure 9. Thermal data showed improvement in the thermal stability of the materials with increasing nanotube contents, as the decomposition temperature increased from 437 °C for the matrix up to 453 °C for solution blending nanocomposites. However, in situ polymerized samples followed the same increasing trend with superior thermal stability and a decomposition temperature extending up to 568 °C with the addition of 10 wt % MWCNTs. This increase in thermal stability may be attributed to the addition of heat resistant reinforcement that made the composite thermally more stable and broadened the temperature range of the materials for various applications. The organic polymer matrix can withstand high temperature, but introduction of heat resistant MWCNTs further improves the thermal stability of the nanocomposites.

The increase in thermal stability was in accordance with the interaction between the polymer matrix and the reinforcement. Intimate mixing with better dispersion and the formation of a charge transfer complex between nanotubes and polymer chains gave rise to high temperature resistant materials as compared to the pure polymer matrix.

4. CONCLUSIONS

SEBS-g-PPy/MWCNTs conductive nanocomposites were successfully synthesized using solution blending and in situ polymerization techniques. Nanocomposites obtained from both the techniques were compared for their morphological, electrical, mechanical, and thermal profiles. MWCNTs were homogeneously distributed within the polymer matrix yielding compatibilized systems due to $\pi-\pi$ interactive forces. These cohesive forces increased interfacial interactions between PPy chains and nanotubes leading to overcome the stress transfer problems. Matrix−nanotubes interactions could be better observed for in situ polymerized in comparison to solution blending nanocomposites. Increased delocalization of π electrons gave improved electrical conductivity, adding a novel conducting material to the list of conductors. These interfacial interactions resulted in better thermo-mechanical characteristics of the designed nanocomposites; however, in situ polymerized nanomaterials were found to be more conductive and thermally resistant with higher tensile strength due to better interaction of the filler with the grafted copolymer. With an increase in nanotubes loading, stress bearing potential and stiffness of nanomaterials significantly improved as a result of ample dispersion and better interactions between the two phases in the nanocomposites.

In this study, the in situ polymerized technique proved to be a better method of fabrication due to ample dispersion of the nanotubes during PPy grafting on the backbone of the SEBS copolymer.

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Notes
The authors declare no competing financial interest.

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