

Mechanical, Thermal, and Electrical Conducting Properties of CNTs/Bio-Degradable Polymer Thin Films

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ABSTRACT: The objective of this study is to increase mechanical, thermal, and electrical properties of plasticizer free thermoplastic bio polymer, BIOPLAST GS 2189 (BP), a blend of poly lactic acid (PLA) and potato starch. This polymer is highly suitable for sheet molding, film processing; blown film extrusion and injection molding and fully biodegradable. Structural, mechanical, thermal, and electrical properties of these films were manipulated by reinforcement of multiwalled carbon nanotubes (CNTs) in BP. Thin films of various (1–5 wt %) percentages of CNTs/BP were prepared by using a high-speed spin coating technique. These as-prepared films are ~60–100 μm in thickness. The thickness measurements of these films were carried out using micrometry and optical microscopy. The maximum tensile strength (200%) and modulus (150%) was observed for 4 wt % loading of CNTs in BP as compared with the neat BP thin film. The X-ray diffraction results show that the addition of CNTs in BP increases the crystallinity of BP. Electrical conductivity of this film also increased by 48% as compared with the neat BP polymer films. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: biodegradable; composites; films; nanotubes; grapheme; fullerenes; synthesis; processing

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INTRODUCTION

Thin films of micrometer thickness are applicable to many technological fields including food packaging, industrial coating, solar cell, and electronics, etc. In such application it is important to evaluate the mechanical performance of thin film in order to understand its application to harsh conditions such as extreme loading and high temperature etc. Polymers such as polyethylene (PE), low density polyethylene (LDPE), and high density polyethylene (HDPE) are widely used in different packaging applications in the form of flexible films and laminates,¹ where thermal conductivity can be an important issue. Some components between conducting lines in the integrated electronic devices may require low thermal conductivity and high dielectric constant, which can be resolved by utilizing some smart thin films.² Thin films with some outstanding electrical properties can be applicable to microelectronic components and micro electro mechanical (MEMs) devices.^{3,4} For example, polystyrene films are widely used as a dielectric material in capacitors.⁵

Biodegradable polymers have recently attracted researcher's interest in polymer composite applications due to their low environmental impacts.⁶ However, in general biopolymers exhibits lower mechanical properties in terms of tensile/flexural strengths and thermal stability due to their hydrophilic nature, incompatibility with general polymers and biodegradability.⁷ The infusion of

nanoparticles as fillers biodegradable polymers can enhance mechanical, thermal, and electrical properties. Films from bio degradable potato starch has naturally lower tensile strength that can be improved by processing with clay and plasticizers.^{8,9} Researchers showed that nonconductive polyaniline biopolymer can be transformed to many biosensor applications by adding conductive nanoparticles such as CNTs and Chitosan.^{10,11} CNTs having a very high strength and high strain to failure results in high tensile strength with a small reduction in tensile ductility in the case of thermoplastics.¹² CNTs are also expected to have good thermal conductivity,¹³ electrical conductivity^{14,15} which may exert a number of reproducible properties to the biodegradable polymers. Numerous studies have shown that, infusion of CNTs into polymers contribute to the enhancement of flexural strength^{16,17} tensile strength,¹⁸ and toughness.¹⁹ In this research project, we have studied the reinforcement of various percentages of CNTs into biodegradable polymer films and tested for their thermal, mechanical, and electrical properties. These results have been compared with the neat systems to estimate the improvements.

EXPERIMENTAL

Materials

Bio polymers films were prepared from BP GS 2189 (Biotec, UK). This is a plasticizer free thermoplastic biobased polymer

synthesized from PLA and potato starch. The polymer was purchased in the form Biotecc, UK in granules/pallets form. According to suppliers specifications this polymer has a bulk density of 880–940 kg/m³ and Melt flow index (MFI) of 190°C at 15–40 g/10 min. The water content of this polymer is ~0.2 wt %, which is very low. The CNTs (purity >95%) were purchased from Nanostructured and Amorphous Materials, USA. The diameter, length, and true density of these CNTs are about 10 nm, 5–15 μm, 2.1 g/cm³, respectively. Chloroform (99%) was obtained from Sigma Aldrich, USA and used as a solvent to dissolve the polymer.

Preparation of CNTs Infused BP Films

BP was first dissolved in chloroform at room temperature at a ratio of 2:9 by weight. CNTs were dispersed in 45 mL chloroform using ultrasonic irradiation for 30 min. The polymer and CNTs in chloroform were then mixed together for another 30 min using ultrasonic irradiation in order to disperse CNTs uniformly. The composite polymer films were fabricated using spin coating technique at a ratio of 1:7 by weight of biopolymer to chloroform. Laurell spin processor (Model WS 650 SZ 6NPP) was used to produce uniform thin films of polymer and polymer/CNTs composite on a silicon wafer (100) substrate. The typical procedure is as follows: The solution was first deposited drop wise onto the steady substrate such that the solution covers the entire 5 inch wafer. Then the substrate was rotated at the preprogrammed speed. The speed of the shaft was gradually increased from 0 to 300 RPM in 5 min and reduced to 0 in 60 s. All the polymer films including neat and 1–5% CNTs reinforced polymer films were prepared using same conditions. These polymer films were further post cured at 60°C for 1 h to remove the chloroform contamination. The polymer films were then separated from the silicon substrate and stored in a desiccator for further testing. Thicknesses of as prepared polymer films were measured using optical microscope and cross checked using digital micrometer. The thickness of these films was in the range of 70–80 μm.

Characterization of BP Films

Rigaku Dmax 2000 X-Ray Diffractometer (XRD) was used to study the crystal structure of neat BP, CNTs, and CNTs infused BP thin film. The XRD measurements were carried out from 2 to 80° of two-theta degrees at a scanning rate of 2° min⁻¹ using Cu K_α radiation at 40 kV and 30 mA. Mettler Toledo TGA/SDTA 851 Thermo Gravimetric Analyzer (TGA) was used to study the thermal stability and solvent residue. For consistency we have used ~10–20 mg of the polymer film sample. These samples were heated from 25 to 800°C in nitrogen atmosphere at a heating rate of 10°C/min. Differential Scanning Calorimetry (DSC) measurements were carried out for neat and CNTs infused polymeric films using Mettler Toledo DSC 882 to study the effect of CNTs reinforcement on glass transition (T_g), melting point (T_m) and crystallization temperatures of thin films. A Zwick Roell Z 2.5 tensile testing machine was used to determine tensile strength, modulus and percentage of elongation of the neat and CNTs reinforced thin films. The samples were prepared according to the ASTM D882 standard test Method.²⁰ The electrical conductivity, I-V measurements were carried out using HP HEWLETT 4155A under dark and light conditions. This

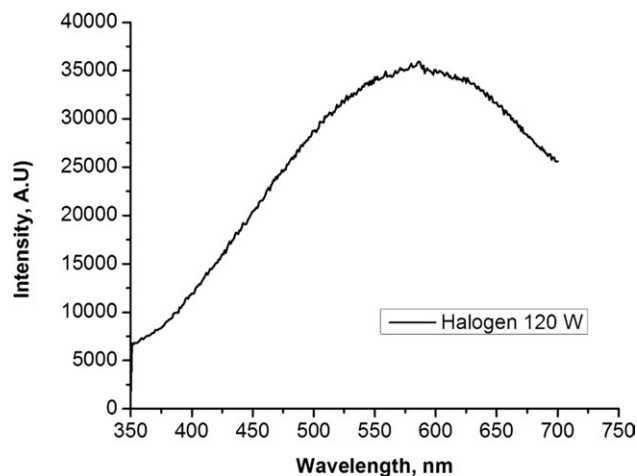


Figure 1. Emission spectra of 120 W halogen lamp sources.

measurement was carried out by two terminal contact resistance methods.²¹ A 120 W halogen light was used for this study and the spectrum wavelength is as shown in Figure 1. Dispersion of CNTs in chloroform was studied using a JEOL-2010 Transmission Electron Microscopy (TEM). A small drop of CNTs/ chloroform was placed on a copper grid and dried before placing on the TEM sample holder. A JEOL 5800 Scanning Electron Microscopy (SEM) was used to investigate the morphology of neat and CNTs reinforced films necked surface due to tensile test. For this test the tensile necked samples were cut carefully and surface was coated with Au-Pd using sputter coating method for 5 min to avoid the charging of the polymer during the test.

RESULTS AND DISCUSSION

X-Ray Analysis

Figure 2 shows the X-Ray diffraction patterns of (a) neat BP thin film, (b) 3 wt % CNTs/BP thin film, (c) 4 wt % CNTs/BP thin film, (d) 5 wt % CNTs BP thin films, and (e) as-received CNTs. Figure 2(a) clearly shows that the as-prepared neat polymer thin film is crystalline and the major peaks are observed at ~16, 19, 30° of 2θ. Since there is no joint committee of powder diffraction standards (JCPDS) is available in the literature for neat BP polymer we have used the XRD pattern of as-prepared BP polymer thin film as a standard to compare the other CNTs infused BP polymer thin films. The XRD spectrum of as-received CNTs shows [shown in Figure 2(e)] a CNTs peaks at ~26 and 43° of two theta and are assigned to (002), (110) planes of CNTs and all the peaks are matched with the JCPDF # 41-1487. Figure 2(b–d) shows the X-ray diffraction patterns of 3–5 wt % CNTs infused in BP polymer film. All the peaks are assigned to the neat BP polymer. The CNTs related peaks in the BP polymer composite are highly suppressed by the crystalline BP polymer peaks. Similar results were reported in the literature.^{22,23} We have also observed that the BP polymer relative XRD peak intensity at ~16° of 2θ is decreased with increase of CNTs concentration in the polymer. The peak at 16° of 2θ is related to the PLA²⁴ which is one of the major components of the BP polymer. The full width at half maximum (FWHM) of BP polymer films were measured for the peak at ~30° of two

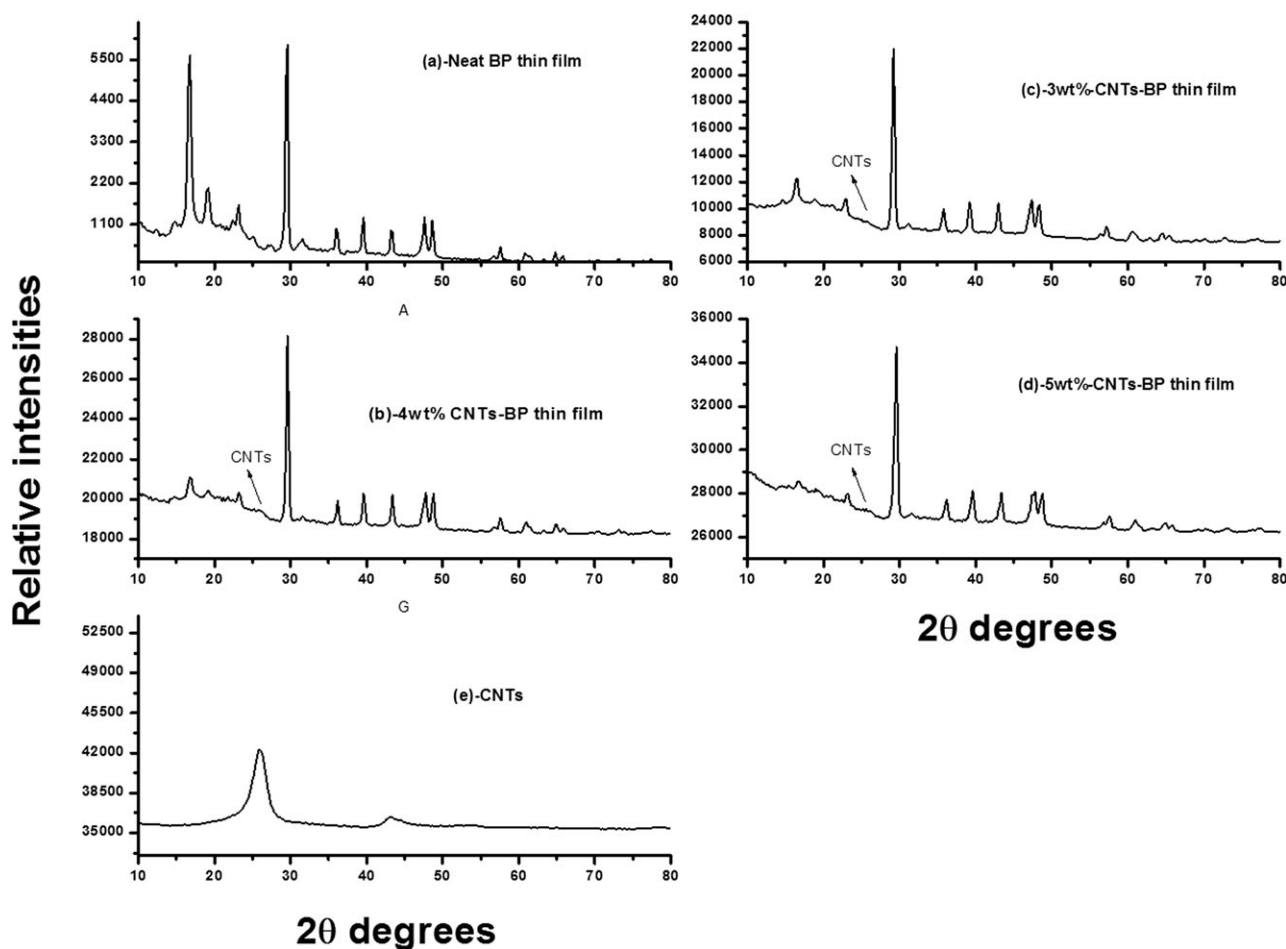


Figure 2. X-ray diffraction patterns of (a) neat BP film, (b) 3 wt % CNTs/ BP film, (c) 4 wt % CNTs/BP film, (d) 5 wt % CNTs BP thin films, and (e) as-received CNTs.

theta to compare the crystallinity of the polymer after and before CNTs infusion. These results show that the FWHM values decrease from 0.459 to 0.423 for 3 and 4 wt % CNTs infusion respectively as compared with the neat BP polymer film. Since the crystallinity of CNTs will not change, the increase in crystallinity of the composite is actually due to increase in crystallinity of BP polymer. In this case the BP polymer is a semi-crystalline polymer and addition of CNTs to the polymer provides a large interface between the CNTs and the polymer, which, in turn, creates very suitable conditions for the nucleation and crystallization process that takes place during the thin film processing from the solution.^{25–27} In addition, the presence of CNTs restricts the entanglement of polymer chains to a lesser extent and allows some degree of orderly orientation during film formation giving rise to increased crystallinity. It is also shown that CNTs nucleate crystallization and accordingly bulk morphological changes take place in the polymer due to such crystallization.²⁵ We have also observed that the higher concentration (5 wt %) of CNTs infusion in BP increases the FWHM to 0.482. This clearly suggests that the crystallinity of the neat BP polymer increased up to 4 wt % loading of CNT and starts decreasing from 5 wt % CNTs infusion in BP polymer thin film. The possible reason for this may be the high agglomeration

of CNTs in the system where the particle–particle interaction is more than the particle–polymer interaction.

Thermal Analysis

Thermogravimetric analysis (TGA) of (a) neat BP thin film, (b) 3 wt % CNTs/BP thin film, (c) 4 wt % CNTs/BP thin film, (d) 5 wt % CNTs BP thin films were shown in Figure 3. The figure inset shown in Figure 3 is the derivative curves of the percentage weight loss versus temperature. In the present TGA analysis the 50% weight loss is considered as a decomposition temperature of the polymer. Neat BP thin film sample shows a decomposition at 330°C whereas, the decomposition for 4 and 5 wt % CNTs reinforced BP films occur at 335 and 340°C, respectively. This indicates that 3–5 wt % of CNTs reinforced films are thermally more stable than neat BP thin film. The residue left in the pan is also estimated at 800°C and found that the neat BP polymer and 3–5 wt % infused CNTs sample residues are ~7.3, 10.77, 12.3, and 14.4 wt %, respectively. These results indicate that the final residue left in the pan for 3 wt % CNTs infused polymer is ~3.5 wt %, for 4 wt % CNTs infused polymer is 5 wt % and for 5 wt % CNTs infused polymer is ~7 wt %. The estimated results from residue calculations are within the error limits of actually added CNTs in the BP polymer. These results

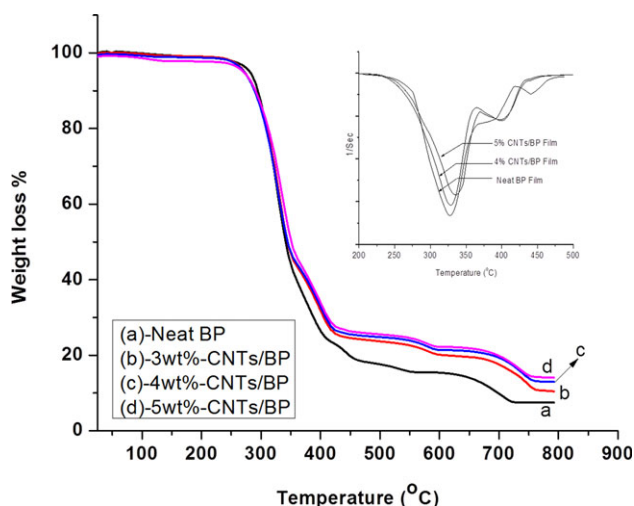


Figure 3. TGA graph of (a) neat BP film, (b) 3 wt % CNTs/ BP film, (c) 4 wt % CNTs/BP film, (d) 5 wt % CNTs BP films. Inset: Derivative curves of weight loss versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are in good agreement with our previous results on similar systems.^{22,28,29}

Differential Scanning Calorimetry (DSC) was performed to measure the glass transition temperature (T_g) and melting temperature (T_m) of BP polymer film before and after addition of 3–5 wt % of CNTs. In this study the T_g s were measured as the inflection points of the heat flow curves.^{30,31} Figure 4 shows the DSC results of (a) neat BP polymer film, (b) 3 wt % CNTs infused BP polymer film, (c) 4 wt % CNTs infused BP polymer film, and (d) 5 wt % CNTs infused BP polymer film. These results indicate that the T_g s increased from $\sim 58^\circ\text{C}$ (neat BP polymer) to 75°C (4 wt % CNTs infused BP polymer film). Whereas the T_g for 5 wt % CNTs infused BP polymer decreased to 55°C . The increase in T_g is due to the presence of CNTs,

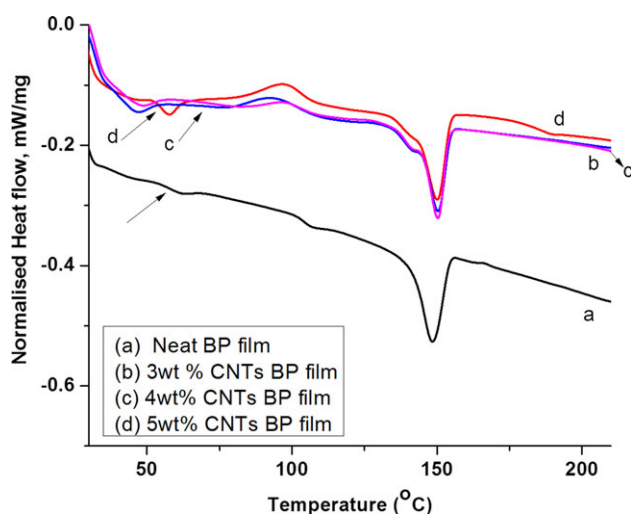


Figure 4. DSC curves of (a) neat BP film, (b) 3 wt % CNTs/ BP film, (c) 4 wt % CNTs/BP film, (d) 5 wt % CNTs BP films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

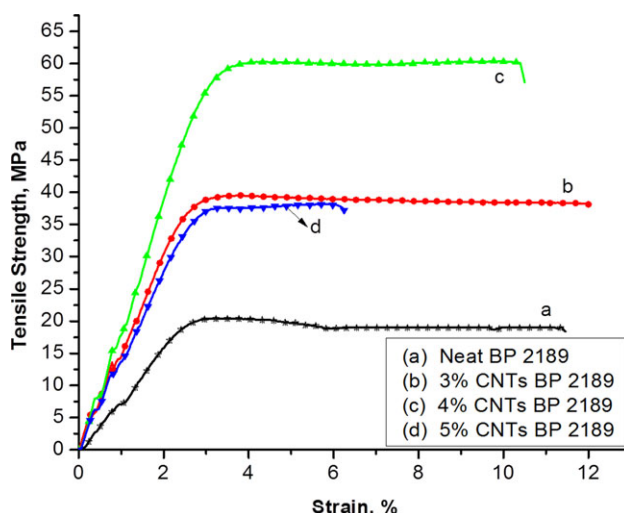


Figure 5. Tensile stress–strain curves of (a) neat BP film, (b) 3 wt % CNTs/BP film, (c) 4 wt % CNTs/BP film, (d) 5 wt % CNTs BP films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which may have imposed restrictions in molecular mobility or decreasing free volume of the polymer. As the temperature of the melt is lowered, the free volume would be reduced until there would not be enough free space to allow molecular motion. With the infusion of CNTs, this free space is evidently further reduced.^{32,33} The decrease in T_g for 5 wt % CNTs infusion may be due to the agglomeration of CNTs in the polymer. This may act as impurity in the system where particle–particle interaction is dominated than the particles–polymer interaction. The T_m measured from the DSC curves for neat BP polymer and CNTs infused BP polymer are ~ 148 and 150°C . The heat of enthalpy measured from these melting curves also show the (15–17 J/g) 2 J/g increase in enthalpy. These results show that there is a slight increase in T_m and heat of enthalpy for CNTs infused BP polymer film as compared with the neat BP polymer film. This indicates that the crystallinities of CNTs infused BP polymer films are higher than the neat BP polymer film.

Tensile Properties

Figure 5 presents tensile strength and elongation of (a) neat BP polymer film, (b) 3 wt % CNTs infused BP polymer film, (c) 4 wt % CNTs infused BP polymer film, and (d) 5 wt % CNTs infused BP polymer film. It is clearly seen from the figure that ultimate tensile strength and modulus increase with gradual increase in CNTs up to 4 wt %. The tensile strength and modulus estimated for neat BP polymer was 20 ± 2 MPa and 0.77 ± 0.02 GPa, respectively. These values are close to the reported values³⁴ and also comparable with conventional nonbiodegradable³⁵ and degradable polymer composites.^{36,37} The tensile strength and modulus measured for 4 wt % infused CNTs BP polymer film is increased to 60 ± 5 MPa (200% increase) and 2.0 ± 0.2 GPa (160% increase) respectively as compared with the neat BP polymer film. Whereas the increase of CNTs concentration to 5 wt % drastically decrease the tensile strength (38 ± 3 MPa) and Young's modulus (1.6 ± 0.18 GPa), respectively. These tensile test results clearly suggest that the increase in

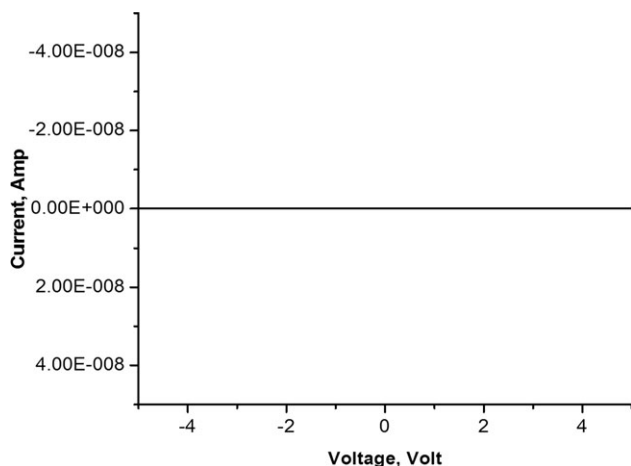


Figure 6. Voltage current behavior of the BP films at dark condition.

tensile strength can be correlated with the increase in crystallinity of 4 wt % CNTs addition in the BP polymer film. These results are consistent with the increase of crystallinity estimated from XRD and DSC results. These results are also very well in agreement with our previous observations.^{22,29}

Electrical Properties

I-*V* characteristics of neat BP polymer film and CNTs reinforced thin films under dark and light conditions are shown in Figures 6 and 7, respectively. In the dark condition almost zero current was observed from the films no matter how the CNTs reinforcement was added in the film, but a significant increase in electrical current was observed when the films were tested under halogen light. It is believed that, the increase in current under light is due to a combined effect of photo resistance/luminescence and reinforcement of CNTs. Under light, changes in electrical current were nonetheless very insignificant with neat and 3 wt % CNTs reinforced films, but a linear and progressive change in current with proportional to applied voltage were

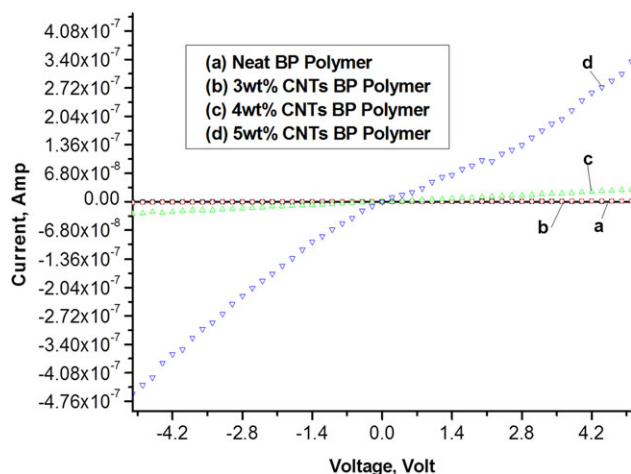


Figure 7. Voltage-current behavior of (a) neat BP film, (b) 3 wt % CNTs/ BP film, (c) 4 wt % CNTs/BP film, (d) 5 wt % CNTs BP films under photo luminescence. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

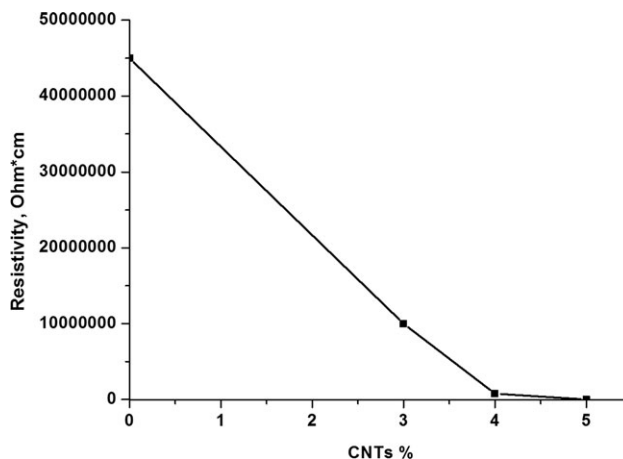


Figure 8. Resistivity of BP film with various percentages of CNTs loading.

observed with 4 and 5 wt % CNTs reinforced films. Although 5 wt % of CNTs infused BP films represented a semiohmic relationship, electrical resistance for each film was measured from the virtually considered slope of each *I*-*V* characteristic plot by assuming simple ohmic relationship between current and voltage. The following equation is used:

$$R = V/I \quad (1)$$

Where, *R* is the resistance, *V* is the applied voltage, and *I* is the current found. Using this resistance, one of the material properties, one can measure resistivity using the following equation:

$$\rho = RA/L \quad (2)$$

Where, *L* and *A* are sample geometry.

The calculated resistivity for thin films with various CNTs loadings are plotted in Figure 8 and summarized in Table I. It is shown in the figure that, the resistivity of neat polymer as comparable with reported value³⁸ is significantly reduced at 4 wt % CNTs infused films. The resistivity of 5 wt % of CNTs reinforced film (with thickness of 40 μm) was found as $50 \times 10^3 \Omega\cdot\text{cm}$. This is clearly a semiconductive in nature and comparable with silicon chips.³⁹ Similarly the films with 4 wt % of CNTs which had the best result in tensile performance also fall in the semiconductor category. Nevertheless, the actual experiment is slightly different from standard test method,²⁸ it reveals

Table I. Resistivity of BP Thin Films with Various Percentages of CNTs Loading

Sample	Thickness μm	Resistivity ohm*cm
Neat BP thin film	90	4.5×10^7
3 wt % CNTs infused BP	50	1×10^7
4 wt % CNTs infused BP	40	8×10^5
5 wt % CNTs infused BP	50	5×10^4

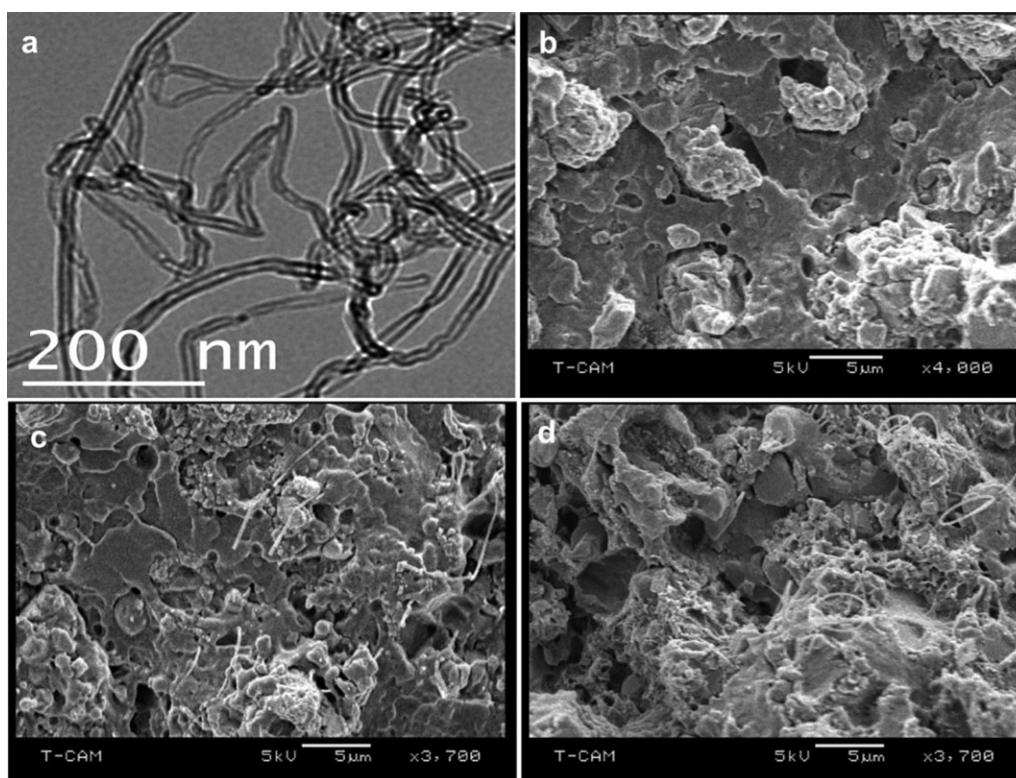


Figure 9. Electron microscopic analyses: (a) TEM micrograph of CNTs, (b) fracture surfaces of neat BP film (c) fracture surface of 4 wt % of CNTs BP film (d) fracture surface of 5 wt% of CNTs BP film.

the photoconductive nature of the CNTs infused films which can be applicable to the photo detection, flexible, and light weight conducting film and photovoltaic etc. These flexible films may be potentially applicable to curved display or solar cells technology,⁴⁰ which may replenish the alternative to petroleum-based solar cells. However, in order for a successful implantation to solar cell back sheet, some other physical properties of these films such as lower thermal conductivity and thermal stability need to be studied.

SEM Analysis

Figure 9 shows electron microscopic analysis of (a) TEM micrograph of CNTs (b) fracture surfaces of neat BP polymer thin film (c) 4 wt % of CNTs BP thin film (d) 5 wt % of CNTs BP polymer thin film. The Figure 9(a) clearly indicates that the CNTs are very well separated in the chloroform and shows minimum entanglement. These CNTs are ~10 nm in diameter and few microns in length. The tensile failure plane of the BP films is observed in the thickness direction. In this analysis almost smooth failure surface was observed from neat BP thin film [Figure 8(b)], whereas for 4 wt % of CNTs-infused BP films represents some randomly spaced nanotubes without any entanglement which is a clear indication of better dispersion. The BP film with 5 wt % of CNTs shows high agglomeration of CNTs in BP thin films. These results are also consistency with the mechanical properties, where the tensile properties are highest for 4 wt % of CNTs in BP thin film when compared with neat BP polymer and the 5 wt % of CNTs infused BP thin films.

CONCLUSIONS

In this study The CNTs were infused in bio-based thermoplastic polymer thin films through as solution spin coating technique. In this study we have shown an increase in crystallinity and as well as thermal stability of the neat BP polymer films with the addition of CNTs up to 4 wt %. Essentially, tensile strength of the BP polymer film has increased up to 200% with the addition of 4 wt % of CNTs. In general most of the biodegradable polymers are dielectric in nature. In this study we have also able to show 99.88% reduction of electrical resistivity of the biodegradable films under photoluminescence. Since this is a naturally crystalline polymer, improvement of such thermal and electrical properties can lead this film into solar cell applications.

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