PREPARATION AND CHARACTERIZATION OF LDPE/CNT

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Abstract— LDPE/CNT composite with 10 wt% CNT content was analyzed under SEM and TEM which resulted uniform CNT dispersion in LDPE matrix.Electrical tests showed enhanced conductivity achievedfor LDPE/CNT composites with CNT addition and frequency raise. DC of composites increased with increasing CNT content up to 3 wt%. Young's modulus and tensile strengthof composites augmented by 96% and 60, when nanotube addition reached 10 wt%. DSC of LDPE/CNT composites improved in crystalline contents compared with pure LDPE resulted into enhanced LDPE/CNT composites thermal stability and hardness. LDPE thermal decomposition was shifted by 87°C on addition of 10 wt% CNT.

Keywords— Low Density Polyethylene; Carbon Nanotube; Nanocomposites.

I. INTRODUCTION

Carbon nanotube (CNT) have paid attention on interest as reinforcing fillers due to its outstanding mechanical and thermal properties [1], but it is also regarded as ultimate fillers for some advanced applications [2]. CNTs hold an extremely high elastic modulus about 1 TPa, comparable to that of diamond (1.2 TPa) and describe strengths of 10-100 times that of strongest steel [3]. In addition, they exhibit electrical conductivity as high as 10^5-10^7 S/m [4] and can convert an insulating polymer into a conducting composite at very low content due to their extraordinarily high aspect ratio [5].

The introduction of nanofillers like CNTs in polymer fibers can direct multifunctional high-performance materials which bring together high strength with electrical conductivity [6]. The keys to achieve maximum performances from composite are to obtain a homogeneous distribution of nanoparticles within polymer matrix, and to have best nanoparticle polymer adhesion, critical for load transfer from matrix to particle [7, 8]. The present research looked into both dependence of CNT content on mechanical, electrical, thermal properties and CNT dispersion/alignment in low density polyethylene (LDPE)/CNT compounds. It was also studied the effects of CNT addition on the improvement of tensile and impact properties of CNTs/LDPE compounds.

II. EXPERIMENTAL

2.1 Materials and Sample Preparation

Low density polyethylene (LDPE) as granules with grade LH0075, density of 0.921 g. cm^{-3} and a MFI of 0.89 g.$(10\ min)^{-1}$, was obtained from the Bandar Imam Petrochemical Company (Iran).Sample preparation LDPE- CNTpowder (CNT) composites were prepared by melt-blending commercial LDPE with CNTpowder in a Brabender mixer. CNT powder was supplied by Nanostructruedand Amorphous Materials Inc. Mixing time was set to 15 min at 120°C to disperse CNT powder into LDPE matrix more uniformly and to avoid thermal degradation of LDPE,LDPE/CNTcompounds were pre-heated for 5 min, and then compression molded according to ASTM D-1928 into sheets (with dimensions of 150×150×2 mm) at 150 ºC under a pressure of 10MPa for 3 min.

2.2 Tensile strength (TS) and Elongation at Break (EB)

TS and EB were determined according to ASTM D-638-03-2003 on an Instron model 4411 testing machine (UK). The test procedure was carried out at a cross head speed of 50 mm/min and room temperature conditions.

2.3 Thermomechanical Analysis (TMA)

TMA of LDPE and its composites was performed with a SETARAM thermomechanical analyzer in penetration mode with 5 mN load. The temperature studied ranged from 30 to 90°C with a heating rate of $3^{\circ}C min^{-1}$.

2.4 Hardness and Impact Strength Tests

The Rockwell hardness test was carried out according to ASTM D785 using HA-101 Rockwell Automatic Digital Hardness Tester. The Rockwell hardness scale used was L (minor load 10 kg, major load 60 kg and Indentor diameter 6.350 mm). The impact strength of composites was measured using an Izod impact testing machine XJU-2.75 supplied by Chengde Testing Instruments Co. Ltd, China. The Izod impact tests were performed at an impact rate of 3.5 m/s using acute notched specimens (notch depth: about

2.5 mm) at a room temperature of 208C. All properties are average value of 4-6 specimens.

2.5 Electrical Properties

Samples for dielectric and conductivity measurements were coated with silver paint prior to measurements. Two metallic electrodes were then connected to samples using silver wires. The Dielectric constant (DC) and resistivity of samples were measured by employing an impedance analyzer (Agilent model 4294) in frequency range of 40–10^7 Hz at room temperature. The DC was determined using an AndoTRS-10T and 6303 dielectric loss measurement system (ANDO Electric Co., Japan and FRIBORG Co. Sweden) in accordance with ASTM D-149 and 150 using an Ando insulation resistance set at 23°C and a frequency of 1 MHz.

2.6 Thermogravimetric Analysis (TGA)

TGA of samples was carried out using Shimadzu Analyzer TGA-50. The TGA test was performed under nitrogen environment and the rate of heating was 10 °C/min.

2.7 Differential Scanning Calorimetry (DSC)

DSC of samples was carried out on a Shimadzu DSC-50 thermal analysis system (Shimadzu, Kyoto, Japan). The test was performed under nitrogen environment and rate of heating of 10°C/min. The specific heat capacity, melting temperature, degree of crystallization, and decomposition temperature of samples were determined from DSC thermograms by ASTM E1269 method.

2.8 Scanning Electron Microscope (SEM)

The morphology of fractured surfaces of specimens was investigated with a JEOL JSM-6335F SEM. The specimens were fractured after cooling in liquid nitrogen, and fractured surfaces were sputter-coated with gold under argon. The electron micrographs were taken using an acceleration voltage of 5.0 kV.

2.9 Transmission Electron Microscopy (TEM)

The electron microstructure of the composite was studied by means of the conventional and high resolution transmission electron microscopy (HRTEM). The conventional TEM studies were performed on a Philips CM12 transmission electron microscope, operating at 120 kV. The HRTEM investigations were performed on a JEOL JEM3000F transmission electron microscope, operating at 300 kV. Thin TEM samples were prepared by slicing the bulk material on a microtome. The curvature of a nanotube segment is defined as 1/R, where R is the radius of a corresponding circle. R is determined from three points along 20 nm long tube segment by means of the image analysis system ‘‘micrograph’’. At least 70 CNTs were examined.

III. RESULTS AND DISCUSSION

3.1. Mechanical Properties

The stress/strain curves of CNT/LDPE composounds with varying tube contents are shown in Figure 1. It is displayed that CNT addition (0-10 wt%) to LDPE affected on increasing chain rigidity and enhanced stress values of compounds. Whereas, CNT addition (0-10 wt%) to LDPE decreased strain values and compound with 10 wt% CNT content broke at 17% strain values. It is understandable that, due to curving and coiling nature of CNTs, strong mechanical interlocking among nanotubes appeared and promoted reinforcement in polymer matrix which restricted chain mobility and made compounds less flexible against stress.

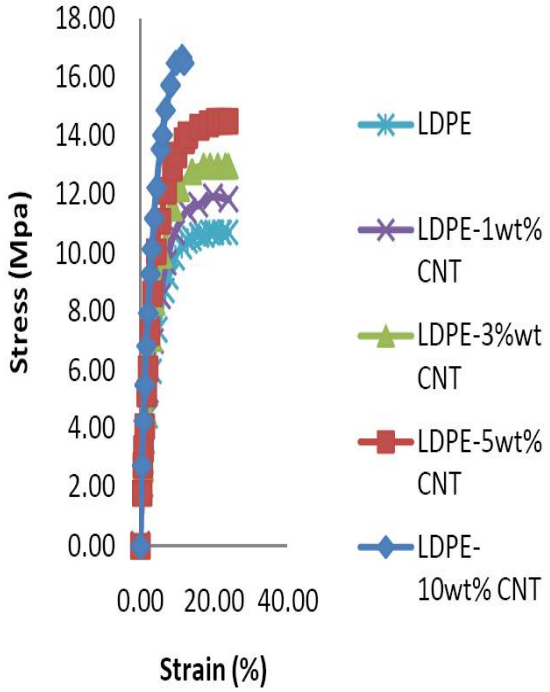


Figure1 LDPE and LDPE/CNTs Stress/strain of composites with varying CNT content

Figure 2 shows elastic moduli of LDPE, as function of CNT percentages. The augmentation of mechanical properties of composites demands a high degree of load transfer between matrix and nanotubes. If interfacial adhesion between phases is weak, nanotubes behave as holes or nanostructured flaws, introducing local stress concentrations, and benefits of CNT properties are lost [9-11]. The nanotubes must be well dispersed. In case of poor dispersion, they will fail by separation of bundle rather than by failure of nanotube itself, resulting in significantly decreased strength [12-15]. Strength in composites is a complicated issue involving load transfer, stress concentrations and defect distribution, especially in case of fibers. The data suggest that significant property enhancement, at low CNT percentages (0-10 wt%), could be attributed to highly

dispersed and well aligned nanotubes and/or good adhesion between nanotubes and polymer matrix.

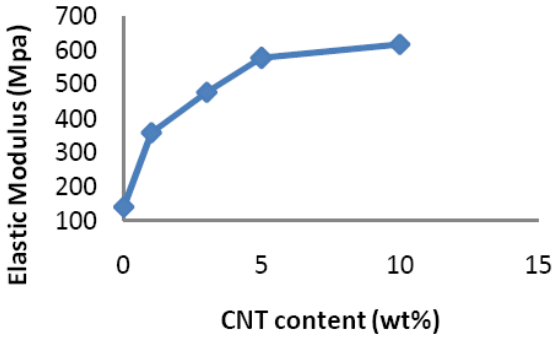


Figure 2 LDPE and LDPE/CNTs elastic modulus asa function of CNT content

Figure 3presents storage modulus of LDPE and LDPE/CNT composites as a function of temperature. LDPE storage modulus and its compositesreduced with temperature increase. Storage modulus of LDPE/CNT composites tended to augment with increasing CNT content. This implied effectiveness of CNTs reinforcing effect. The storage modulus maximum value wasgained with 10wt% CNT content. Figure3displays LDPE and its compositestangent delta versus temperature. A broad peak located at -20°C for LDPE, and -10°C for LDPE/CNT composites that can be attributed to LDPE glass transition temperature (*T*g). LDPE molecular chains are frozen below glass transition temperature and LDPE chains mobility increases above *T*g.

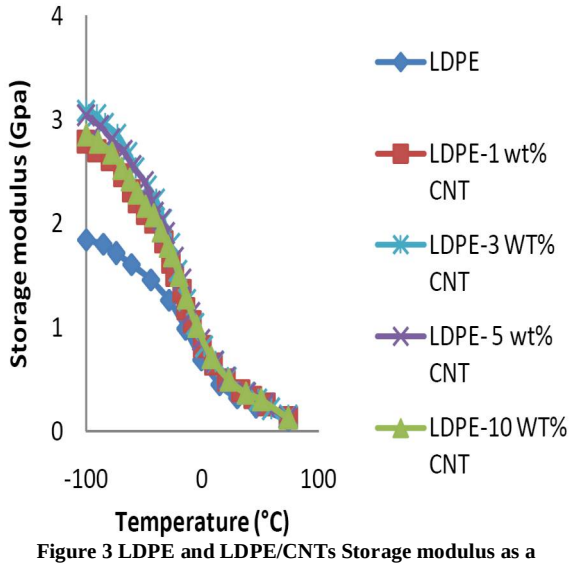


Figure 3 LDPE and LDPE/CNTs Storage modulus as a function of temperature

Figure 4 displays LDPE loss modulus as function of temperature and CNT content. Figure 4 presents tangent delta of pure LDPE and its composites versus temperature. A wide peak placed at ~--16°C for LDPE, and ~-6°C for LDPE/CNT composites, can be attributed to LDPE glass transition temperature (*T*g). Below glass transitiontemperature, LDPE molecular chains were frozen and above*T*g, LDPE chains mobility increased.

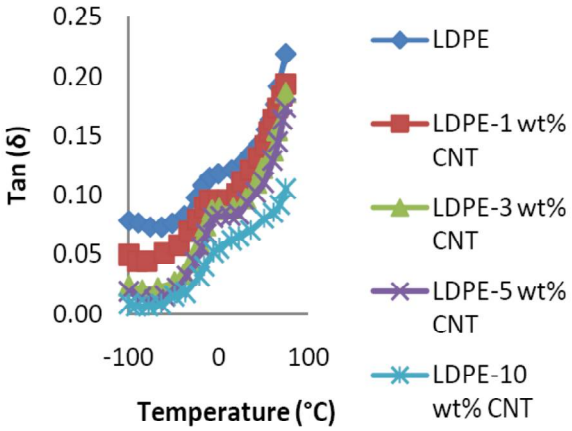


Figure 4 LDPE and LDPE/CNTs loss modulus as a function of temperature

It was studied that there is a moderate enhancement of Young's modulus when CNT content changes from 0 to 10wt%, as shown in Figure5. The structural change of composites with increasing CNT content is responsible for this, because when CNT content was increased to 5 wt%, a continuous CNT network is formed throughout polymer matrix, as confirmed by rheological tests as discussed earlier [15-17]. It is understandable that, due to curving and coiling nature of CNTs, strong mechanical interlocking among nanotubes appears and promotes reinforcement.

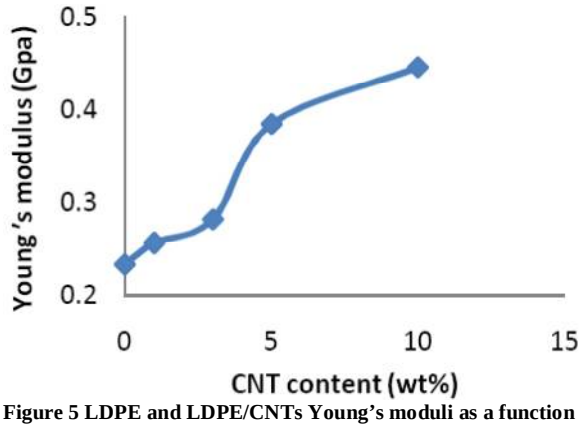


Figure 5 LDPE and LDPE/CNTs Young's moduli as a function of CNTs content

Figure 6 displays LDPE TMA and its composites. TMA measures finite changes in a sample height as it undergoes higher temperature. Displacement for LDPE and its composites augments with temperature increase in temperature investigated range which was related to thermal expansion of polymer matrix and associated with LDPE macromolecular chains movement. LDPE/CNT composites displacement inclined to decrease with increasing CNT content at various temperatures, indicating that CNT introduction blocks mobility of LDPE macromolecules to some degree. This blocking effect is particularly marked for LDPE/CNT composite with

10 wt% where CNT network formed throughout entire matrix of composite. CNTs curving and coiling nature acted an important role in composite modulus enhancement and provided network throughout polymeric matrix which promoted CNTs reinforcement [1-5].

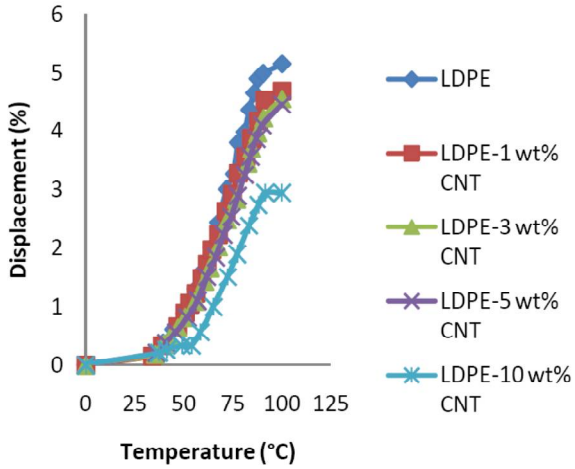


Figure 6 LDPE and LDPE/CNT compositesTMA

The Izod impact strength of compositesispresented in Figure 7. The impact strength of acute notched specimens is augmented with increase of CNT content.Figures 7 shows that CNTs reinforced LDPE matrix due to its large aspect ratio and high stiffness.The reason possibly attributed toCNTs entrance into polymer defects and changed strain concentration of matrix, and absorbed a lot of energy, so impact strength of acute notched specimens increased and consequently,CNT addition increasedLDPE toughness.

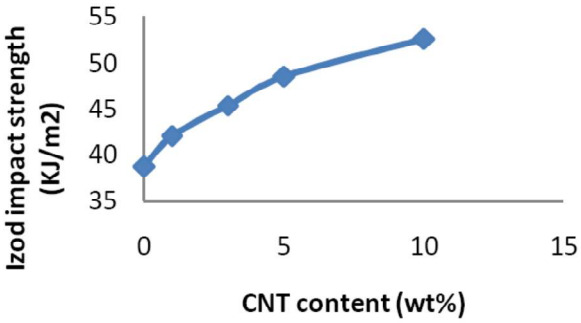


Figure 7 LDPE Izod impact strength changes with variousCNTs content

The CNT/LDPE composites hardness measured with Shore-D hardness test shown in Figure 8. A significant hardness augmentationwasexamined by extra CNTs (0-10 wt%) in LDPE matrix. Compared to pure LDPE matrix,LDPE/CNTs bulk composites brought a considerablehardness amendment from 57 to 68.5 Mpa. LDPE/CNT hardness with 10 wt% CNTwas about 1.2 times higher than that of LDPE without CNTs. It was studied, when polymer/CNTs compositeswere formulated by microstructural level process, enormous contact area which provided a strong physical bonding amongCNTs and polymer matrix, which fixed homogeneous CNTs dispersion as well as high interfacial strength [18, 19].

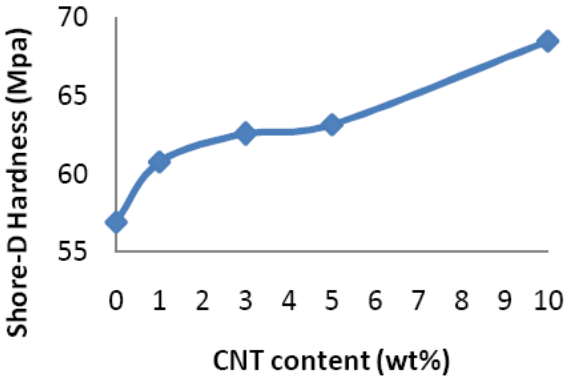


Figure 8 LDPE/CNTs composites hardness with different CNT contents

3.2 Electrical Properties

Figure9presents DC changes with various CNT contents for LDPE/CNT composites. The DC of LDPE/CNT compositesaugmented slightly with increasing CNT content up to 3wt%. Above this content, DC of compositesenhanced sharply. The DC of LDPE/5wt%CNTcompositewasfour orders of magnitude higher than that of LDPE/3wt%CNT. No sharp increase in DC was observed even CNT content reached10wt%. In most polymer/CNTcomposites, bundle structure is formed resulting from agglomeration of filler particles at vicinity of percolation threshold. Such a structure is favorable at relatively lower filler volume fraction [20]. In this respect, it becomes apparent that fillers of LDPE/CNT composites containing lower CNT weight content are dispersed as isolated agglomerates in the matrix rather than a network of linked particles. Figure15 and 16 show typical SEM micrograph of fracture surface of LDPE/10wt% CNT composite. CNTs are detected as white spots dispersed individually throughout polymer matrix and a network of CNT particles was formed within matrix of composite, consequently, leading to anintense increase in dielectric constant.

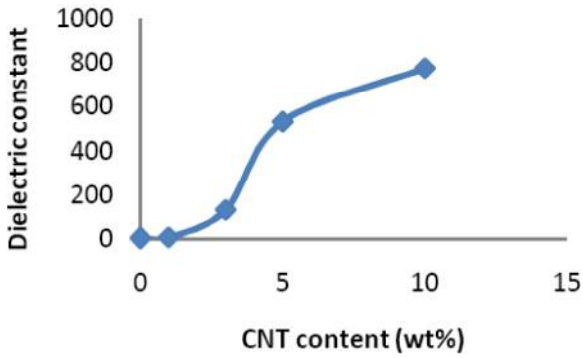


Figure 9 LDPE/CNT compositesDC as a function of CNT content

Figure10 shows DC dependence on LDPE/CNT compositesfrequency in range of 10^2–10^7 Hz. The

pure LDPEDC and its composites with low CNT content (1 wt%)was independent of frequency. However, as CNT content reached 3 wt%, a noticeable DC dependence on frequency was observed. The frequency dependence of DC of materials having percolation threshold which can be expressed as[21]:

$$DC \propto \omega^{-\mu} \quad (1)$$

Where $\omega = 2\pi f$ and μ are critical exponent. The μ for LDPE/ 10wt% CNT compositewas determined to be 0.26 [10].

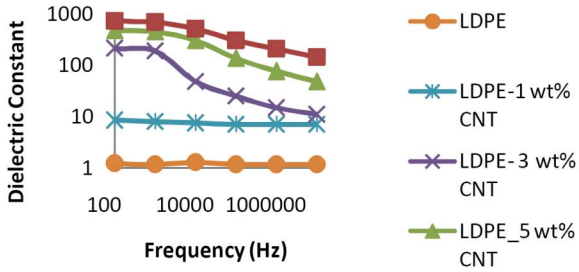


Figure 10 LDPE and LDPE/CNT composites as a function of frequency

Figure 11 shows conductivity dependence of LDPE/CNT composites and frequency at room temperature. Figure 11 reveals that conductivity increased with CNT content (0-10 wt%) and frequency range of $1–10^7$ Hz.The LDPE conductivity and its compositesaugmented almost linearly with frequency. However, conductivity of LDPE/10 wt% CNT composite was frequency independent below a critical value (i.e. < 20Hz) which was characteristic of a nondielectric material with a pronounced direct current.

The dependence of conductivity, conductivity, on frequency of dielectric materials can be described by [21]:

$$\text{conductivity} \propto \omega^{\nu} \quad (2)$$

where ω is$\omega = 2\pi f$ and ν value for LDPE/10wt% CNT compositewas determined to be ~0.66 at higher frequency regime. The low ν value is associated with polarization effect between CNT clusters [22-24]. This condition was almost obeyed for LDPE/10wt% CNT composite, indicating that this compositewas confined in percolation regime, facilitating formation of CNT network within LDPE matrix. The conductivity did not have a significant increment with increasing f <20 HZ, which suggested that electrical conducting networks were not formed in LDPE/CNT composites. Specifically, at low CNT concentration, CNT are individually dispersed within polymeric matrix. This leads to composites having a low electrical conductivity. Above f_{CNT}>20, increase in conductivity is very remarkable. Such a marked increase in conductivity values proposed there was a critical concentration, known also as percolation threshold of fillers(f_c) [10].Definitely, when $f_{CNT}$was above the f_c, electrons could easily transfer between CNT through a tunnel effect and an Ohmic contact because distance between CNT was very short and electrical conducting networks were formed in LDPE/CNT composites.

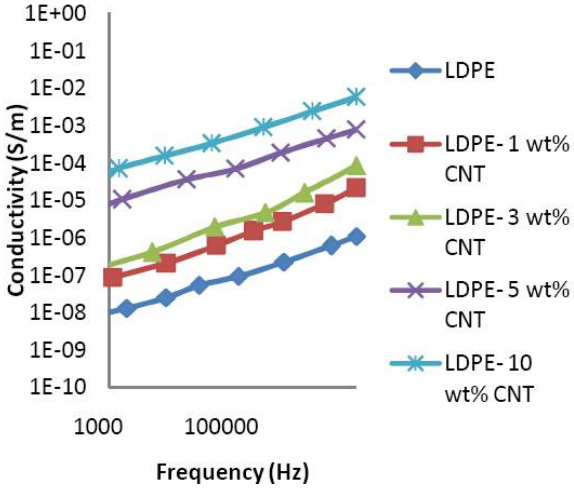


Figure 11 LDPE and LDPE/CNT composites conductivity as a function of frequency

Figure12expressesconductivity values of LDPE/CNTs, as a function of CNT content. Percolation theory deals with effect of varying in a random system and number of interconnections present [9, 10]. In this case filler bundles began to connect each other to form a filler network throughout entire composite, resulting in several orders of magnitude increased in electrical conductivity of composites. The transition from isolated bundle to connected network of conducting filler was referred to as percolation transition [10-17]. However, It wasemphasized that electrical conductivity of LDPE, soon after percolation, resultedincrease of about nine orders of magnitude at nanotube loadings (0-10 wt%).

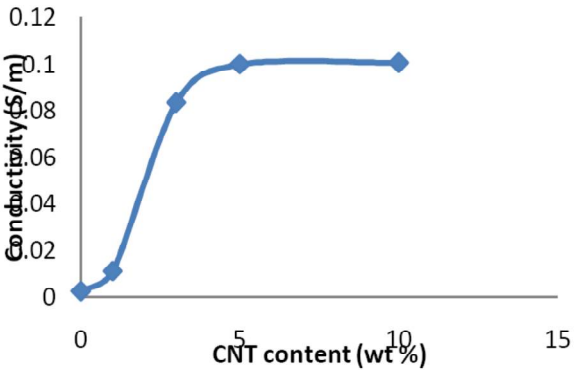


Figure12 LDPE electrical conductivity as function of CNT content

3.3 Thermal Properties

Figure 13 shows TGA of LDPE and its composites with different CNT contents (0-10 wt%). It is revealed that LDPE had thermal stability up to 350°C

and suddenly lossed 90% weight. This was attributed to complete breakdown of polymeric backbone. However, CNT addition to LDPE (0-10 wt%) shifted weight loss initiation temperature to higher temperature, i.e., 437°C for LDPE/CNT10 wt%, showing better thermal stability after CNTaddition. This was attributed to CNT reinforcing effecton LDPE and LDPE crystallization increased as observed by DSC [11-14].

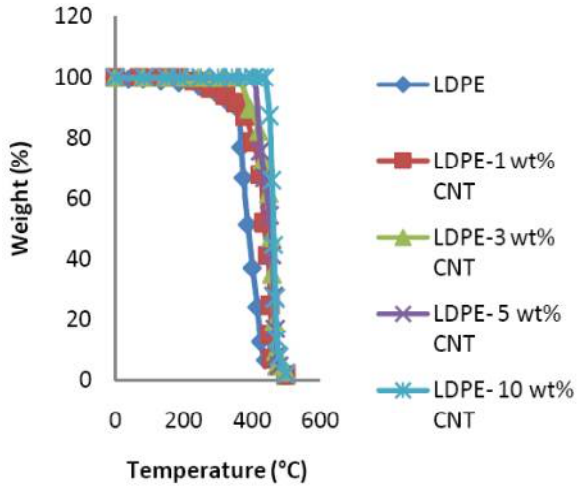


Figure13 TGA of LDPE and LDPE/CNT composites

Thermal analysis (DSC) of LDPE and LDPE/10wt% CNT are shown in Figure 14. In case of 3LDPE/10wt%CNT, slope of beginning stage of endotherm peak for LDPE/10wt% CNT looks a slight change and maximum peaks are same at 108^{o}C, which impliesLDPE molecular weightwas not changed during CNT addition and area under DSC curve presents bigger than pure LDPE which reveals increasing of LDPE crystallization region with CNT addition..

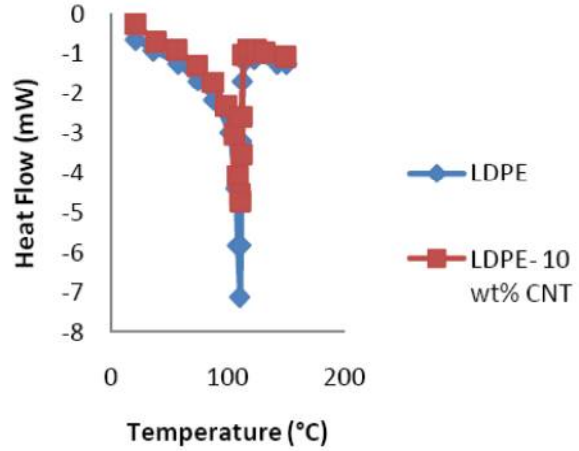


Figure14 DSCof LDPE andLDPE/10wt%CNT

3.4 Characterization

Figure15shows morphology of CNT/LDPE composite with different magnifying values which presents typical SEM micrograph of fracture surface of LDPE/10wt% CNT composite. It is obvious to see from images that most CNT are uniformly dispersed within LDPE/CNT matrix and there is no CNT agglomeration at fractured cross-surfaces of LDPE/CNT composites. CNTs are observed as white spots dispersed independently throughout matrix which, with further increasing CNT content, a network of CNT particles is gradually formed within matrix of composite, consequently, lead to a sharp increase in DC and conductivity for polymer composite. This study displays that CNT dispersed homogeneity among LDPE matrix and caused effective influences on electrical, mechanical and thermal properties of composite samples which are justified by different experiments have been done in this study.

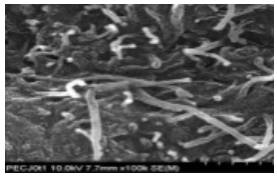


Figure15SEMof LDPE/10 wt%CNT

The electron micrograph of LDPE/ CNT with 10 wt% content is presented in Figure16.Itis clear that CNTs are consistently dispersed in matrix, but most of them are curved.Figure16displays a high resolution TEM picture of CNTs in LDPE. It is seen from Figure 16 that CNTs and matrix form close interfaces without gaps. This implies a good wetting of CNTs. The mismatch in coefficients of thermal expansion between CNT and polymer leads to a compressive radial residual stress along tube when polymer is cooled down from its melt [12-18]. However, no tube collapse in this study was observed, signifying that stress was below critical resisting threshold of CNTs.

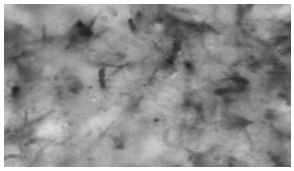


Figure 16 TEMof LDPE/CNT 10 wt%

CONCLUSION

This study revealed that 10 wt% CNTs addition to LDPE increased young's modulus and TS of composites by 96% and 60%, respectively. However, superior property of high tensile modulus of CNTs has not been fully utilized in composites because of curving and coiling nature of nanotubes. It can be concluded from SEM and TEM that CNTs have some dispersion and orientation in LDPE matrix. Meanwhile, mechanical properties of composites increased when a suitable CNTs level was present and compared with pure LDPE. It was resulted that homogeneous CNTs distribution with interface in matrix was an important issue to enhance hardness property of LDPE/CNTs composites. Electrical properties of LDPE/CNT composites as a function of

CNT content, and frequency have been studied that DC of LDPE/CNT compositesaugmented slightly with increasing CNT content up to 3 wt%. Above CNT 3 wt% content, DC of composites increased sharply. DC of LDPE/10 wt% CNT composite was much bigger than pure LDPE. Frequency dependence of electrical properties of LDPE/10 wt% CNT composite could be well described by percolation theory. Conductivity and DC of LDPE/CNT composites first increased gently with increase of CNT concentration, and then increased significantly as CNT weight fraction was above 3 wt%. The results were explained well by employing percolation theory. DSC and TGA analysis showed a high thermal stability improvement for composite samples due to CNT content and improvement in crystallinity of CNT reinforced LDPE matrix. Hardness property of fabricated LDPE/CNT composites was significantly increased by enhancing CNTs weight content. It is resulted that homogeneous CNTs distribution in polymer matrix was an important issue to improve LDPE/CNT composites hardness property. The enhancement resulted more pronounced at low nanotubes loading (above 3 wt%). Electrical properties showed that electrical conductivity of LDPE matrix, resulted a significant increase, with quite low nanotube loadings (above 1 wt%).

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