Mechanical and electrical properties of low density polyethylene filled with carbon nanotubes

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Abstract. Carbon nanotubes (CNTs) reveal outstanding electrical and mechanical properties in addition to nanometer scale diameter and high aspect ratio, consequently, making it an ideal reinforcing agent for high strength polymer composites. Low density polyethylene (LDPE)/CNT composites were prepared via melt compounding. Mechanical and electrical properties of (LDPE)/CNT composites with different CNT contents were studied in this research.

Keywords: Low density polyethylene, Carbon nanotube, Composites, Properties

1. Introduction
Carbon nanotube (CNT) have gained attention as reinforcing fillers due to its outstanding 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 and electrical properties in low density polyethylene (LDPE) contain CNT compounds.

Experimental
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-CNT powder (CNT) composites were prepared by melt-blending commercial LDPE with CNT powder in a Brabender mixer. CNT powder was supplied by Nanostructured and 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/CNT compounds 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 °C under a pressure of 10MPa for 3 min.

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.

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 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 dielectric constant 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.

**Results and Discussion**

**Mechanical Properties**
The stress/strain curves of CNT/LDPE composites 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.

![Figure 1. LDPE and LDPE/CNTs Stress/strain of composites with varying CNT content](image)

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 3 presents storage modulus of LDPE and LDPE/CNT composites as a function of temperature. LDPE storage modulus and its composites reduced 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 was gained with 10 wt% CNT content. Figure 3 displays LDPE and its composites tangent 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 $T_g$.

It was studied that there is a moderate enhancement of Young’s modulus when CNT content changes from 0 to 10 wt%, as shown in Figure 4. 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.
Electrical Properties

Figure 5 presents dielectric constant changes with various CNT contents for LDPE/CNT composites. The dielectric constant of LDPE/CNT composites augmented slightly with increasing CNT content up to 3 wt%. Above this content, dielectric constant of composites enhanced sharply. The dielectric constant of LDPE/5 wt%CNT composite was four orders of magnitude higher than that of LDPE/3 wt%CNT. No sharp increase in dielectric constant was observed even CNT content reached 10 wt%. In most polymer/CNT composites, 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 [18-20]. 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.

Figure 6 shows dielectric constant dependence on LDPE/CNT composites frequency in range of $10^2$–$10^7$ Hz. The pure LDPE dielectric constant and its composites with low CNT content (1 wt%) was independent of frequency. However, as CNT content reached 3 wt%, a noticeable dielectric constant dependence on frequency
was observed. The frequency dependence of dielectric constant of materials having percolation threshold [21] which can be expressed as below:

\[
\text{Dielectric constant } \propto \omega^{-\mu}
\]  

(1)

Where \(\omega = 2\pi f\) is the radial frequency and \(\mu\) are critical exponent. The \(\mu\) for LDPE/ 10 wt% CNT composite was determined to be 0.26 [10].

Figure 6. LDPE and LDPE/CNT composites as a function of frequency

Figure 7 shows conductivity dependence of LDPE/CNT composites and frequency at room temperature. Figure 7 reveals that conductivity increased with CNT content (0-10 wt%) and frequency range of 1–10^7 Hz. The LDPE conductivity and its composites augmented almost linearly with frequency. However, conductivity of LDPE/10 wt% CNT composite was frequency independent below a critical value (i.e. < 20 Hz) which was characteristic of a non-dielectric material with a pronounced direct current [21].

The dependence of conductivity, \(\sigma\), on frequency of dielectric materials can be described by:

\[
\sigma \propto \omega^{-\nu}
\]  

(2)

where \(\omega = 2\pi f\) and \(\nu\) value for LDPE/10 wt% CNT composite was determined to be ~0.66 at higher frequency regime. The low \(\nu\) value is associated with polarization effect between CNT clusters [22]. This condition was almost obeyed for LDPE/10 wt% CNT composite, indicating that this composite was 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 \(f_{\text{CNT}} > 20\), 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 [10]. Definitely, when \(f_{\text{CNT}}\) 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 7. LDPE and LDPE/CNT composites conductivity as a function of frequency

Figure 8 expresses conductivity 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 was emphasized that electrical conductivity of LDPE, soon after percolation, resulted increase of about nine orders of magnitude at nanotube loadings (0-10 wt%).

Figure 8. LDPE electrical conductivity as function of CNT content

Conclusion
It was revealed that 10 wt% CNTs addition to LDPE increased young’s modulus and TS values of composites by 96% and 60%, respectively. Mechanical properties of pure LDPE augmented with CNTs addition. Electrical tests presented that DC value of LDPE content 10 wt% CNT composite was much bigger than pure LDPE and it is augmented slightly with further CNT addition up to 3 wt%. Above 3 wt% CNT content, DC of composites increased sharply. The frequency dependence of electrical properties of LDPE content 10 wt% CNT was well described with percolation theory. Conductivity and DC properties of LDPE/CNT composites first increased
gently with addition of CNT content, and raised significantly as CNT weight fraction was above 3 wt%.
Electrical properties also showed that electrical conductivity of LDPE matrix, resulted a significant increase,
with quite low nanotube loadings (above 1 wt%).

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