Effect of Microfiber Reinforcement on the Morphology, Electrical, and Mechanical Properties of the Polyethylene/Poly(ethylene terephthalate)/Carbon Nanotube Composites

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In situ microfiber reinforced conductive polymer composites consisting of high-density polyethylene (HDPE), poly(ethylene terephthalate) (PET), and multiwalled carbon nanotube (CNT) were prepared in a twin screw extruder followed by hot stretching of PET/CNT phase in HDPE matrix. For comparison purposes, the HDPE/PET blends and HDPE/PET/CNT composites were also produced without hot stretching. Extrusion process parameters, hot-stretching speed, and CNT amount in the composites were kept constant during the experiments. Effects of PET content and molding temperature on the morphology, electrical, and mechanical properties of the composites were investigated. Morphological observations showed that PET/CNT microfibers were successfully formed in HDPE phase. Electrical conductivities of the microfibrillar composites were in semi-conductor range at 0.5 wt% CNT content. Microfiber reinforcement improved the tensile strength of the microfibrillar HDPE/PET/CNT composites in comparison to that of HDPE/PET blends and HDPE/PET/CNT composites prepared without hot stretching.

INTRODUCTION

Recently, there is a great interest in industry on electrically semiconductor materials with superior mechanical properties and thermal stability [1]. Especially, conductive polymer composites have received significant attention for use in various engineering applications such as sensors, antistatic coatings, electromagnetic interference shielding, and electrolytes in the fuel cells [2, 3]. They are generally a synergetic combination of conductive filler and insulating polymer matrix. They exhibit a series of unique features, such as a percolation phenomenon, sensitivity to pressure, temperature and gas, improved mechanical and thermal properties.

Conductive polymer composites are usually prepared by incorporating conductive fillers into polymer matrix through melt mixing either by using an extruder or an internal mixer. However, to obtain high electrical conductivity with this method, high loadings of the conductive fillers are usually required, which may result in poor mechanical properties and high cost [4–8]. In the literature, several processing techniques have been used to lower the percolation threshold, in which electrical conductivity of composite increases by several orders of magnitude with the formation of current conductive structures [2]. These techniques are in situ polymerization of the polymer in the presence of conductive particles [9] and selective localization of conductive filler in one of the phases or at the interface of a polymer blend composed of two polymer constituents, in which filler forms the conductive network in the dispersed phase. This phase also constitutes continuous conductive structure in the major phase, which is called as double percolation [10–12]. However, in situ polymerization technique is hard to apply in the industrial scale, and in the second technique the incompatible nature of the polymer constituents of the composite lowers the mechanical properties.

A suitable processing technique must be performed for the preparation of the conductive polymer composites with lower filler loadings and better mechanical properties. The processing technique may change the morphology, which affects the properties of the polymer composites. It is well known that fibrillar morphology can greatly improve the mechanical properties of the fiber/polymer composites. Composites containing conductive fibers have lower percolation thresholds than the ones having spherical conductive particles [13, 14]. Microfiber reinforced conductive polymer composites are generally prepared by extrusion of an incompatible thermoplastic polymer pair with conductive filler in which the conductive particles selectively locate in the dispersed polymer phase, and the dispersed polymer/conductive filler phase forms microfibers in situ by hot stretching [1, 15, 16]. In this method, polymer matrices should have a distinct dif-
ference between their melting temperatures and melt viscosities. Polymer with higher melting point and lower melt viscosity is the dispersed phase in which the conductive filler particles distribute, and forms the microfibers in the matrix polymer with lower melting point. The electrical and mechanical properties of the composites are mainly affected by the amount, size, and distribution of the dispersed polymer/conductive filler microfibers in the matrix, processing conditions, hot-stretching speed, and molding temperature [17, 18].

Microfiber reinforcement has been proved to be a desirable method to improve the mechanical and electrical properties of polymer composites in contrast to the conventional melt mixing [1, 15, 16]. The composites, which are prepared by in situ microfiber reinforcement, have high electrical conductivity, lower percolation threshold and better mechanical properties, due to the selective localization of the conductive filler in microfiber phase, double percolation phenomena in a co-continuous polymer blend and reinforcement of microfibers.

In this study, conductive polymer composites with high electrical conductivity and improved mechanical properties at low carbon nanotube (CNT) loadings were obtained by preparing in situ microfiber reinforced high-density polyethylene (HDPE)/poly(ethylene terephthalate) (PET)/CNT composites through extrusion and hot stretching. Apart from the studies reported in the literature, CNT was used as conductive filler during the preparation of the microfiber reinforced polymer composites. The effect of PET content and the melting temperature of the composites on the microfibrillar morphology were mainly investigated. In addition, microfiber composites were compared with conventional melt mixed HDPE/PET blends and HDPE/PET/CNT composites in terms of morphology, electrical, mechanical, and thermal properties.

BACKGROUND

The dispersion of the CNT particles in an immiscible blend is a critical issue to obtain enhanced composite properties. When CNT particles are mixed with an immiscible polymer blend, it can be dispersed in one of the polymer phases or at the interface between the polymers. The important issue is to optimize the dispersion of CNT in the composite and obtain electrically conductive composite at low CNT concentrations [10, 11].

The surface energy components of the conductive filler and the polymers at the room temperature (20°C), can be determined by measuring the contact angles of the certain probe liquids on the samples of the filler and polymers [19, 20].

The dispersive (γ\text{solid}^d), electron acceptor (γ\text{solid}^A), and electron donor (γ\text{solid}^B) components of the total surface energy can be calculated with “Young equation” (Eq. 1), by using contact angles of probe liquids measured on the sample surface [19]:

\begin{equation}
(1 + \cos \theta_{\text{liquid}})\gamma_{\text{liquid}}^\text{d} = 2\left(\gamma_{\text{liquid}^\text{d}}^\text{d} + (\gamma_{\text{liquid}^\text{A}}^\text{A} + \gamma_{\text{liquid}^\text{B}}^\text{B})^{1/2}\right),
\end{equation}

in which \(\theta_{\text{liquid}}\) is the contact angle values of the probe liquid, \(\gamma_{\text{liquid}}^\text{d}\) is the total surface energy of the probe liquid, \(\gamma_{\text{liquid}^\text{d}}^\text{d}\) is the dispersive component of the probe liquid surface energy, \(\gamma_{\text{liquid}^\text{A}}^\text{A}\) is the electron acceptor component of the probe liquid surface energy and \(\gamma_{\text{liquid}^\text{B}}^\text{B}\) is the electron donor component of the probe liquid surface energy. Polar component of the surface energy (\(\gamma_{\text{solid}}^\text{P}\)), consists of electron acceptor (\(\gamma_{\text{solid}^\text{A}}^\text{A}\)) and electron donor components (\(\gamma_{\text{solid}^\text{B}}^\text{B}\)).

\begin{equation}
\gamma_{\text{solid}}^P = 2(\gamma_{\text{solid}^\text{A}}^\text{A} + \gamma_{\text{solid}^\text{B}}^\text{B})^{1/2}.
\end{equation}

Moreover, the total surface energy, \(\gamma_{\text{solid}}\), can be calculated by using dispersive (\(\gamma_{\text{solid}^\text{d}}\)) and polar components (\(\gamma_{\text{solid}^\text{p}}\)).

\begin{equation}
\gamma_{\text{solid}} = \gamma_{\text{solid}^\text{d}} + \gamma_{\text{solid}^\text{p}}.
\end{equation}

The interfacial tensions between two composite constituents (\(\gamma_{1-2}\)) can be determined by using the surface energy components of the materials from general equation with harmonic mean.

\begin{equation}
\gamma_{1-2} = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1\gamma_2}{\gamma_1 + \gamma_2}\right).
\end{equation}

Surface energies of the polymers and filler determine the location of the filler in the polymer composite. Generally, the lower interfacial tension between the polymer and conductive filler makes the adsorption of the filler by the polymer easier. Sumita et al. proposed that the selective localization of the filler in a polymer blend can be estimated by the wetting coefficient (\(w\)), which is defined by the following Eq. 5 [21];

\begin{equation}
w = (\gamma_{T-B} - \gamma_{T-A})/\gamma_{A-B}.
\end{equation}

where \(\gamma_{T-A}\) is the interfacial tension between the polymer A and filler, \(\gamma_{T-B}\) is the interfacial tension between the polymer B and filler, and \(\gamma_{A-B}\) is the interfacial tension between two polymers. If \(w > 1\), the filler particles locate within polymer A. If \(w < 1\), the filler particles locate within polymer B. Otherwise the filler particles distribute at the interface [21].

EXPERIMENTAL

Materials

In this study; HDPE, PET, and multiwalled CNT were used for the preparation of the composites and blends. Information on these materials are given in Table 1.
Microfiber reinforced composites and conventional systems were prepared in a two-step extrusion process. Before blending, HDPE and PET pellets were dried in a vacuum oven at 60 °C for 4 h and at 90 °C for 24 h, respectively. During the first extrusion HDPE and PET were mixed in a corotating twin screw extruder (Thermo-mopris TSE 16 TC, L/D = 24). The HDPE/PET ratios were selected as 90/10, 80/20, 70/30, 60/40, and 50/50. HDPE/PET blends, which were obtained in first extrusion, mixed with CNT in the second extrusion and the mixture from the extruder die was hot stretched by using a speed adjustable take-up device (Siemens Micromaster 440) to form the PET/CNT microfibers in the HDPE matrix at the hot-stretching speed of 5.8 m/min. The hot-stretching ratio (the ratio of the areas of extrudate to hot stretched sample which was drawn by the take-up device) was 19.6, as it was related to the ultimate speed of the take-up device at which continuous microfibrillar composite processing with uniform dimensions could be performed. Moreover, well-defined microfibers were obtained for the composites at similar hot-stretching ratio (19.2) in the literature [17, 18]. The HDPE/PET part was (100 − x) % of the composite, where x was the CNT amount in the composite and it was kept constant as 0.5 wt%. Conventional composites and blends were prepared according to the same procedure given above without the hot-stretching process. Extrusion processes were performed at a barrel temperature profile of 190–210–230–250–270 °C, which is typical for the processing of HDPE/PET, blends in the literature [16–18] and a screw speed of 120 rpm.

Tensile testing and electrical conductivity measurement specimens of microfiber reinforced composites were prepared by using injection and compression molding devices, respectively, at 210 °C. The PET based microfibers were considered to be preserved at this temperature because of the high melting point of PET (~255 °C). To observe the effect of melting temperature on microfiber structure, composites were also molded at 240 °C and 280 °C. During compression molding, samples were pre-heated and molded at 50 bar oil pressure for 1.5 min and 150 bar oil pressure for 1 min, respectively. Compression molded samples were quenched to room temperature by tap water. Injection moldings (DSM Micro 10 cc Injection Molding Machine) of the samples were conducted under 15 bar pressure and at 30 °C mold temperature. Conventional composites and blends were molded at the same conditions used for the microfiber reinforced composites.

Sample Characterization

The electrical resistivities were measured with two point probe method, in which probes were connected to a Keithley 2400 source meter. Samples for the electrical resistivity measurements were prepared by using compression molding technique. The volume resistivity $\rho$ was calculated from the relationship:

$$\rho = \frac{(V)/(I)}{(S)/(L)},$$

in which $V$ is the voltage drop, $I$ is the current, $L$ is the length, and $S$ is the cross-sectional area of the sample.

The tensile properties were investigated by using a Shimadzu Autograph AG-100 KNIS MS universal tensile testing instrument according to ISO 527-2 5A standard. Test specimens had thickness of 2 mm, width of 4 mm, and gauge length of 20 mm. According to the gauge length and a strain rate of 0.1 min$^{-1}$, the crosshead speed of testing instrument was selected as 2 mm/min. Impact strength of the samples were determined by using a Ceast Resil Impactor 6967 impact testing device according to ASTM D 5942 standard, instrumented with a 7.5 J hammer. The samples had thickness of 4 mm and width of 10 mm. Five specimens of each sample were tested in both tests and average of the test results were illustrated in graphics with their standard deviations.

Melt viscosities of the HDPE, PET, and PET/CNT composites were determined with Dynisco LCR-7001 (Capillary Viscometer) at 260 °C in a shear rate range from 10 to 600 1/s. Although CNT content of the HDPE/PET/CNT composite systems is constant (0.5 wt%), the CNT amount in PET phase differs as PET composition changes from 10 to 50 wt%. Hence, the melt viscosities of PET/CNT composites containing 1, 1.25, 2.5, and 5 wt% CNT were measured and illustrated. The morphological analyses were performed by using a Scanning Electron Microscope (JEOL JSM-6400). Prior to morphological analysis, selected samples were etched in hot xylene at 135 °C for 45 min to remove the HDPE phase from the composites and observe microfibrillar morphology easier. In addition, some of the samples were etched in trifluoro acetic acid at room temperature for 6 h, for determining the size of the PET and PET/CNT phases. As trifluoro acetic acid etching removes the PET and PET/CNT phase from the composites, these phases are observed as hollow spherical particles dispersed in HDPE phase in the SEM micrographs. Domain sizes of the PET and PET/CNT
phases in the blends and composites were determined from the SEM micrographs by using image analysis software (Image J). Two SEM micrographs were analyzed for each sample and at least 300 hollow spherical particles were taken into account.

Thermal characteristics of the samples were investigated by differential scanning calorimetry (DSC). The analyses were conducted from \(20^\circ C\) to \(300^\circ C\) at a heating rate of \(5^\circ C/\text{min}\). Crystallinities of the HDPE and PET phases in the samples were calculated by using the equation below:

\[
X_c = \left( \frac{\Delta H_m}{\Delta H_m^0 \times w_{\text{poly}}} \right) \times 100 \tag{7}
\]

where \(\Delta H_m^0\) is the melting energy of the 100% crystal structure, \(\Delta H_m\) is the melting energy, \(X_c\) is the percent crystallinity, and \(w_{\text{poly}}\) is the weight fraction of the polymer in the composite. \(\Delta H_m^0\) values of the HDPE and PET are 207 and 138 J/g, respectively [22].

Surface energy components of the HDPE, PET, and CNT were determined by measuring the contact angles of probe liquids on CNT and polymer surfaces. CNT particles were pressed as discs under 150 bar pressure and contact angles of probe liquids were determined from these pressed surfaces [20]. Diiodomethane (DIM), ethylene glycol (EG), and formamide were used as probe liquids. DIM was selected to calculate the dispersive component of surface energy, \(\gamma^d\). Meanwhile, EG and formamide were used to calculate the polar component of surface energy, \(\gamma^p\). Surface energy components of probe liquids are given in Table 2 [19].

\[\text{TABLE 2. Surface energy components of probe liquids (mN/m) [19].}\]

<table>
<thead>
<tr>
<th>Probe liquid</th>
<th>(\gamma^\text{liquid})</th>
<th>(\gamma^\text{solid})</th>
<th>(\gamma^d)</th>
<th>(\gamma^p)</th>
<th>(\gamma^A)</th>
<th>(\gamma^B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIM</td>
<td>50.80</td>
<td>50.80</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Formamide</td>
<td>48.00</td>
<td>29.00</td>
<td>19.00</td>
<td>3.00</td>
<td>2.30</td>
<td>39.60</td>
</tr>
<tr>
<td>EG</td>
<td>58.00</td>
<td>39.00</td>
<td>19.00</td>
<td>2.30</td>
<td>3.00</td>
<td>39.60</td>
</tr>
</tbody>
</table>

Surface energy components of the matrix polymers and carbon nanotube (mN/m).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\gamma^\text{solid})</th>
<th>(\gamma^d)</th>
<th>(\gamma^p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>33.32</td>
<td>32.20</td>
<td>1.12</td>
</tr>
<tr>
<td>PET</td>
<td>36.96</td>
<td>29.06</td>
<td>7.90</td>
</tr>
<tr>
<td>CNT</td>
<td>46.14</td>
<td>35.67</td>
<td>10.47</td>
</tr>
</tbody>
</table>

Results and Discussion

Surface Energy Measurements and Selective Localization of Carbon Nanotube

Surface energies and melt viscosities of the polymers, mainly determine the location of the conductive filler in the polymer composites consisting of two immiscible polymers [23]. Surface energies of HDPE, PET, and CNT, which are calculated from contact angle measurements (Eqs. 1–3), are shown in Table 3 and used in the determination of the surface tensions between the composite components.

Surface energy measurements show that CNT has higher surface energy (\(\gamma^\text{solid}\)) than HDPE and PET, due to its larger surface area and functional groups present on its surface. The polar component of HDPE (\(\gamma^p\)) is close to zero, due to the lack of the functional groups. PET has higher polar surface energy component due to the presence of carboxylic end groups, when compared with that of HDPE, which can increase the affinity between CNT and PET, rather than HDPE. Surface tensions (Eq. 4), between PET and HDPE, PET and CNT, HDPE and CNT, are calculated as 5.28, 1.05, and 7.74 mN/m, respectively. Wetting coefficient (\(w\)) is calculated as 1.27 from the Eq. 5, which means that CNT particles should disperse in PET phase theoretically. In addition, lower interfacial tension between PET and CNT, makes the dispersion of CNT in PET phase easier [24]. This result is associated with the fact that carbon based conductive particles prefer to locate in the phase which has lower melt viscosity [3, 21, 23]. Rheological analyses show that PET has much lower melt viscosity than HDPE at the extrusion temperature (see Fig. 1). Also, SEM analysis reveals that CNT (see Fig. 2) selectively disperse in the PET phase of HDPE/PET/CNT system (Figs. 3 and 4). In Fig. 2, individual CNTs are recognizable in CNT agglomerate, as long fibers with a diameter of around 10 nm. Figures 3 and 4 show the PET phase contacting with HDPE phase. As it can be seen from the figures, CNT particles are not distributed homogeneously in the composite. PET surface is rough, without any sign of elongation due to the brittle nature of PET, and CNT particles selectively locate on its surface as fibrillar particles. On the other hand, HDPE phase is stretched due to ductile nature with a smooth surface structure and it is very hard to observe any CNT particles on its surface.

\[\text{FIG. 1. Shear viscosity vs. shear rate graphs for HDPE, PET, and PET/CNT composites.}\]
Morphology Studies

The SEM micrographs of the HDPE/PET blends and HDPE/PET/CNT composites (Figs. 5 and 6) show that PET and PET/CNT phases disperse in HDPE up to 30 wt% PET composition. A wide distribution of dispersed particle size is generally observed in the blends examined, due to the occurrence of coalescence phenomena of the minor phase during the melt mixing. The average diameter of PET and PET/CNT phases, which are etched away with trifluoro acetic acid, increases from 0.49 to 1.41 μm and 0.36 to 0.84 μm, respectively, as the PET content in the blend increases from 20 wt% to 30 wt%, due to droplet coalescence (Table 4) [25–27]. PET/CNT domain sizes in composite systems are smaller than the PET domain sizes in the blend systems (Table 4). The decrease in the size of the PET phase after CNT addition to the HDPE/PET blends can be explained in terms of the reduction in the coalescence of the PET phase due to the presence of the rigid CNT particles in the PET phase and at the interface between the HDPE and PET. During the melt blending of the HDPE/PET/CNT composites, the interfaces act as solid-like barriers which repulse each other, owing to the rigidity, and lower mobility of the CNT particles. This lowers the melt coalescence of the PET/CNT phases. Moreover, CNT addition decreases the interfacial tension between the HDPE and PET, which can also cause a reduction in the size of the PET phase. The interfacial tension between the HDPE and PET decreases from 5.28 to 5.04 mN/m (calculated from the surface energy measurements of the composite constituents) in the presence of CNT particles. These phenomena can decrease the size of the PET/CNT phase in HDPE/PET/CNT composites when compared with the size of the PET phase in HDPE/PET blends. This was also observed in the literature for similar composite materials [26, 27]. The difference in PET

FIG. 2. SEM micrograph of carbon nanotube.

FIG. 3. (a) SEM micrograph of the HDPE/PET/CNT (70/30/0.5) composite system, (b) magnified micrograph of the rectangular region in (a), (c) is the magnified PET/CNT phase in (b) and (d) is the magnified micrograph of rectangular region in (c).
domain size in the blends and composites affects the tensile properties of the samples. According to melt viscosity based morphology model [12], which claims that the co-continuous morphology starts to form when the melt viscosity and the volume ratios of the polymer phases are equal to each other in a composite system, the co-continuous morphology starts to form when the melt viscosity and the volume ratios of the polymer phases are equal to each other in a composite system, the co-

FIG. 4. (a) SEM micrographs of the HDPE/PET/CNT (60/40/0.5) composite system, (b) and (c) are the magnified micrographs of the rectangular regions in (a).

FIG. 5. SEM micrographs of the selected blend samples (HDPE/PET). (a) 80/20, (b) 70/30, and (c) 50/50 (etched by trifluoro acetic acid).
ous morphology start to develop after 30 wt% and 40 wt% PET loading for HDPE/PET and HDPE/PET/CNT systems, respectively. SEM results are in accordance with the Paul and Barlow model. A co-continuous morphology is observed when PET content in the blends and composites are 50 wt% (Figs. 5 and 6).

Micrographs of the hot-stretched HDPE/PET/CNT systems (see Fig. 7) exhibit the in situ PET/CNT microfiber structure formed in HDPE phase for all composites. However, the structure and concentration of the microfibers are different for all compositions [28, 29]. The changes in the surface structure of the microfibers are due to the diversity in the amounts of CNT in PET phase for various composite systems. Difference in the CNT concentration of the PET phase directly changes the microfiber structure [16]. Deformation of PET/CNT phase into microfibers during elongational flow, strongly depend on the interfacial interactions between composite constituents and melt viscosity of the dispersed phase. The poor interfacial interactions between PET and HDPE, due to the incompatible nature of these polymers, do not create a remarkable resistance for the elongation of PET/CNT phase and enhance the formation of microfibers. However, the fibrillation of the PET phase in the presence of CNT particles also depends on the concentration of CNT in this phase. CNTs are rigid particles, which limit the flow of the polymer melt and increase the melt viscosity (see Fig. 1). As the CNT amount in the PET phase decreases, hot stretching can facilitate the deformation and fibrillation of the dispersed PET/CNT phase in the composite, more effectively due to the lower melt viscosity of dispersed phase. The concentration of the microfibers grows up and the average diameter of them decreases as PET content of the composites increases (CNT content in PET phase

<table>
<thead>
<tr>
<th>Sample (HDPE/PET/CNT)</th>
<th>Morphology</th>
<th>Average diameter (µm)</th>
<th>Minimum diameter (µm)</th>
<th>Maximum diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/20 (Fig. 5a)</td>
<td>PET phase dispersed in HDPE</td>
<td>0.49 ± 0.09</td>
<td>0.05</td>
<td>1.67</td>
</tr>
<tr>
<td>70/30 (Fig. 5b)</td>
<td>PET phase dispersed in HDPE</td>
<td>1.41 ± 0.38</td>
<td>0.09</td>
<td>23.13</td>
</tr>
<tr>
<td>50/50 (Fig. 5c)</td>
<td>Co-continuous</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>80/20/0.5 (Fig. 6a)</td>
<td>PET/CNT phase dispersed in HDPE</td>
<td>0.36 ± 0.27</td>
<td>0.05</td>
<td>3.40</td>
</tr>
<tr>
<td>70/30/0.5 (Fig. 6b)</td>
<td>PET/CNT phase dispersed in HDPE</td>
<td>0.84 ± 0.45</td>
<td>0.05</td>
<td>10.29</td>
</tr>
<tr>
<td>50/50/0.5 (Fig. 6c)</td>
<td>Co-continuous</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>80/20/0.5 microfiber injection molded (Fig. 8d)</td>
<td>PET/CNT phase dispersed in HDPE</td>
<td>0.93 ± 0.34</td>
<td>0.05</td>
<td>5.93</td>
</tr>
<tr>
<td>80/20/0.5 injection molded (Fig. 8e)</td>
<td>PET/CNT phase dispersed in HDPE</td>
<td>0.94 ± 0.48</td>
<td>0.06</td>
<td>10.85</td>
</tr>
</tbody>
</table>
decreases). The average diameters of the microfibers in the 80/20/0.5 microfiber and 50/50/0.5 microfiber systems are around 8 and 4 μm, respectively.

Microfiber reinforced composites are generally molded at a lower temperature than the melting temperature of the microfiber phase, to preserve the microfiber structure and perform the transformation of the composite into isotropic material reinforced with the microfibers [30, 31]. Figure 8a and b show that the microfiber structure is protected in the composites which were molded at 210°C. This is necessary for the achievement of the desired electrical and mechanical properties. Moreover, most of the microfibers are oriented along the injection molding direction, as they leave a long section being vertical to the fracture surface (Fig. 8a) [15]. However at 240°C, some of the microfibers melt, as the molding temperature is close to the melting point of PET (Fig. 8c). When the molding temperature is raised to 280°C, microfiber struc-

FIG. 7. SEM micrographs of the selected hot-stretched samples [(a), (a')] 90/10/0.5 microfiber, [(b), (b')] 80/20/0.5 microfiber, [(c), (c')] 70/30/0.5 microfiber, and [(d), (d')] 50/50/0.5 microfiber reinforced composites (etched by hot xylene).
tures totally disappear and is reconverted into randomly distributed spherical particles as a result of melting of the PET phase (Fig. 8d). SEM micrographs of the hot-stretched and conventional 80/20/0.5 composites, which are molded at 280°C resemble each other (Fig. 8d and e) with the average diameters of the PET/CNT phases as 0.93 and 0.94 μm, respectively (Table 4).

**Electrical Resistivity**

Electrical resistivity of HDPE + 0.5 wt% CNT composite is around $10^{10}$ Ω cm, which is in insulator range ($>10^7$ Ω cm). On the other hand, the electrical resistivity of PET/CNT system containing same amount of CNT in it, is around $10^7$ Ω cm (see Fig. 9). This noticeable difference is due to the distinction between melt viscosities of these two polymers and affinities of the polymers to CNT. PET has higher affinity to CNT, due to the polar end groups present in the chemical structure and this improves the wetting of CNT by polymer matrix. Lower melt viscosity of PET causes a larger agglomerate size of CNT in the composite, which makes the conductive network formation and current conduction easier in PET matrix [27]. In addition, all the PET/CNT composites should exhibit low electrical resistivity (<100 ohm-cm) above 0.5 wt% CNT loading. This means that all the PET/CNT

![FIG. 8. SEM micrographs of the selected molded samples. (a) 80/20/0.5 microfiber (210), (b) 80/20/0.5 microfiber (210) (etched by hot xylene), (c) 80/20/0.5 microfiber (240) (etched by hot xylene), (d) 80/20/0.5 microfiber (280) reinforced composites (etched by trifloro acetic acid), and (e) 80/20/0.5 composite (etched by trifloro acetic acid).](image)

![FIG. 9. Electrical resistivity values of the microfibrillar and conventional composites.](image)
phases in the microfiber reinforced and conventional composites have enough electrical conductivity to form conductive networks in the samples.

In the microfibrillar and conventional HDPE/PET/CNT system, the percolation threshold depend on two interconnected points; first one is the percolation threshold of nanotube particles in PET phase and the second one is the percolation threshold of PET/CNT phase in the HDPE matrix [3]. Before the percolation threshold concentration, tunneling distance is so much that HDPE dominates the conduction mechanism. Free charge carriers of conductive PET/CNT phase have to pass through microspaces between microfibers, which are filled with insulating HDPE. However, beginning from percolation content, the conductive PET/CNT microfibers will dominate the current conduction mechanism. PET-based composite containing 0.5 wt% CNT has an electrical resistivity value of 100 Ω cm. As a result of this, when PET/CNT phase forms a continuous structure in HDPE matrix, electrical conductivity of the composites passes from insulator range to semiconductor range (<10^7 Ω cm) as seen in Fig. 9. Direct contact between the microfibers can dominate the electron conduction in the microfibrillar composite, as CNT particles can directly touch each other when individual fibers contact with other fibers [11, 32]. The percolation threshold of the PET/CNT microfibers in the microfiber reinforced composites is below 10 wt% PET/CNT loading, since the electrical resistivity value of 90/10/0.5 microfiber system is about 10^7 Ω cm (see Fig. 9). Electrical resistivities of microfiber reinforced composites molded at 210°C decrease as the PET content in the composite is increased (see Fig. 10), due to rise of the number of contact points between the microfibers providing the electron transportation [16]. However, the decrease in the CNT amount in the PET/CNT phase as the PET content in the composites increases, do not have a significant effect on the electrical resistivity results of the composites. On the other hand, the electrical conductivities of the composites prepared without hot stretching and microfiber reinforced composites molded at 280°C are in the insulator range when PET/CNT content in the composite is below 40 wt% (see Fig. 9). As PET/CNT phase in the composite is not continuous below this composition (Figs. 6 and 8), electrical conductivity of the composites are low and falls in the insulator range.

Electrical resistivities of the microfiber reinforced composites increase when the molding temperature is increased from 210°C to 280°C (see Fig. 10). Molding temperatures above the melting point of PET, causes PET/CNT phase to melt and lose the microfiber characteristics. Thermodynamically when microfiber phases melt, they have a spherical shape (see Fig. 8) and continuity of the PET/CNT phase in the composite disappears below 40 wt% PET loading (see Fig. 6). 80/20/0.5 microfiber (210) system has an electrical resistivity of 10^8 Ω cm, whereas the electrical resistivity of the 80/20/0.5 microfiber (280) system is around 10^10 Ω cm (see Fig. 10).

Samples, which are molded at 240°C, have electrical resistivity values between the composites molded at 210°C and 280°C. Before the characterization experiments, it was expected that PET/CNT microfibers could soften and attach each other without damaging their structures when the molding temperature (240°C) is close to the melting point of PET, which may improve the current conduction by increasing the number of contact points between the microfibers.

**Mechanical Properties**

SEM micrographs of the HDPE/PET/CNT composites show a typical incompatible morphology with discrete PET/CNT domains dispersed within a continuous phase of HDPE (Figs. 3 and 4) [33]. No evidence of interfacial interactions or adhesion between both phases exists. The immiscible nature between two polymer phases leads to unstable morphology and poor mechanical properties in the composites. However, microfibrillar morphology can greatly improve the mechanical properties of the polymer/microfiber composites when the mechanical properties of the fibers with high aspect ratio are greater than the polymer matrix [17, 18, 34]. Microfiber reinforcement improves the tensile strength and modulus of the samples compared to that of the blends and composites prepared without hot stretching up to 30 wt% PET loading (Figs. 11 and 12). Direct short fiber strengthening and residual thermal stress in microfibers are the main factors in reinforcement mechanism of in situ microfibrillar composites. The difference in the thermal expansion coefficients of HDPE and PET/CNT phases results in thermal residual stresses. During injection molding of composites at 210°C, PET/CNT microfibers are solid but HDPE is in molten phase. When the composite starts to cool from processing temperature to mold temperature microfibers have little thermal contraction; however, HDPE undergoes crystallization and contracts strongly [23]. Microfiber reinforced composites containing 40 wt% and 50 wt% PET could not be molded at 210°C and when these composites are molded at 240°C, their tensile strength and modulus...
are lower than the blends and conventional composites having the same composition, due to partial melting of the PET phase. Microfiber reinforced composites which are molded at 210°C, show a maximum for tensile strength and modulus values at 20 wt% PET loading. Tensile strength and modulus values of 80/20/0.5 microfiber (210) are 44 and 950 MPa, respectively. The optimum PET content for having improved mechanical properties is around 20–30 wt% for HDPE/PET/CNT system, as also observed by other researchers before [35]. The increases in the concentration of the microfibers (see Fig. 7) do not improve the tensile strength and modulus, due to the poor interfacial adhesion between HDPE and PET/CNT phase [34]. It can be concluded that presence of more microfibers in the sample is not sufficient for increasing the tensile strength without the compatibility of the polymer phases after a certain PET composition (30 wt%). Tensile strength values of the HDPE/PET/CNT composites are higher than HDPE/PET blends (see Fig. 11), as a result of the smaller domain size of the PET/CNT phase in the composites than the PET domain size in blends (Table 4) and presence of the reinforcing CNT particles in the composite structure.

Increasing the molding temperature, decreases the tensile strength and modulus values of microfiber reinforced composites up to 30 wt% and 40 wt% PET loading, respectively (Figs. 13 and 14). At high temperature molding, microfibers with high aspect ratio transform into spheres with low aspect ratio and the reinforcing effect of microfibers diminishes (see Fig. 8) [36]. Microfiber reinforced composites molded at 280°C and conventional composites have nearly the same tensile strength modulus values. Both 80/20/0.5 microfiber (280) and 80/20/0.5 systems have tensile strength of approximately 35 MPa. Also, 70/30/0.5 microfiber (280) and 70/30/0.5 systems have tensile modulus of around 600 MPa.

Microfiber reinforcement enhances the impact strength values when compared with that of blends and composites prepared without hot stretching, except for 90/10 systems (see Fig. 15). Parallel to tensile strength and modulus results, 80/20/0.5 microfiber (210) system has the highest impact strength among the microfiber reinforced composites molded at 210°C. Microfibers present in the composite decrease the crack formation and propagation in the sample during the impact test. When the growing crack reaches the microfiber phase, the microfiber nucleates the formation of many tiny craze cracks, which produces a large free surface that absorbs the mechanical energy as the potential surface energy [7]. As a result of this, when the microfiber concentration in the composite increases, the impact strength also increases with respect to the blend without CNT. The percent increase of impact strength for 80/20/0.5 microfiber (210) and 70/30/0.5
microfiber (210) systems, when compared with the blend systems, are approximately 50% and 350%, respectively (see Fig. 15). However, when PET content in the composites are higher (40–50 wt%), microfiber formation do not have a distinctive effect on the impact strength. The brittle nature of PET overcomes the microfiber reinforcement and decreases the impact strength. Molding temperature increment generally decreases the impact strength of the microfiber reinforced composites due to the melting of PET phase (see Fig. 16).

**Thermal Properties**

Thermal properties and crystallinities of the polymer constituents of the blends are investigated by using DSC. Melting points and percent crystallinities of HDPE and PET are given in Table 5. Melting temperatures ($T_m$) of HDPE and PET phases are determined as 131°C and 251°C, respectively for all blends and composites. The observed changes in the crystallinities could be explained on the basis of the CNT in the PET phase and effect of the physical state of the second polymer phase in the samples [37]. Percent crystallinity ($X_c$) of the HDPE phase decreases as the PET amount in the composite is increased. Crystallization of HDPE phase in the samples occurs in the presence of rigid PET phase due to the high melting temperature of PET ($\sim$ 250°C). This restricts the crystal growth in HDPE phase and descends the percent crystallinity [38]. However, percent crystallinities of the hot-stretched and molded microfiber reinforced composites are nearly same for both polymers. Degree of crystallinities of PET phases in the samples increases with the decreasing amount of HDPE. Crystallization of PET in the samples occurs in the presence of molten HDPE phase, which could again hinder the crystallization of PET phase and decrease the percent crystallinity [37]. In addition, the presence of CNT in PET phase ascends the percent crystallinity. CNTs are nano-sized particles and they can enhance the crystallization of PET phase due to the nucleation effect [39].

**CONCLUSIONS**

Microfiber reinforced HDPE/PET/CNT composites were prepared through extrusion and hot stretching. According to surface energy measurements and SEM analysis, CNT particles were selectively located in PET phase of the composite. This result was coherent with the fact that in a polymer blend system carbon-based conductive filler particles prefer to locate in the phase which has lower melt viscosity. The concentration of the microfibers ascended as the amount of PET increased in the composites. Also the microstructures of the fibers were diverse for different PET compositions. The change in the structure of the microfibers was due to the difference in the amounts of CNT in PET phase for microfibrillar composites. The increase in the melt viscosity of PET phase influenced the microfiber formation and structure. Electrical conductivities of the microfibrillar composites were higher than composites prepared without hot stretching due to the continuous PET/CNT microfiber network formed during hot stretching. However, an increase in the molding temperature decreased the electrical conductivity of the microfibrillar composites, as the PET/CNT microfibers could not be preserved at elevated temperatures and

<table>
<thead>
<tr>
<th>Sample (HDPE/PET/CNT)</th>
<th>$T_m$ (HDPE) ($^\circ$C)</th>
<th>$T_m$ (PET) ($^\circ$C)</th>
<th>$X_c$ (HDPE) (%)</th>
<th>$X_c$ (PET) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/20</td>
<td>132</td>
<td>251</td>
<td>77.7</td>
<td>18.5</td>
</tr>
<tr>
<td>70/30</td>
<td>132</td>
<td>251</td>
<td>74.0</td>
<td>20.8</td>
</tr>
<tr>
<td>50/50</td>
<td>129</td>
<td>251</td>
<td>63.2</td>
<td>24.3</td>
</tr>
<tr>
<td>80/20/0.5 microfiber</td>
<td>130</td>
<td>251</td>
<td>72.8</td>
<td>24.8</td>
</tr>
<tr>
<td>70/30/0.5 microfiber</td>
<td>129</td>
<td>251</td>
<td>67.5</td>
<td>28.5</td>
</tr>
<tr>
<td>50/50/0.5 microfiber</td>
<td>129</td>
<td>251</td>
<td>62.8</td>
<td>30.3</td>
</tr>
<tr>
<td>80/20/0.5 microfiber (210)</td>
<td>130</td>
<td>250</td>
<td>72.4</td>
<td>25.4</td>
</tr>
<tr>
<td>80/20/0.5 microfiber (240)</td>
<td>132</td>
<td>251</td>
<td>74.9</td>
<td>25.6</td>
</tr>
<tr>
<td>80/20/0.5 microfiber (280)</td>
<td>130</td>
<td>250</td>
<td>75.4</td>
<td>25.5</td>
</tr>
<tr>
<td>70/30/0.5 microfiber (210)</td>
<td>131</td>
<td>251</td>
<td>65.6</td>
<td>27.4</td>
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<tr>
<td>50/50/0.5 microfiber (210)</td>
<td>130</td>
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<td>63.4</td>
<td>30.8</td>
</tr>
<tr>
<td>80/20/0.5</td>
<td>131</td>
<td>251</td>
<td>72.8</td>
<td>26.2</td>
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</tbody>
</table>
deform into spherical particles. Microfiber reinforcement improved the tensile and impact strength of the samples, when compared with those of blend and conventional composite systems, up to 30 wt% PET loading. After this amount, the improvement in mechanical properties diminished due to incompatible nature of HDPE and PET. Percent crystallinities of HDPE and PET decreased as the amount of second polymer phase in the composite and blend systems increased.

REFERENCES

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