Effects of Reprocessing on the Structure and Properties of Polycarbonate/Multi-Walled Carbon Nanotube Based Electrostatic Dissipative Composites

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ABSTRACT
Polycarbonate (PC)/multi-walled carbon nanotube (MWCNT) based electrostatic dissipative (ESD) composite was reprocessed by repeated injection molding to investigate if this material can be successfully recycled. The varied parameter was the number of cycles (1-6) at the processing temperature of 235-280°C. The effects of reprocessing on the structure, rheological, electrical and mechanical properties were studied. The ESD properties such as electrical resistance, tribo-charge voltage, and decay time were in the static dissipative range for ESD application after reprocessing. The decreases in heat deflection temperature were insignificant. The tensile strength was slightly increased and almost no change was observed at the higher number of injection molding cycles (4-6 cycles). In contrast, the elongation at break and impact strength were decreased and began to slightly change at injection molding cycles of 4-6. The changes in mechanical properties partly resulted from the larger exposure to the shear stresses in the melt as the number of injection molding cycles increased, leading to better dispersion level of MWCNTs in the polymer matrix. There was no observable chemical change as well as material degradation after reprocessing for 1-6 cycles. However, the polymer chain scission was observed since the melt flow index increased and the storage modulus, loss modulus, and complex viscosity decreased when the number of injection molding cycles increased. Overall, it was concluded that the PC/MWCNT composite had high possibility for reprocessing because there were only minor material property changes after 6 injection molding cycles, except for its mechanical and rheological properties.

Keywords: polycarbonate, muti-wall carbon nanotube, reprocessing, injection molding

1. INTRODUCTION
Polymer recycling is of great interest in respect of economical and environmental concerns [1, 2]. For economic reasons, the reprocessing of scrap material from molding processes such as sprues, runners, and unwanted parts is usually performed especially for high performance and expensive polymers. Moreover, polymer recycling is currently used...
to reduce the environmental problems caused by the increasing quantity of post-consumer plastic products in the waste stream. Increasing environmental concerns and legislation have resulted in significant pressure to reduce, reuse or recycle various waste polymer products. Mostly, polymer recycling is carried out by reprocessing, involving several high temperature shearing cycles that lead to material deterioration such as the occurrence of thermal and/or mechanical degradation, the consequence of chemical and physical changes, and the damage of final properties. Therefore, knowledge of the nature and intensity of the degradation is significantly important to prevent such material detriments by selecting a suitable stabilizer and/or the maximum amount of recycled material which may be added to the virgin material with an acceptable level in the ultimate properties.

A number of studies on reprocessing and its effects on material properties have been published for many kinds of polymers such as polyolefins [3, 4], polycarbonate (PC) [5], poly(ethylene terephthalate) [6], and polyamides (PAs) [7-11]. Reprocessing of polymer blends such as PC/ poly (butylenes terephthalate) (PBT) [12], PA6/polypropylene (PP) [13], and PP-(ethylene-propylene (EP)) copolymer/ poly(ethylene-co-vinyl acetate) (EVA) [14] has been conducted as well as that of reinforced materials [15-18] and nanocomposites [19-22].

Electronic components are susceptible to damage from electrostatic discharge (ESD). A variety of materials has been developed to package sensitive electronic devices and prevent damage during storage and shipping. For many articles in ESD protected environments, the optimal surface resistivity is in the range of 10^6-10^9 \text{ \Omega} /\text{sq} [23]. Even higher values may be accepted if the article is capable of dissipating charge fast enough. Too high surface resistivity results in an uncontrolled discharge [23]. Static dissipative materials are often used to slow down the charge removal process and prevent a damaging ESD event. Electrostatic dissipating thermoplastic compounds have successfully eliminated ESD failures in many applications in the electronics industry. A variety of conductive fillers is presently available to material engineers, including carbon black (CB), carbon fibers (CF), carbon nanotubes (CNT), metallic powders, flakes or fibers, and glass spheres or glass fibers coated with metals [23]. Among of these fillers, CNT is considered as a perfect candidate for the development of electrically/thermally conductive polymer-based composites due to its exceptional electrical and thermal conductivity, high strength and stiffness and large aspect ratio [24-30]. The conductivity of ESD compounds depends not only on the filler type and concentration, but also on the specific polymer matrix used and on the generated morphology [31].

This work investigates the impact of reprocessing on properties of the PC/MWCNT composite such as chemical structures, ESD properties, and rheological and mechanical properties, by means of repeated injection molding cycles. The number of injection molding cycles was 1-6.

2. MATERIALS AND METHODS
2.1 Materials and Sample Preparation
The commercial PC/MWCNT composite (EA-3240, injecting molding grade for ESD applications) was kindly provided by Cheil Industries Inc., Korea. The virgin PC/MWCNT pellets were dried in hopper dryer at 80°C for 3 h prior to processing. The injection molding of the PC/MWCNT composite was carried out using a Fanuc Roboshot 2000i 100B
reciprocating screw injection molding machine to obtain tensile, impact, and HDT/VICAT specimens. The plasticization unit consists of a standard screw with a diameter of 32 mm, L/D ratio of 20/1, and compression ratio of 4D. The temperature profile was 235, 260, 290 and 280°C from rear zone to the nozzle and the mold temperature was set at 100°C. The screw rotation speed was 50 rpm. The injection speed and pressure were 20 cm³/s and 80 bar, respectively. After the first injection cycle, some specimens were kept for properties evaluation, and others were ground into appropriate size by a plastic crusher. The granulated material was dried and injected using the same conditions as above and the resultant specimens were repeatedly processed until the 6th cycle of injection molding was completed. Specimens from each reprocessing cycle were kept to condition for 24 h in a desiccator before characterization.

2.2 Characterization

The electrical resistance of injection-molded samples was measured according to ANSI/ESD STM11.13-2004 using a resistance meter (3M-701). The tribo-charge voltage and decay time were determined based on ESD ADV11.2-1995 using an electrostatic voltage meter (Trek-520), and a charged plate monitor system (Trek Model 150A), respectively. Tensile properties were carried out according to ASTM D638 using a Universal testing machine (Instron 4502), at a crosshead speed of 5 mm/min and test temperature of 25°C. The specimen dimensions were 12.7 mm × 165 mm × 3.2 mm (W×L×T). The Young’s modulus and elongation at break were determined from the load-displacement curves. Izod impact tests were performed on an impact tester (Radmana model ITR 2000) based on ASTM D256. The notched sample had a size of 12.7 mm × 63.5 mm × 3 mm (W×L×T). A HDT/VICAT softening temperature tester (Yasuda model HD-PC) was used for measuring the HDT of specimen. The samples were prepared with the dimensions of 13 mm × 127 mm × 5 mm (W×L×T). Tests were in accordance with ASTM D648 at a load of 1.82 MPa. TGA measurements were carried out using a TA instruments thermobalance (TGA Q500) under nitrogen atmosphere and at a heating rate of 20°C/min. Dynamic measurements were carried out using an advanced rheometric expansion system (ARES). The frequency sweep from 0.1 to 100 rad/s was performed at 260°C under dry nitrogen condition. For all the measurements, the PC/MWCNT samples were tested within the linear viscoelastic strain range. The MFI was measured with an extrusion plastometer (Davenport model 10, Lloyd Instruments), according to ASTM D1238 at 260°C, with a 2.16 kgf weight. TEM samples were ultra-thin-sectioned at 70 nm using an ultramicrotome. The morphology of the nanocomposites was obtained using a JEOL JEM-2010, LaB6 filament at an accelerating voltage of 200 kV. To verify the effect of reprocessing on chemical structures and bonding between MWCNTs and PC matrix, attenuated total reflectance ATR-FTIR measurement was carried out on the samples at different injection molding cycles. FTIR spectra were recorded using a Thermo Nicolet 6700 spectrometer. Single beam spectra were collected from 16 scans at resolution of 4 cm⁻¹ and the measurement range was 4000-600 cm⁻¹. All experiments were performed at ambient temperature, 25 ± 2°C. Five specimens were tested for each set of measurements.
3. Results and Discussion

3.1 Morphology

Figure 1 (a-f) shows the TEM images of the PC/MWCNT injection-molded samples at different injection molding cycles. As can be seen, MWCNTs were well separated and uniformly distributed in the PC matrix. The structure and dimension of MWCNTs for each injection molding cycle were very similar, indicating that the aspect ratio of MWCNTs remained the same after reprocessing and MWCNT agglomeration was not observed. Reprocessing may improve dispersion due to the longer exposure to the shear stresses. This occurred in the case of polyolefin-clay nanocomposites [22] because exfoliation and dispersion are difficult to attain for such kind of nanocomposites. In this study, the lack of agglomeration upon reprocessing by the injection molding method was attributed to the high screw speed in the injection machine which favors MWCNT dispersion.

3.2 ESD Measurement

An ESD control system should be introduced in the production and handling of electronic parts and devices. Static dissipative materials are often used to slow down the charge removal process and prevent a damaging ESD event. The Electronic Industry Association (EIA) specifies that the typical requirements for surface resistivity, tribo-charge voltage, and decay time are $10^6$-$10^9$ $\Omega$/sq, less than 25 V, and less than 5 sec, respectively [23]. In this experiment as presented in Table 1, the injection-molded PC/MWCNT composite

![Figure 1. TEM photographs of the PC/MWCNT injection-molded samples at different injection molding cycles: (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, (d) 4th cycle, (e) 5th cycle, and (f) 6th cycle.](image-url)
Table 1. ESD results for injection-molded specimens using PC/MWCNT composites at different injection molding cycles.

<table>
<thead>
<tr>
<th>Injection molding cycle</th>
<th>Tribo-charge voltage (V)</th>
<th>Standard deviation</th>
<th>Surface resistivity (Ω/sq)</th>
<th>Standard deviation</th>
<th>Decay time (sec) from 1000 to 100 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Positive charge</td>
</tr>
<tr>
<td>1</td>
<td>2.7</td>
<td>0.15</td>
<td>7.83 × 10^9</td>
<td>0.029</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>0.26</td>
<td>5.94 × 10^9</td>
<td>0.042</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.80</td>
<td>7.01 × 10^9</td>
<td>0.037</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>2.1</td>
<td>0.35</td>
<td>6.74 × 10^9</td>
<td>0.017</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>2.2</td>
<td>0.74</td>
<td>7.96 × 10^9</td>
<td>0.010</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>2.6</td>
<td>0.23</td>
<td>2.82 × 10^9</td>
<td>0.015</td>
<td>0.11</td>
</tr>
</tbody>
</table>

ESD properties such as electrical resistance (3-8 × 10^9 Ω/sq), tribo-charge voltage (2-3 V), and decay time (<0.1 s), suitable for ESD protection. As the injection molding cycles increased from 1 to 6, the ESD properties of specimens were slightly changed but remained in the acceptable range for ESD protection. Based on TEM topology (see Figure 1 (a-f)), there was no observable change in the MWCNT aspect ratio since the tube length was unchanged. The slight change in filler dispersion did not affect the conductivity of the composite since the resistivity change may be still in the steepness range (the percolation threshold) of the percolation curve. The percolation threshold indicates the critical amount of filler necessary to initiate a continuous conductive network, which varies from polymer to polymer for a given conductive filler type [23].

3.3 Rheology

Figures 2-4 show the storage modulus ($G'$), the loss modulus ($G''$), and the complex viscosity ($\eta^*$) of the PC/MWCNT composite at different injection molding cycles processed at 260°C. The $G'$ and $G''$ of the PC/MWCNT composites tended to decrease with increasing injection molding cycles. The $G'$ and $G''$ of the 6th injection molding cycle significantly decreased compared with the 1st injection molding cycle, which suggested that the rheological properties of the PC/MWCNT composite were influenced by the injection molding cycle. The effect of polymer chain scission might be larger than the effect of MWCNTs distribution. Therefore, the rheological properties of PC/MWCNT composites decreased with increasing injection molding cycles. The $G'$ and $G''$ increased with increasing the frequency for all injection molding cycles. It is suggested that the increase of rheological properties of the PC/MWCNT composites at high frequency is related to an increase of the MWCNT-MWCNT network structure because of low degree of aggregation of MWCNTs at high frequency [30]. Moreover, the increase of the rheological data of the PC/MWCNT composites at high frequency suggests that the interaction between PC and MWCNT may exist in the PC/MWCNT composites. The rheological properties of polymer composites at high frequency region reflect the dynamics of polymer entanglement [30].

In Figure 4, shear-thinning behavior was observed for the $\eta^*$ of the PC/MWCNT composites at different injection molding cycles. The shear-thinning behavior and long time relaxation suggest a pseudo-solid-like behavior of the
**Figure 2.** Effect of reprocessing on the storage modulus ($G'$) of the PC/MWCNT composites at 260°C.

**Figure 3.** Effect of reprocessing on the loss modulus ($G''$) of the PC/MWCNT composites at 260°C.

**Figure 4.** Effect of reprocessing on the complex viscosity ($\eta^*$) of the PC/MWCNT composites at 260°C.
PC/MWCNT composites. The $\eta^*$ insignificantly decreased with the increase of injection molding cycle. From the results of the $G'$ and $G''$ shown in Figures 2 and 3, the decrease of the $\eta^*$ of the PC/MWCNT composites at high injection molding cycle is mainly due to the decrease of the $G'$ and $G''$ since the $\eta^*$ is related to both the $G'$ and $G''$ ($\eta^* = [(G')^2 + (G'')^2]^{1/2}/\omega$, where $\omega = \text{frequency}$) [32].

The rheological results corresponded to the increasing of MFI of the PC/MWCNT composite when the injection molding cycle increased as shown in Figure 5. The MFI increased from 29.57 to 79.75 g/10 min as the injection molding cycle increased from 1 to 6. This may result from the molecular chain scission of PC due to high shear stress during the injection molding process. Liu and et.al. [5] reported that the occurrence of polymer chain scissions mostly occurred near the chain ends. This might be the reason why there were no large increases in MFI and decrease in $G'$, $G''$, and $\eta^*$ upon reprocessing.

### 3.4 Mechanical Properties

The tensile strength and elongation at break of injection-molded specimens are given in Figure 6. The tensile strength values after reprocessing insignificantly increased (1-4 cycles) from 60.66 to 62.02 MPa and remained at constant level of about 62 MPa at higher recycled process (4-6 cycles). The ductility results measured as the elongation at break and impact strength are presented in Figures 6 and 7, respectively. The elongation at break decreased from 45.32 to 13.37% (1-4 cycles) and slightly reduced at higher injection molding cycles of 4-6 from 13.37 to 7.66%. The impact strength decreased from 221.69 to 93.86 J/mm at injection molding cycles of 1-4 and slightly reduced at higher injection molding cycles of 4-6 from 93.86 to 67.97 J/mm. The tensile strength and ductility results corresponded to the degree of MWCNT fillers dispersion due to the larger exposure to the shear stresses in the melt. The dispersion of MWCNTs was slightly increased together with the lack of change of MWCNT aspect ratio at injection molding cycles of 1-4, but the improvement of MWCNTs distribution at injection molding cycles of 4-6 was hardly observed from TEM topologies. Furthermore, this possibility indicated that full dispersion of MWCNT powder in PC matrix was not
achieved after the first injection molding cycle because of the low interfacial interaction between MWCNTs and polymer leading to poor dispersion of MWCNTs in common polymer matrices. This agreed with the TEM results where slight change in the extent of dispersion was observed as injection molding cycle increased. For a glassy, amorphous material like PC, the key parameters controlling the mechanical performance are expected to be the molecular weight, the free volume, the chemical nature, as well as the molecular orientation. In the case of PC composite, the characteristic and distribution of fillers in the polymer matrix also play an important role on mechanical properties of the composite.

Figure 8 shows the relationship of heat deflection temperature (HDT) versus number of injection molding cycles of the PC/MWCNT injection-molded samples. The HDT slightly decreased from 118 to 113°C as the injection molding cycle increased from 1 to 6. The slight variation of HDT values also implied that the polymer chain...
scission insignificantly occurred at the main chain since the change of HDT is mainly depended on the molecular weight of based polymer.

3.5 Chemical Structure

The TGA results on PC/MWCNT injection-molded samples at different numbers of injection molding cycles from 1-6 are reported in Figure 9. All the TGA curves were identical and they exhibited first significant weight loss at about 400°C, which was well above the experimental processing temperature (235-280°C). This agreed with the excellent degree of stability observed for the PC/MWCNT composite after reprocessing, resulting in only slightly changes in its properties after reprocessing.

The FTIR result was used to detect possible changes in the chemical structure of the PC/MWCNT composite as the injection molding cycle increased. As shown in Figure 10, the peaks at 1728 and 3000 cm\(^{-1}\) indicate the existence of an ester group...
and some stretching of C=C in the aromatic ring of PC in the composite. The bands at 1015 and 1776 cm\(^{-1}\) are ascribed to internal planar bending vibrations of aromatic rings and stretching of the carbonyl groups, respectively [5]. However, the bands at 3673 and 3531 cm\(^{-1}\) assigned to vibrations of methyl groups and stretching vibrations of hydroxyl groups [5] were not clearly seen. No significant change of FTIR spectra was observed indicating that any possible change of the chemical structure might be slight. This may be because either the MWCNTs may obscure the peak being sought, or the extent of the degradation caused by high temperature and shear stress was too low and thus the concentration of the functionalities was simply below the sensitivity of the instrument. In addition, reprocessing can break down the polymer chains but does not change the chemical structure significantly.

4. CONCLUSION

Detailed structural and property characterizations suggested that the PC/MWCNT composite had high possibility for reprocessing since most of its properties did not significantly change after six injection molding cycles, except for its mechanical and rheological properties. The PC/MWCNT composite had high thermal stability after reprocessing up to 6 cycles at 235-280\(^\circ\)C. Moreover, the electrical properties and HDT were insignificantly varied. The \(G', G'',\) and \(\eta^*\) decreased with increasing number of injection molding cycles, relating to the increase in MFI values. This indicated a decrease of PC molecular weight due to some degree of the polymer chain scission caused by high shear stress in the injection molding process. The MWCNT structure was not deteriorated by high shear stress during several injection molding cycles since the aspect ratio of MWCNTs remained unchanged. The tensile strength insignificantly increased whereas the elongation at break and impact strength decreased at injection molding cycles of 1-4, and then slightly changed at injection molding cycles of 4-6, corresponding to the dispersion results of MWCNTs in the composite as observed from TEM micrographs. The effect of type and content of antioxidants in the PC/MWCNT composite on rheological properties after reprocessing cycles will be further investigated.
for a better understanding of the degradation mechanism of the nanocomposite.

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