Electrical Conductive CNT-PVA/PC Nanocomposites with High Tensile Elongation

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Electrically conductive CNT reinforced polycarbonate matrix nanocomposites with high strain-to-failure were fabricated by inserting polyvinylalcohol as a surface modifier through a melt blending process. The addition of PVA by coating the CNT through a simple ball milling process before melt blending with a polycarbonate matrix resulted in an increased percolation limit as compared to that prepared using uncoated CNTs, while the electrical conductivity was maintained at a similar level of $2 \times 10^{-2}$ S/cm. However, tensile elongation was considerably improved by the addition of PVA and remained at 81% even though 5 wt% of the CNTs were added for electrical conductivity, while elongation dropped to 25% when the CNTs were not coated with PVA. The addition of PVA induces homogeneous dispersion of CNTs during the melt blending process and can enhance both electrical conductivity and mechanical durability.

Keywords: PVA Coating MWNT, Polycarbonate, Nanocomposites.

1. INTRODUCTION

Carbon nanotubes (CNTs) are considered to provide promising nanosized reinforcement due to their light weight, high aspect ratio, and excellent mechanical, electrical and thermal properties.¹ ² They thus open a new area with high driving force to develop nanocomposites reinforced with CNTs. In particular, CNTs have given rise to the possibility of producing new polymeric materials capable of high mechanical performance and, at the same time, electrical conductivity.³ ⁴

Of the many polymers, polycarbonate (PC) is one of the most important engineering plastics and is widely used for laser optical data storage, optical fibers, membranes and structural parts substituting metals due to its outstanding properties including excellent toughness, dimensional stability, transparency and thermal stability. This wide range of applications of PC can be enlarged by obtaining electrical conductivity. The addition of CNTs is one way to give PC electrical conductivity.⁵ ⁷

Previous studies on CNT/PC nanocomposites, generally prepared by solution blending or melt blending process, have identified the problem of fracture toughness, even though electrical conductivity has been obtained.⁸ ¹¹ Although the addition of CNTs in PC can enhance strength and promote electrical conductivity, the strain-to-failure ratio is considerably degraded and sometimes the PC becomes very brittle. It is generally accepted that this degradation comes from poor dispersion of CNTs within the PC matrix and weak interfacial adhesion between the CNTs and PC matrix. Some modification of interface and dispersion by using epoxide-modified CNTs⁸ or a hybrid composite with P3HT-g-PCL⁹ cannot improve their fracture toughness, and can result in severe brittleness.

Here, we suggest a new melt blending-based process using PVA as an interfacial modifier to disperse CNTs homogeneously and, at the same time, provide sound interfacial strength. The PVA at the interface between CNT and PC can provide much enhanced strain-to-failure in a tensile loading condition, while at the same time having little affects on electrical conduction through CNT networks within the PC matrix. In addition, the CNT/PC nanocomposites can be prepared by means of a simple melt blending process, suitable for mass production, by the addition of a small amount of PVA during the blending step.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The multi-walled CNTs (MWNTs) used in this study were synthesized through the chemical vapor deposition method
by Iljin Nanotech Co. Ltd. Korea. Polyvinylalcohol (Acros Organics, Mw: 88,000) and polycarbonate (Cheil Industries) were used as purchased without further treatment.

2.2. Fabrication Process for CNT-PVA/PC Nanocomposites

For the homogeneous dispersion of CNTs and the sound interface between the CNTs and the PC matrix, PVA-coated CNTs are used following the melt blend process. The PVA coated CNTs were fabricated according to the following process steps. First, the CNTs were dispersed in water by ultra-sonication and an aqueous PVA solution was added to the dispersed CNT while stirring at 80 °C. Second, the mixture was ball milled using zirconia balls for 24 hours. The ball milled solution was then dried in a vacuum oven at 100 °C for 24 hours.

The dried CNT-PVA mixtures were mixed with PC powder and ball-milled again for 24 hours. The ball-milled CNT-PVA/PC mixture powder was melt-blended using a Brabender mixer at 55 rpm at 260 °C for 15 minutes, and hot press at 260 °C to 280 °C.

2.3. Characterization of CNT/Polycarbonate Nanocomposites

The microstructure of CNT/PC nanocomposites was observed by scanning electron microscope (SEM, Hitachi S-4800) after Pt coating by sputter. The mechanical properties of the PC/MWNT composites were investigated by tensile testing according to ASTM D638, using a universal testing machine (Instron 5538). The speed of cross-head movement for the tensile test was 10.0 mm/min, and the averaged value from at least 5 specimens was used. Electrical conductivity measurement was performed using a probe station (Semiconductor Characterization System 4200 SCS/F and Summit 11862B, Keithley and Cascade) in the voltage range of −0.5 V to +0.5 V.

3. RESULTS AND DISCUSSION

3.1. Microstructure and Electrical Conductivity

Coating CNTs with PVA contributes considerably to the homogeneous dispersion of CNTs within the PC matrix in the melt-blending process, as shown in Figure 1. CNT/PC nanocomposites without PVA coating have severely agglomerated CNTs in the PC matrix, which induces a CNT-rich zone and a CNT-free zone. However, with the addition of PVA coated CNTs, where the weight fraction of PVA and CNT is 1:10, the CNTs were homogeneously dispersed within the PC matrix. The role of PVA in dispersing CNTs in molten PC is not clear. However, it could be expected that the coating of a small amount of PVA considerably suppresses the van der Waals force between CNTs during the blending process. It should be noted that the CNTs were not chemically treated for surface functionalization.

It is expected that coating each CNT with PVA degrades the electrical conductivity of CNT-PVA/PC nanocomposites as compared to CNT/PC composites without PVA coating. Actually, the relationship between electrical conductivity and the amount of CNTs added to the CNT/PC or CNT-PVA/PC nanocomposite, shown in Figure 2, indicates that the percolation limit, meaning the minimum CNT content for electrical conductivity, increased as an increasing amount of PVA coated the CNTs. However, the electrical conductivity of CNT-PVA/PC nanocomposites is not much
affected when the amount of CNT added exceeds the percolation limit.

There are several theories on the electrical conductivity of CNT reinforced polymer composites. One of them concerns the quantum tunneling of electrons between CNT networks jumping over the polymer matrix between each CNT. In this theory, the distance between the CNTs should be close to allow electrons to jump between them. The insertion of PVA inhibits this electron movement by inserting an additional barrier between the CNTs. However, the homogeneous dispersion of CNTs within the PC matrix decreases the mean free path of the matrix, i.e., the average thickness of the PC matrix between the CNTs, compensating for the additional PVA barrier. By increasing the CNT content, the CNTs are mechanically connected to each other, ultimately resulting in saturated electric conductivity. It should be noted that the CNTs are not chemically treated except for the PVA coating in the ball milling process. Therefore, CNTs are not severely damaged in maintaining homogeneous CNT dispersion, and saturated electrical conductivity, obtained by keeping the CNTs in contact with each other, shows little differences from the PVA coating.

3.2. Mechanical Properties of CNT-PVA/PC Nanocomposites

The tensile deformation behaviors of CNT-PVA/PC nanocomposites and CNT/PC nanocomposites have shown dramatic differences, as illustrated in Figure 3. In the stress–strain relationship during the tensile test shown in Figure 3, stress increases and reaches a peak level and then decreases rapidly to saturated stress with increasing strain. After reaching saturated value, the stress slightly increases with increasing strain until fracture. The differences in the stress–strain curve in Figure 3, according to the addition of CNT or PVA coated CNT to PC, are shown mainly in elongation. The elastic modules increase from 489 MPa to 555 MPa with the addition of 5 wt% of CNTs and to 564.5 MPa with the addition of 5 wt% of PVA coated CNTs. Peaks stress improved 63.4 MPa to 66.9 MPa with the addition of the same amount of CNT and to 70 MPa with the addition of PVA coated CNTs. However, elongation decreased from 179% to 25% with the addition of 5 wt% of CNTs to PC. Just a 1 wt% addition of CNTs to PC decreases elongation to 65%.

Coating CNTs with a small amount of PVA dramatically enhances the elongation of CNT-PVA/PC nanocomposites. Elongation decreases to 81% with the addition of 5 wt% of PVA coated CNTs, which is a much higher elongation than that of CNT/PC nanocomposites with 1 wt% of uncoated CNTs. When 1 wt% of PVA coated CNTs are added, elongation is maintained 134% as shown in Table I.

Table I. Elongation of CNT/PC nanocomposite and PVA-CNT/PC nanocomposite.

<table>
<thead>
<tr>
<th>Contents of CNTs (wt%)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT/PC</td>
<td>179 ± 4</td>
</tr>
<tr>
<td>1</td>
<td>65 ± 20</td>
</tr>
<tr>
<td>2</td>
<td>38 ± 5</td>
</tr>
<tr>
<td>5</td>
<td>25 ± 2</td>
</tr>
<tr>
<td>PVA-CNT/PC</td>
<td>134 ± 0.74</td>
</tr>
<tr>
<td>1</td>
<td>116 ± 15.1</td>
</tr>
<tr>
<td>2</td>
<td>81 ± 0.27</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

The enhancement of elongation by coating CNTs with PVA is more clearly apparent in the relationship between peak stress and elongation shown in Figure 4. In the case of CNT/PC nanocomposites, elongation decreases rapidly with increasing peaks stress, and is maintained at high values in the case of CNT-PVA/PC nanocomposites.

The role of PVA in the enhancement of elongation is not clear because only a small amount of PVA is added...
Electrical Conductive CNT-PV A/PC Nanocomposites with High Tensile Elongation  

Jung et al.

4. CONCLUSIONS

In this study, CNTs were coated with PVA through a ball milling process and PVA-CNT/PC nanocomposites were fabricated by a melt blending process. The electrical, morphological and mechanical properties of the PVA-CNT/PC nanocomposites were investigated by electrical conductivity, SEM, and tensile strength measurements.

From the results of the morphology of the PVA-CNT/PC nanocomposites, it was observed that the CNTs were dispersed homogeneously in the PC matrix. The percolation threshold of the PVA-CNT/PC nanocomposite was shown to be in the range of 1 wt% to 2 wt% of the CNTs. The electrical conductivity of the 5 wt% PVA-CNT/PC nanocomposite was about $2 \times 10^{-2} \, \text{S/cm}$, which was almost the same as that of the 5 wt% CNT/PC nanocomposite. This is because the PVA film on the surface of the CNTs inhibits electron movement by imposing an additional barrier between the CNTs. However, as the CNT content increases, the CNTs become connected to each other and finally lead to saturated electric conductivity.

The mechanical properties of PVA-CNT/PC nanocomposites increased with increasing volume fraction of adding CNTs. Young's modulus of the PVA-CNT/PC nanocomposite was increased from 489.1 MPa to 564.3 MPa by increasing the carbon nanotube content from 0 wt% to 5 wt%. Tensile strength of the PVA-CNT/PC nanocomposite was increased from 63.37 MPa to 66.99 MPa. The elongation of 5 wt% PVA-CNT/PC nanocomposite showed a very high elongation of 81%. It is suggested that the homogeneous dispersal of the CNTs prevents stress concentration within the PC matrix, which induces fracture during tensile loading. The morphology of the fractured surface of the CNT-PVA/PC nanocomposites does show evidence of strong bonding between the CNTs and the PC matrix. Therefore, it can be expected that the PVA at the interface also enhances interfacial bonding strength.

From the above results, PVA-CNT/PC nanocomposite can be a good candidate as an advanced electronic material such as ESD and EMI shielding materials due to its high electrical conductivity, strength, modulus, and elongation.

Acknowledgments: This research was supported by a grant (KFR-2007-313-D00362) from the Korea Research Foundation and also partly supported by Nano R&D program through the Korea Science and Engineering Foundation funded by the Ministry of Science and Technology (Grant 2008-02631).

References and Notes

Jung et al. Electrical Conductive CNT-PVA/PC Nanocomposites with High Tensile Elongation


Received: 26 August 2009. Accepted: 28 December 2009.