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Effects of matrix viscosity, mixing method and annealing on the electrical conductivity of injection molded polycarbonate/MWCNT nanocomposites

Jinguang Kim, Younggon Son*

Division of Advanced Materials Science and Engineering, College of Engineering, Kongju National University, Cheonan, Chungnam 331717, Republic of Korea

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ABSTRACT

Effects of the compounding equipment, the viscosity of the matrix, and the annealing on the electrical resistivity of polycarbonate (PC)/MWCNT nanocomposites were investigated. Two different types of compounding equipment (a batch mixer and a twin screw extruder) produced a huge difference in the resistivity in an injection molded PC/MWCNT nanocomposite while the resistivity of compression molded samples showed only small differences. It was also observed that the viscosity of the PC matrix affected the resistivity of the injection molded nanocomposites to a great extent. The resistivity of the nanocomposites increased with the viscosity of the PC matrix. This is attributed to two factors. When the PC/MWCNT nanocomposites are fabricated, interpenetration of the PC matrix into MWCNT bundles is easier for a less viscous matrix. Another factor is that lower viscosity PC induces less orientation of MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) have attracted widespread interest as a reinforcing material for polymer based nanocomposites due to their unique mechanical, electrical, and thermal properties. During the past two decades, a large number of studies have been conducted on various aspects of polymer/CNT nanocomposites, including their electrical, rheological, and mechanical properties [1–4]. Although pristine CNTs have outstanding mechanical properties, the incorporation of CNTs into a polymer provides only a slight increase in the mechanical properties due to several reasons. One of the reasons is that CNTs are not easily dispersed in the polymer matrix but instead exist as agglomerates, leading to insufficient mechanical bonding across the CNT/polymer interface.

On the other hand, the electrical conductivity of a polymer can be remarkably increased by the incorporation of CNTs in small quantities due to the high aspect ratio of the CNT structure [1]. Accordingly, industrial interest in CNT has focused on the electrical conductivity of the polymer/CNT nanocomposites rather than their mechanical properties. In particular, conductive composites can be applied to antistatic, electrostatic dissipative (ESD), and electromagnetic interference (EMI) shielding applications [5].

It is well understood that the percolation threshold, where the conductivity shows a dramatic increase upon a small increment of the conductive filler loading, is influenced by the aspect ratio of the conductive fillers [6]. Since the filler network or interconnecting structure is established at relatively low concentrations of a filler with a high aspect ratio, the percolation threshold point decreases with the aspect ratio. CNTs, which often have an aspect ratio over 500, therefore show a much lower percolation threshold point (<volume fraction of 0.004) than other conductive fillers such as carbon black (>0.1) and carbon fiber (0.05–0.1).

Until recently it was not believed that the electrical percolation threshold point of polymer/CNT nanocomposites is affected by the polymer processing method [7–11]. Abbasi et al. investigated the effects of processing methods including compression molding, injection-compression molding, and injection molding on CNT alignment and on the electrical properties of polycarbonate/CNTs nanocomposites [9]. They observed that the degree of CNT alignment is greatly affected by the processing method and CNTs are preferentially aligned to the flow direction. By estimating effective shear rates for each processing method, it was shown that the CNT alignment increased with the effective shear rate. When the CNTs are aligned, the probability of tube–tube contact decreases [8], and consequently a high degree of alignment results in a significant increase in the electrical percolation threshold. Villmow et al. [10]

* Corresponding author.
E-mail address: songy@kongju.ac.kr (Y. Son).

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investigated the influence of injection molding conditions on the electrical conductivity of PC/multiwall carbon nanotube (MWCNT) nanocomposites. They found that the highest influence on the electrical conductivity was the injection velocity followed by the melt temperature. Holding pressure and mold temperature were found to have only very slight influences. Transmission electron microscopic (TEM) investigations revealed that a high injection velocity led to a highly orientated skin layer with well-separated MWNTs, which provides electrical insulation due to the absence of tube–tube contact. Several other works on the effects of high speed polymer processing on the electrical conductivity of polymer/MWCNT nanocomposites have also been reported, and the findings were summarized in a recent review paper [12].

Polycarbonate (PC) is an important commercial engineering plastic for various electronic goods such as mobile phones and high definition televisions. PC manufacturers are very interested in PC/CNT nanocomposites to expand the usage of PC to ESD and EMI shielding applications. Since the injection molding method is the only choice in these applications due to the demands of mass production, clear understanding of the relationship between the injection molding conditions and the electrical conductivity of the PC/CNT nanocomposite is an important research topic. Numerous studies have been carried out on PC/MWCNT nanocomposites processed by high speed polymer processing such as an injection molding process. Two theories have been elaborated to explain the reduced electrical conductivity of PC/MWCNTs by high speed polymer processing. These two theories will be discussed in the 'Results and Discussion' section of this paper with our experimental results and we provide evidence supporting one theory in particular.

We also investigated various factors affecting the electrical conductivity of injection molded PC/MWCNT nanocomposites, including the compounding equipment, the viscosity of the matrix, and the incorporation of third components, aspects that have not yet been studied. We believe that this information will be helpful to reduce the amount of CNT loading in the nanocomposite while maintaining the same level of conductivity. Since high electrical conductivity with a small amount of CNT loading is desirable from an economical perspective, the findings of this study will be valuable to the research and industrial communities.

2. Experimental

Materials: The MWCNTs used in this study were purchased from Nanocyl (trade name: NC7000, diameter; 9.5 nm, length; 1.5 μm, carbon purity > 90%). They are produced by thermal chemical vapor deposition and directly used without further treatment. Polycarbonates (PCs) with three different molecular weights were obtained from Cheil Industries Inc. Characteristics of the PCs are summarized in Table 1.

Preparation of the nanocomposites: PC/MWCNT nanocomposites were prepared in an internal batch mixer (at a rotor speed of 100 rpm for 10 min) and a twin screw extruder (at a speed of 150 rpm.) at 280 °C. Prior to mixing, the PC and MWCNTs were dried at 110 °C in a vacuum oven for a day. The batch mixer used was a Brabender batch mixer W30 EHT (Brabender® GmbH & Co., Germany). The extruder was a co-rotating twin screw extruder (BA-11, BAUTEK Com., Republic of Korea) with a screw length of 440 mm and a screw diameter of 11 mm. Table 2 shows the notation and compositions of the prepared nanocomposites.

Sample preparation: Compression molding and injection molding were employed to investigation the effects of processing on the electrical properties of the PC/MWCNT nanocomposites. Prior to each processing, the PC/MWCNT nanocomposites were dried in an air circulating oven at 110 °C for 24 h. Compression molding was performed using a laboratory press at 270 °C. Each disc shaped sample of 25 mm diameter and 1.5 mm thickness was cooled to room temperature. For injection molding, a laboratory scaled injection molding machine was used at various injection speeds, temperatures, and mold temperatures. Dried samples were then injection-molded into rectangular plates (13 mm × 65 mm × 2 mm).

Characterization: The surface resistivities of the samples were measured by using two resistivity meters (SRM-110, Wolfgang Warmbier, Ltd, Germany for a high resistance range $>10^6$ Ω/sq and LLORESTA-UP, Mitsubishi-Chemicals for a low resistance range $<10^6$ Ω/sq.). Because the surface resistivity is very sensitive to temperature and humidity, all measurements were conducted at 23 °C, 50% RH according to ASTM D257. Each sample was cleaned with ethanol prior to measurements.

The glass transition temperatures (Tg) of pure PC, PC/MWCNT nanocomposite (both compression molded and injection molded), and purified PC were determined by a differential scanning calorimeter (DSC Q20™, TA Instrument) under a nitrogen atmosphere. First, the samples were heated at 200 °C and maintained for 5 min to erase the thermal history. The samples were then cooled to room temperature quickly, equilibrated for 3 min, and heated to 200 °C at a rate of 10 °C/min.

The purified PC is the sample from the PC/MWCNT composite after removal of MWCNTs. 1 g of PC/MWCNT4 nanocomposite was dissolved in 10 ml of THF. The solution was centrifuged at 5000 rpm in a centrifuge (Model Hanil Fleta5) for a day. The supernatant of the centrifuge tube was removed by a syringe and filtered through a syringed filter (Thermo Scientific Nalgene™ 50 mm Inline Syringe Filter with PTFE Membrane, pore size = 0.22 μm). The solution was dried and then purified PC was obtained.

Complex viscosities (η^*) as a function of frequency (ω) were determined with a strain-controlled rheometer (Physica MCR301 from Anton Paar) in dynamic oscillatory mode with a parallel-plate configuration of 25 mm diameter and 1 mm gap size at 280 °C.

Table 1
Characteristics of PC used in this study.

Index	Grade name	M_n (g/mol)	M_w (g/mol)	PDI	η_0 at 280 °C[a] (Pa s)
PC-L	SC1620	17,200	27,600	1.60	185
PC-M	SC1280	23,700	37,200	1.57	340
PC-H	PTULG	29,000	38,100	1.31	610

[a] η_0: Zero shear viscosities.

3. Results and discussion

3.1. General theories on the effect of high speed processing

A number of groups have studied the effects of high speed

Table 2
Index and composition of the PC/MWCNT nanocomposites.

Index	PC-L	PC-M	PC-H	MWCNT	LCP
PC-**L/MWCNT0.5**	99.5	0	0	0.5	0
PC-**L/MWCNT1**	99	0	0	1	0
PC-**L/MWCNT2**	98	0	0	2	0
PC-**L/MWCNT4**	96	0	0	4	0
PC-**M/MWCNT0.5**	0	99.5	0	0.5	0
PC-**M/MWCNT1**	0	99	0	1	0
PC-**M/MMWCNT2**	0	98	0	2	0
PC-**M/MWCNT4**	0	96	0	4	0
PC-**H/MWCNT0.5**	0	0	99.5	0.5	0
PC-**H/MWCNT1**	0	0	99	1	0
PC-**H/MMWCNT2**	0	0	98	2	0
PC-**H/MWCNT4**	0	0	96	4	0