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Polycarbonate carbon nanofiber composites

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Abstract

Carbon nanofiber (CNF) composites have the potential for creating inexpensive, semiconducting polymers. These composites require a homogeneous dispersion within the polymer. Many groups have focused on high shear methods such as twin screw extrusion. Although high shear methods produce a homogeneous dispersion, the aspect ratio of the nanofibers is reduced by the mechanical force. In this report, we present results for low shear composite formation via in situ polymerization of cyclic oligomeric carbonates. The composites were characterized by thermal gravimetric analysis, electrical conductivity, scanning electron microscopy and transmission electron microscopy. The composites exhibit minimal aggregation of the carbon nanofibers even at high weight percents. The polycarbonate/CNF composites exhibit an electrical conductivity percolation threshold of 6.3 wt% which is higher compared with similar CNF composites. The composites also show an increase in thermal stability of 40 °C as the CNF loading increases from 0 to 9 wt%.

Keywords: Ring-opening polymerization; Nanocomposites; Carbon nanofibers

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1. Introduction

Polymers are designed for specific applications based on their structure and properties. Often a polymer requires modification for a greater range of applications that may require different structural or physical properties [1,2]. One modification method is the addition of a filler to create a composite where the polymer may exhibit improvements in mechanical strength, electrical conductivity, or thermal stability [3–5]. Carbon nanofibers (CNF) and nanotubes (CNT) have been used to modify several polymers including poly(propylene) [6–8], poly(methyl methacrylate) [9,10], poly(ethylene terepthalate) [11], poly(styrene) [12] and poly(carbonate) [4,7,13]. The advantage of CNFs compared to conventional fillers like carbon black and silica is the higher aspect ratio [1,4]. The high aspect ratio is important for mechanical and electronic applications.

Ring-opening polymerization (ROP) of cyclic polycarbonate oligomers has been previously used to make polymer/clay nanocomposites [14]. The advantages of this process include the low viscosity of the cyclic oligomers, the lack of volatiles and better control over the molecular weight [14]. Several research groups have thermally polymerized bisphenol A polycarbonate oligomers in a twin screw extruder with CNFs [4,7,9,13]. Most well dispersed, electrically conductive and thermally stable materials are made by high shear methods like twin screw extrusion [4,7,13]. High shear methods are efficient at making a well dispersed sample; however, the aspect ratio of the CNFs are significantly reduced.

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The reduction of the CNF aspect ratio leads to decreased mechanical properties and conductivity. Although a homogeneous dispersion is obtained with high shear methods and a percolation threshold between 1 and 2 wt% for PC–MWNT composites [4] or 5–10 wt% for PC–CNF composites [7] has been reported, the length of the CNT decreases from 1 μm to 200 nm [13]. The resistivity for the PC–CNF samples decreases from 10^{16} to 10^{6} Ω cm [7]. We propose that low shear methods combined with ROP will produce a PC/CNF composite that exhibits improved conductive and physical properties.

2. Experimental

2.1. Materials

All materials were used as received unless otherwise noted. Poly(bisphenol A carbonate) oligomers were obtained from Cyclics Corporation. Tetrabutylammonium tetraphenylborate (99%) was obtained from Aldrich. Methylene chloride was obtained from Fisher Scientific. Polygraf III (PR-19-HHT-LD) carbon nanofibers were used as received from Applied Sciences, Inc. Conductive silver paint was obtained from SPI Supplies. The probe sonicator was an Autotune Series High Intensity Ultrasonic Pricessor Model GE130.

2.2. Characterization

Resistivity measurements were made using the four point probe technique with a Keithley Model 6514 system electrometer and a HP 6112A DC power supply. Melt pressing was done with a Hakke heated press. Thermal gravimetric analysis measurements were made using a Hi-Res TGA 2950 thermogravimetric analyzer (TA instruments) in the temperature range of 25–900 °C and at a heating rate of 20 °C/min in air. Scanning electron micrographs (SEM) were made by freezing substrates in liquid nitrogen, mounting, and using SPI Sputter™ Model 12121 for ion sputter coating with platinum. SEM images were taken using a JEOL JSM-5300 Scanning Microscope. Transmission electron micrographs (TEM) were made using a FEI Technai 12; samples were prepared by imbedding samples in epoxy and microtoming to a thickness of less than 60 nm.

2.3. In situ ring-opening polymerization

Typically, 10 g of polycarbonate cyclic oligomer and the appropriate weight percent of carbon nanofibers were weighed out. The carbonate oligomer and CNF were ground together with a mortar and pestle until a homogeneous dispersion was observed. The homogeneous mixture was put into a test tube and warmed to melt the oligomers. The warmed mixture was sonicated at 40% amplitude (12 output watts) for 15 min and allowed to cool to room temperature. Tetrabutylammonium tetraphenylborate (44 mg; 0.4 wt%) was dissolved in 5 mL methylene chloride. The methylene chloride mixture was added to the oligomer/CNF mixture and the sample was sonicated again at the same amplitude for 15 min. The tube was put under vacuum and placed into a sand bath at 80 °C overnight to remove the solvent. The ring-opening polymerization was conducted for 30 min at 285 °C in vacuo. The tube was broken and the sample removed for characterization and testing.

2.4. Melt pressing

The powdered samples of polycarbonate/CNF were put into a mold and subjected to a pressure of 15–20 tons between 325 and 365 °F. Approximately 1 h melt pressing times were used for all of the samples.

2.5. Resistivity testing

The pressed samples were coated with silver paint where the probe tips touched the sample and put into the four point conductivity apparatus with 1 V through the samples. The current and voltage were measured, and using the following equations the resistivity in ohm cm was calculated. (R = resistance, V = voltage, I = current, ρ = resistivity, ω = width of sample, τ = thickness of sample, l = length between inner probes.)

$$R = V/I$$

$$\rho = (R^{*}\omega^{*}\tau)/1$$

3. Results

To improve dispersion for in situ polymerized composites, many groups have used high shear methods like twin screw extrusion [4,12]. This method decreases the aspect ratio of the carbon nanotubes or carbon nanofibers [7]. The decreased aspect ratio will decrease the network formation of the CNF within the composites and raise the percolation threshold for conductivity. In this research we have used low shear methods and probe sonication to increase the dispersion and minimize the reduction of the aspect ratio of the nanofibers. We have combined this with the ring-opening polymerization of cyclic polycarbonate oligomers.

Fig. 1 depicts the synthesis of the polycarbonate/CNF composites. The cyclic oligomers were mixed with the carbon nanofibers prior to addition of the tetrabutylammonium tetraphenylborate catalyst. Following the ring-opening polymerization, the samples were black solids except for the sample containing no CNF.