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European Polymer Journal 41 (2005) 889–893
EUROPEAN POLYMER JOURNAL
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# Polycarbonate carbon nanofiber composites

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Received 21 November 2004; accepted 27 November 2004
Available online 26 January 2005

**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

## 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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doi:10.1016/j.eurpolymj.2004.11.040

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 $10^{6}\,\Omega\,cm$ [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, $\rho$ = resistivity, $\omega$ = width of sample, $\tau$ = 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.

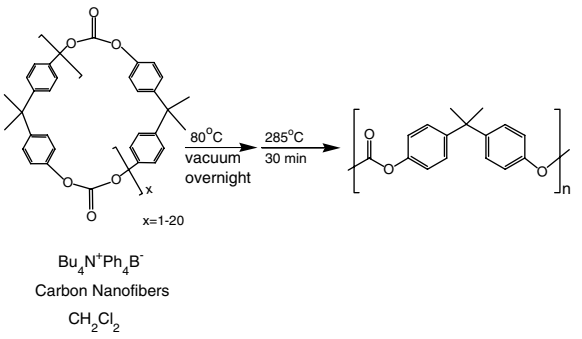


Fig. 1. Ring-opening polymerization of PC/CNF composites.

Thermal gravimetric analysis (TGA) verified the amount of CNF present in the composites. TGA (Fig. 2) analysis also demonstrated a slight increase in the thermal stability of the CNF composites with increasing CNF content. At 9 wt% CNF the 5 wt% loss of the polycarbonate occurred at a temperature of 382 compared with 379 °C for the control sample containing 0 wt% CNF. The secondary decomposition of the polycarbonate had a more significant difference between 9 and 0 wt % from 577 to 512 °C respectively. In some polymer–CNF or polymer–CNT composites, the increase in thermal stability has been attributed to restricted macromolecule mobility imposed by the CNFs [8,10].

The conductivity results in Fig. 3 show a percolation threshold at 6.3 wt%. The increase in conductivity is 5 orders of magnitude between the 6.3 ($10^8$ Ω cm) and 9 wt% ($10^3$ Ω cm) CNF, and the increase is 8 orders of magnitude compared to 0 wt%. The percolation threshold reported by Hammel et al. [7] for CNF/PC composites formed by high shear methods was between 5 and 10 wt% and only dropped to $10^6$ Ω cm.

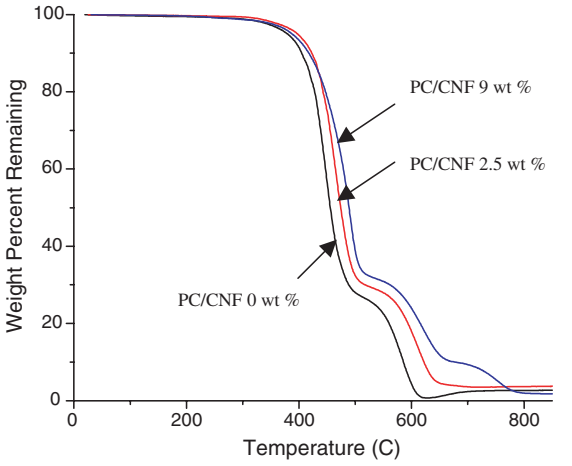


Fig. 2. TGA results for the PC/CNF composites, only 0, 2.5 and 9 wt% are shown for simplicity.

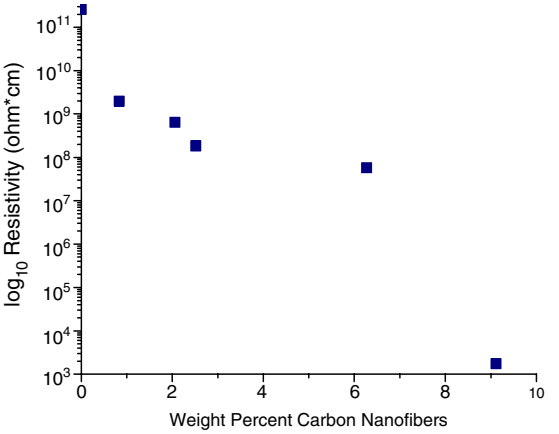


Fig. 3. Resistivity results for the PC/CNF composites.

TEM and SEM analysis is depicted in Figs. 4 and 5. The TEM (Fig. 4) shows the dispersion of CNF in a matrix of polycarbonate for 1 wt%, 6.3 wt% and 9 wt%. The SEM images (Fig. 5) correspond to the same weight percents and show the CNF emerging from the fractured surface.

## 4. Discussion

### 4.1. Thermal stability

Fig. 2 indicates a 40 °C increase in the thermal stability as the fiber loading increased from 0 to 9 wt%. This is not a large increase in the thermal stability, but is consistent with literature results on polymer–CNF composites [8,10]. A likely interaction is π–π stacking of the CNF aromatic groups and the phenyl groups in the backbone of the polycarbonate. The decomposition of the PC/CNF composites occurs in three steps. The first process occurs at approximately 375 °C, the second at approximately 500 °C, and both are due to the decomposition of the PC. The final decomposition occurs between 620 and 640 °C and is due to the breakdown of the CNF.

### 4.2. Dispersion and network formation

The dispersion can be deduced by analysis of the TEM and SEM images in Figs. 4 and 5. The 1 wt% sample displays single CNFs in both the SEM and TEM images (Figs. 4a and 5a) consistent with uniform dispersion. The SEM of the 6.3 wt% CNF (Fig. 5b) composite shows single CNFs. In the TEM image in Fig. 4b, most CNFs appear to be dispersed singly; however, there appears to be some aggregate formation on the composite surface that we speculate corresponding to 2–3 CNFs per aggregate, compared with multiple CNFs aggregates in the TEM image of CNFs alone (Fig. 6). We also observed a shortening of the CNF from the initial 30–

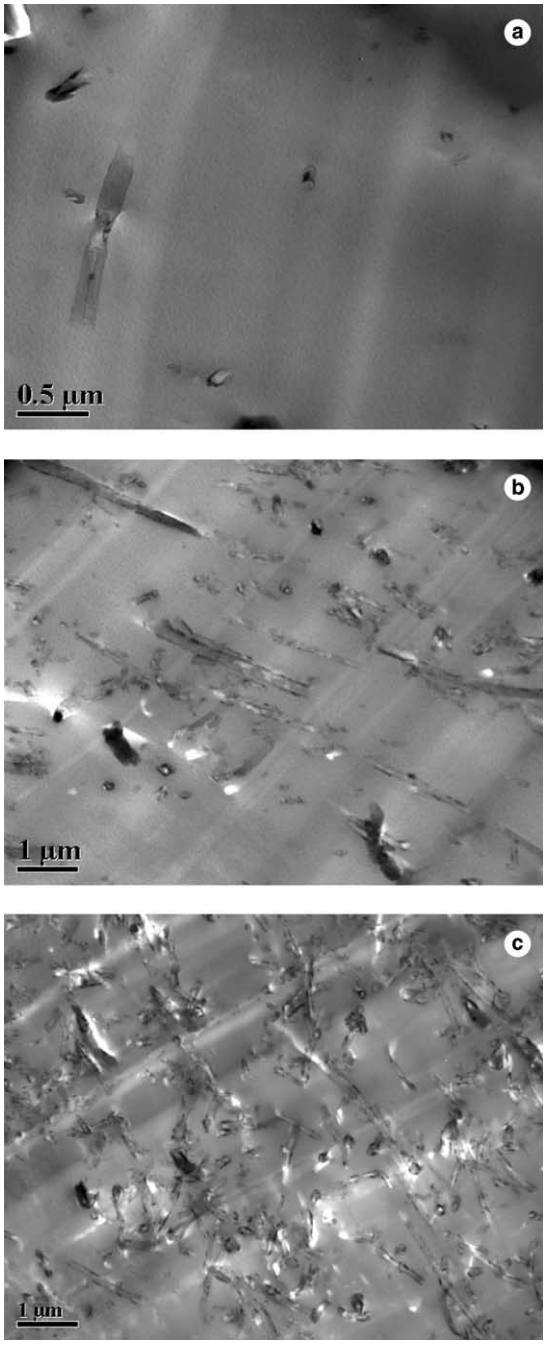


Fig. 4. TEM of PC/CNF composites (a) 1 wt%, (b) 6 wt%, (c) 9 wt%.

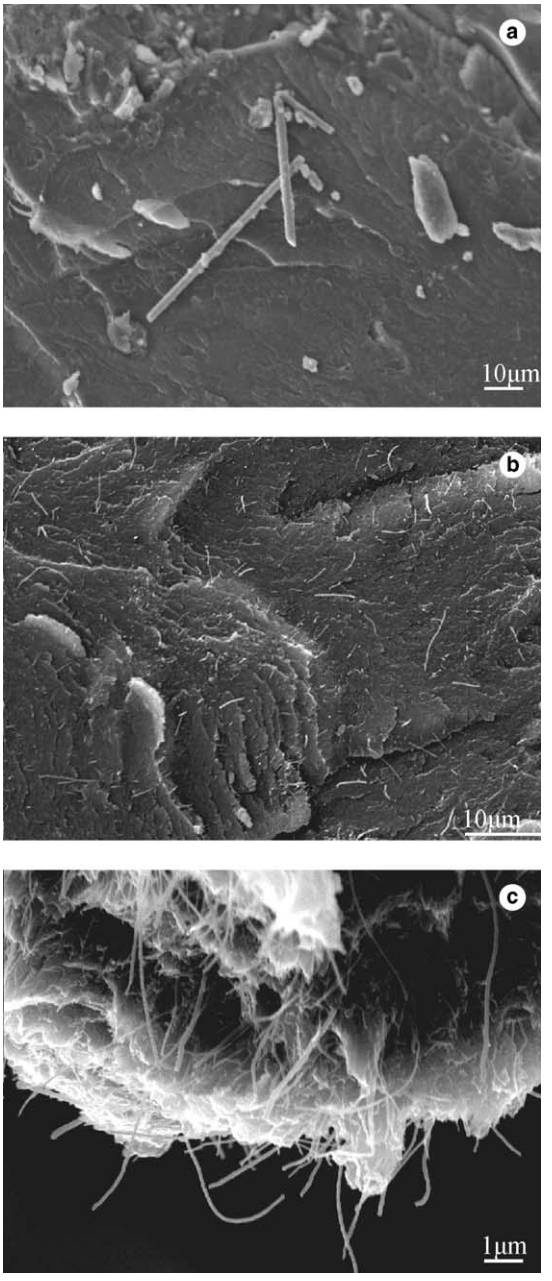


Fig. 5. SEM of PC/CNF (a) 1 wt%, (b) 6 wt%, (c) 9 wt%.

100 μm length reported by Applied Sciences, Inc. to 5–10 μm after composite fabrication. We speculate that this shortening occurs during sonication or grinding with the mortar and pestle. Undoubtedly this shortening of the CNF has affected the network formation and the percolation threshold. The lengths observed in this research are significantly larger than the high shear methods where after 10 min of mixing in a twin screw extruder the nanotube length decreases from 1 μm to 500 nm [13]. Although there is still some aggregation in the 9 wt%, the CNF appear to be uniformly dispersed throughout the sample and a network formation is observed in the TEM (Fig. 4c). We have defined a 'network' when it appears that all of the CNFs overlap throughout the sample. This network formation is criti-

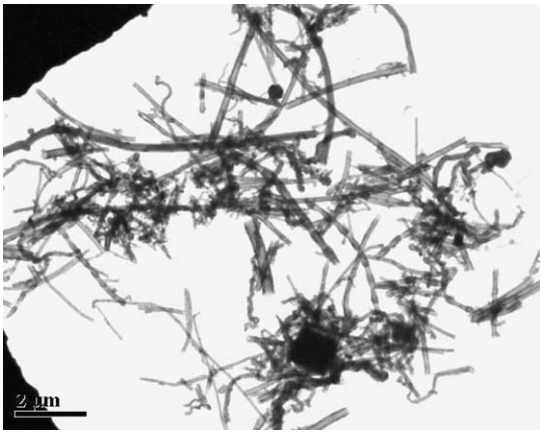


Fig. 6. Initial starting CNF sonicated for 30 min in ODCB. Average length approximately 10–20 μm.

cal for good conductivity. In the 1 wt% CNF sample (Fig. 4a) the network formation has not formed because we do not observe overlapping of CNFs.

### 4.3. Percolation threshold

The reason that the conductivity percolation threshold of these samples is high may be due to a lower aspect ratio of the CNF compared with the CNT used in other research groups [4] or the averaging of the concentric carbon shells on the CNF. SWNT and MWNT are typically synthesized so that the walls are conductive or semiconducting leading to a low percolation threshold. CNF have a larger diameter and more walls of carbon. The walls could be conducting, semiconducting, insulating, or a combination of all three. Therefore, CNFs are intrinsically less conductive than either SWNTs or MWNTs. This is also true for carbon black composites which also require a larger weight percent of filler to display conductivity.

## 5. Conclusion

Compared to high shear methods, the percolation threshold is higher for the samples in this research; the composites do not become semiconducting until 9 wt% of CNF. We speculate that while our method better preserves the aspect ratio of the CNFs, we obtain a less uniform dispersion compared to high shear methods. We observed an increase in thermal stability that suggests an interaction between the CNF and the PC matrix. SEM and TEM analysis indicates that the CNFs are homogenously dispersed. TEM of the 9 wt% CNF composite indicates a continuous network consistent with the low resistivity of these samples.

## Acknowledgments

This research was supported by the DURINT on Microstructure, Processing and Mechanical Performance of Polymer Nanocomposites, Air Force Contract No. F49620-01-1-0447. The authors also thank Applied Science, Inc. for samples of carbon nanofibers.

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