

# Preparation and Properties of Cyclic Olefin Copolymers Multiwalled Carbon Nanotube Nanocomposites

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**ABSTRACT:** Nanocomposites of cyclic olefin copolymer (COC) and two types of multiwalled carbon nanotubes (MWCNTs) with different aspect ratios were prepared. The morphology, thermal behavior, and electrical conductivity of the nanocomposites were investigated by scanning electron microscopy, differential scanning calorimetry, thermal gravimetric analysis, and the DC conductivity measurement. It was found that the developed nanocomposite preparation method resulted in good nanotubes dispersion in the polymer matrix for both types of MWCNTs. No appreciable differences in glass transition temperatures were observed between the pure COC and nanocomposites. On the other hand, CNTs significantly

improved the thermo-oxidative stability of the COC. The nanocomposites showed significant delay in onset of degradation and the degradation temperature was  $\sim 40^\circ\text{C}$  higher than that of the pure COC. The nanocomposites also showed substantially higher DC conductivity, which increased with the nanotube concentration and aspect ratio. An increase of DC electrical conductivity over  $10^9$  times can be achieved by the addition of 2 wt % CNTs. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** cyclic olefin copolymer; carbon nanotubes, nanocomposites; thermal properties; electrical conductivity

## INTRODUCTION

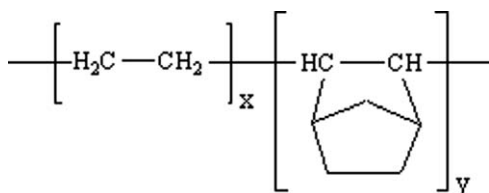
Recently, polymer nanocomposites have attracted a great deal of research interest because of the potential properties enhancement by incorporation of nanosized particles into the polymer matrices. Among a myriad of nanoparticles, carbon nanotubes (CNTs) are among the most promising as they possess excellent physical properties such as extremely high mechanical strength and stiffness, high electrical, and thermal conductivity.<sup>1</sup> The polymer nanocomposites are further benefited by the low density and high aspect ratio (thereby high reinforcement efficiency) of the CNTs. To date, a great variety of polymer/CNTs nanocomposites have been prepared with improved properties, e.g., stiffness,<sup>2–4</sup> toughness,<sup>4–6</sup> dimensional stability,<sup>7</sup> thermal stability,<sup>8,9</sup> flammability,<sup>9,10</sup> electrical conductivity,<sup>11–14</sup> etc, when compared to the neat polymers.

Cyclic olefin copolymers (COCs) are thermoplastics prepared from the copolymerization of cycloolefin (typically norbornene and its derivative) and

olefin (ethylene or propylene).<sup>15</sup> By controlling the COCs chemical compositions and microstructures, a wide range of properties has been realized. As a relatively new group of thermoplastic materials, the interest in COCs has steadily increased. The present COCs are primarily being explored as materials for optical data storage, lenses, packaging, medical devices, etc,<sup>16,17</sup> taking advantage of their exceptional optical transparency. COCs also possess good mechanical properties, high glass transition temperatures and high thermal stability, low dielectric constants and dielectric loss, excellent chemical resistance, low moisture uptake, and good barrier properties. In particular, the combination of excellent mechanical and thermal properties make them viable alternative to polyolefins. They have been used in nonoptically related applications, such as housings, gears, powder coatings, toner binder resin, and filter media for air and other gases.<sup>18,19</sup>

Further improving the properties of COCs by using nanoparticles is an intriguing approach but to date studies concerning with the preparation and characterization of COCs nanocomposites are scarce. Ou and Hsu prepared COC silica nanocomposites using solution blending and the nanocomposites exhibited higher glass transition temperature,<sup>20,21</sup> higher decomposition temperature, and significantly

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**Figure 1** Chemical structure of cyclic-olefin copolymer (COC).

reduced oxygen permeability.<sup>20</sup> Wu and Wu prepared COC nanoclay nanocomposites via solution blending and observed increased storage modulus and reduced water permeability in the nanocomposites.<sup>22</sup> Nanocomposites were also prepared by melt compounding using polyhedral oligomeric silsesquioxanes (POSS) COC<sup>23</sup> and fumed silica COC.<sup>24</sup> To the best of our knowledge, there is no report on the study of COC CNTs nanocomposites despite the great potential these nanocomposites might possess.

In this study, we prepared COC nanocomposites using two types of multiwalled carbon nanotubes (MWCNTs) with comparable diameters but significantly different lengths. The effects of CNTs aspect ratio and concentration on the nanocomposites morphology, thermal, and electrical behavior were investigated. Although these nanocomposites are not suitable as optical materials, the enhancement of other properties through the incorporation of CNTs is beneficial to expand the use of COCs in other applications where optical clarity is not of critical importance.

## EXPERIMENTAL

### Materials

The COC used in the study (Topas 6017) was kindly supplied by the manufacturer (TOPAS Advanced Polymers, Florence, KY). It is a copolymer of ethylene and norbornene. A schematic of the copolymer is shown in Figure 1. The norbornene content was 82 wt % according to the manufacturer. The molecular weights were determined by gel permeation chromatography (PL-GPC220, Polymer Lab, Santa Clara, CA). Measurements were performed at 423.15K with 1,2,4,-trichlorobenzene as the solvent. The weight-average and number-average molecular weights were  $2.14 \times 10^5$  g/mol and  $1.05 \times 10^5$  g/mol, respectively. 1,2-Dichlorobenzene (*o*-DCB, pu-

rity 99%) and ethanol (purity  $\geq 99.5\%$ ) were purchased from Aldrich (St. Louis, MO) and used as received. Two types of multi-walled carbon nanotubes (MWCNTs) were used for the nanocomposites preparation, Nanocyl 3101 (Nanocyl Inc., Sambreville, Belgium) and Flotube 7000 (CNano Inc., San Francisco, CA). The characteristics of the two MWCNTs are summarized in Table I. Flotube 7000 (denoted as LMWCNTs) is a pristine nanotube and has a significantly larger average tube length and aspect ratio than the Nanocyl 3101. On the other hand, the Nanocyl 3101 (denoted as SMWCNTs) is pre-functionalized with carboxylic groups.

### Preparation of nanocomposites

Nanocomposites with three different nanotubes concentrations (0.5 wt %, 1 wt %, 2 wt %) were prepared by the antisolvent precipitation method.<sup>25</sup> COC was firstly dissolved in the *o*-DCB to form a homogeneous solution. Separately an appropriate amount of nanotubes were suspended in *o*-DCB (0.25 mg/ml) and sonicated for 4 hours using a probe sonicator (Misonix Sonicator 3000, Farmingdale, NY). The COC solution was then added to the CNT suspension and sonicated for additional 30 min. Subsequently, the mixture was dropwise added to large quantity of ethanol under vigorous stirring. The nanocomposites precipitated from the solvent and were collected by filtration. They were further dried in vacuum oven under elevated temperature to remove the residual solvent.

### Characterization of nanocomposites

#### Carbon nanotube dispersion

Dispersion of the CNTs in the polymer matrix was observed by scanning electron microscopy (SEM, JOEL JSM-7401 F, Tokyo, Japan). Samples were firstly freeze-fractured in liquid nitrogen before mounted on stubs and sputter-coated with a thin gold layer. Images were obtained using an accelerating voltage of 10 kV and a working distance of 8 mm.

#### Glass transition temperature

The glass transition temperatures ( $T_g$ ) of the COC and nanocomposites were measured by differential

**TABLE I**  
Characteristics of Multi-Walled Carbon Nanotubes (MWCNTs)

Supplier	Carbon purity	Average diameter (nm)	Average length ( $\mu\text{m}$ )	Aspect ratio
NANOCYL <sup>TM</sup> NC3101	>95%	9.5	1.5	~ 160
CNano Flotube 7000	95.3%	8.5	40–80	>4500

scanning calorimetry (DSC) (DSC Q100, TA Instruments, New Castle, DE) in nitrogen atmosphere. Samples were thoroughly dried before measurement. To remove the thermal history, samples were first heated to 250°C at a rate of 10°C/min before cooling down 25°C at a rate of 10°C/min. Subsequently, a second heating was conducted from which the  $T_g$  was determined. For each sample, three measurements were conducted and the average was taken as the sample  $T_g$ .

#### Thermal stability

To study the effect of the CNTs on the thermal stability of the polymer, thermal gravimetric analysis (TGA) were performed (TGA Q50, TA Instruments, New Castle, DE) from room temperature to 800°C under both nitrogen and air atmosphere, using a rate of 10°C/min.

#### Electrical conductivity

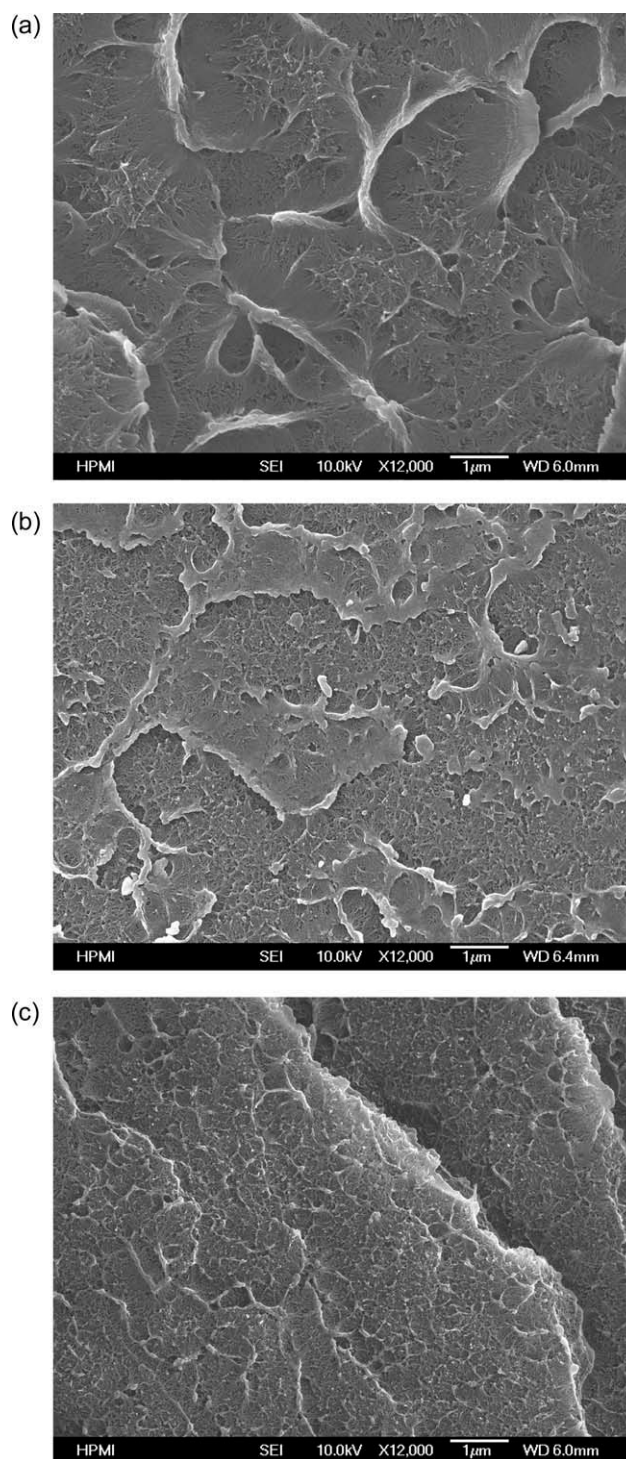
Standard two-probe method was used to measure the electrical conductivity. Samples (disks with diameter of 25.4 mm and thickness of 1mm) were prepared by compression molding at 260°C using a Carver Laboratory Press (Wabash, Wabash, IN). Before measurement both sides of the disk sample were coated with conductive adhesive and connected to an electrometer (Keithley 6514, Keithley Instruments Inc., Cleveland, Ohio) by silver wires. A minimum of three measurements was conducted for each sample to calculate the average value.

## RESULTS AND DISCUSSION

### Nanocomposites morphology

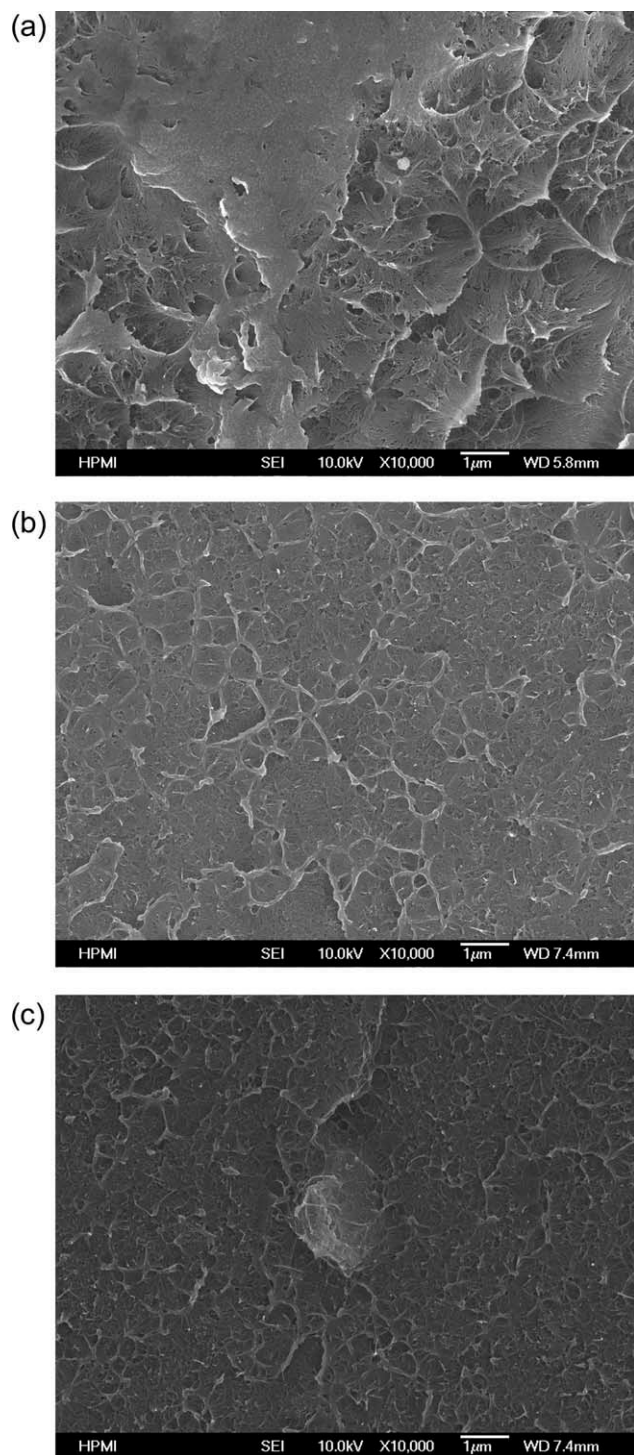
The dispersion of CNTs in COC was observed by SEM. Shown in Figures 2 and 3 are the SEM micrographs of the nanocomposites COC/SMWCNTs and COC/LMWCNTs, respectively. The bright spots are the CNTs. The LMWCNTs indeed have significantly larger length than the SMWCNT. Both types of nanotubes were well dispersed in the polymer matrix for each of the nanotube concentration investigated herein (0.5, 1, and 2 wt %). A significant portion of CNTs was dispersed at individual nanotube level. In addition, the COC polymer appeared to adhere to the CNTs rather well, and CNTs "pull-out" was not observed. This might result from the favorable hydrophobic interaction between the norbornene component and the CNTs.

In nanocomposites synthesis, achieving good nanoparticle dispersion is one of the key challenges. Due to the large specific areas and strong van der Waals interaction, nanotubes exist as bundles or



**Figure 2** SEM micrographs showing SMWCNT dispersion in COC: (a) 0.5 wt % SMWCNTs, (b) 1 wt % SMWCNTs, (c) 2 wt % SMWCNTs.

aggregates. If not properly dispersed, the aggregates act as flaws leading to the reduction of properties. An efficient dispersion method is of critical importance for achieving good dispersion of CNTs in polymers. The good CNTs dispersion realized in the current study is the result of judicious design of process technology and selection of appropriate solvent.



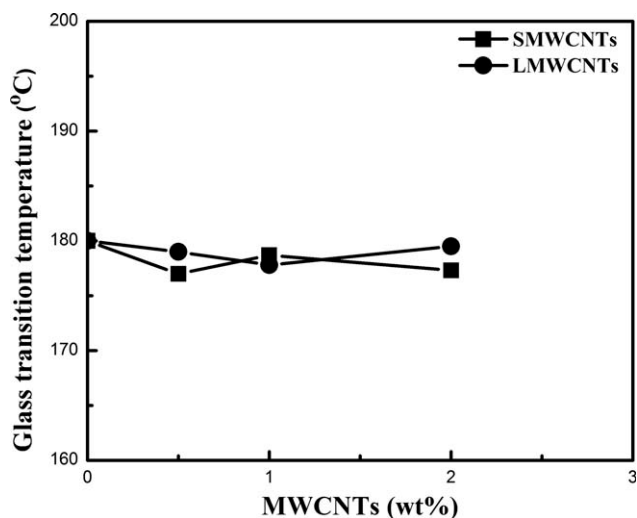
**Figure 3** SEM micrographs showing LMWCNT dispersion in COC: (a) 0.5 wt % LMWCNTs, (b) 1 wt % LMWCNTs, (c) 2 wt % LMWCNTs.

First, high power sonication, one of the most effective methods for nanoparticles dispersion, was employed to disentangle the CNTs bundles and disperse the nanotubes in the solvent. Secondly, the solvent also plays a critical role in dispersing the nanotubes, and stabilizing the dispersed suspension and preventing reaggregation. The choice of solvent in

the preparation of COC CNTs nanocomposites is particularly challenging. Because of its excellent chemical and solvent resistance, not many commonly used organic solvents are capable of dissolving COC. Considering the solvent shall also be a good dispersing agent for the CNTs the situation is even more demanding. We have done extensive solvent screening before deciding on *o*-DCB. *o*-DCB is one of the few solvents in which COC has substantial solubility. In addition, *o*-DCB is one of the best agents for CNTs dispersion.<sup>26,27</sup> Through strong  $\pi$ - $\pi$  and hydrophobic interaction, and dipole-dipole interaction,<sup>28-31</sup> it is possible to disperse CNTs at individual nanotube level in *o*-DCB. Thirdly, the CNTs dispersion state must be preserved and reaggregation prevented during nanocomposites preparation. This was realized by the antisolvent precipitation process. Upon combining the polymer solution and the CNTs suspension, the polymer was able to wrap around the nanotubes to form a stable structure where CNTs were well separated. The well-dispersed state was preserved by subjecting the polymer-CNTs suspension to an antisolvent (ethanol). Rapid diffusion of *o*-DCB into ethanol led to fast precipitation of the nanocomposites and effective lock-down of the dispersed structure.

#### Thermal properties of COC and nanocomposites

The glass transition temperatures of the COC 6017 and nanocomposites were measured by DSC. The results are summarized in Figure 4. The addition of either type of nanotubes into the COC matrix did not affect the polymer glass transition temperature. The glass transition is the onset of coordinated polymer chain segmental motion that involving only about  $\sim 20$ – $25$  monomer units.<sup>32</sup> It is conceivable



**Figure 4** Glass transition temperature of COC and COC/MWCNTs nanocomposites.

TABLE II  
TGA Data of COC and COC/MWCNTs Nanocomposites in Nitrogen and Air Atmosphere

Sample	N <sub>2</sub>				Air			
	T <sub>2%</sub> (°C)		T <sub>d</sub> (°C)		T <sub>2%</sub> (°C)		T <sub>d</sub> (°C)	
	SMWCNTs	LMWCNTs	SMWCNTs	LMWCNTs	SMWCNTs	LMWCNTs	SMWCNTs	LMWCNTs
Pure COC	442.7		481.2		399.9		441.4	
0.5 wt % MWCNTs	443.7	444.2	484.2	483.1	405.8	402.6	477.5	477.0
1 wt % MWCNTs	443.1	441.2	484.9	484.6	403.1	403.3	481.1	480.9
2 wt % MWCNTs	442.4	440.0	484.5	485.5	415.9	419.8	483.6	478.9

that this small-scale molecular motion is not perturbed by the presence of the multiwalled nanotubes, which have significantly larger dimensions. Even single-walled CNTs, which has much smaller dimensions, has shown no effect on polymer glass transition in several studies.<sup>33,34</sup> It shall be noted that however, for strongly interacting polymer-nanoparticles systems with high particle concentration, constrains of the motion may occur, leading to an increase of the glass transition temperature.<sup>35</sup>

The effects of CNTs on the thermal stability of COC were examined by TGA. Under nitrogen atmosphere TGA traces of both pure polymers and nanocomposites of either type (data not shown) exhibited single peak of weight loss rate, suggesting that degradation proceed via a one-stage process. The presence of CNTs did not change the polymer degradation mechanism. Similar effect was observed before in LLDPE MWCNT nanocomposites.<sup>36</sup> The onset degradation temperature (defined as the temperature at which 2% weight lost occurred  $T_{2\%}$ ) and degradation temperature at which maximum weight loss rate occurred ( $T_d$ ) are summarized in Table II. The presence of either type of CNTs has negligible effects on both temperatures.

Oxidative degradation behavior was investigated by using TGA in air and the results are shown in Figures 5 and 6. The oxidative degradation of COC commenced about 400°C (Table II), significantly lower than the onset of degradation in nitrogen. The degradation involved two major stages of weight loss. The primary weight loss occurred ~ 440°C, which was close to the onset degradation of COC in nitrogen. A much smaller secondary weight loss peak occurred ~ 520°C. The nanocomposites exhibited similar two-step weight loss with significantly improved thermal stability. The onset of degradation was delayed in the presence of CNTs, and the effect was more prominent at higher CNTs concentrations. Comparing to the pure COC, the nanocomposites with 2% CNTs had an onset degradation temperature ~ 15–20°C higher. Furthermore, all nanocomposites showed significantly higher degradation temperature. The major weight loss peak shifted to ~ 480°C, an increase of ~ 40°C than that of pure COC, independent of CNTs type and concentration.

In addition, the secondary weight loss peak temperature was also higher for the nanocomposites than the pure COC.

CNTs may improve the thermal stability of polymers through several mechanisms as reported in the literature. The presence of CNTs or nanoparticles

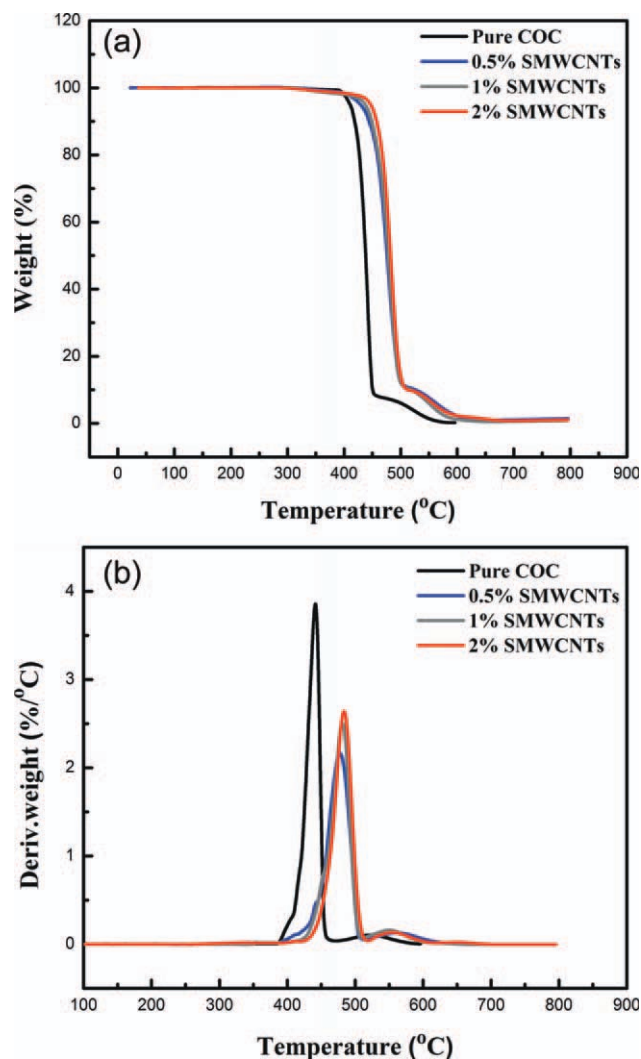
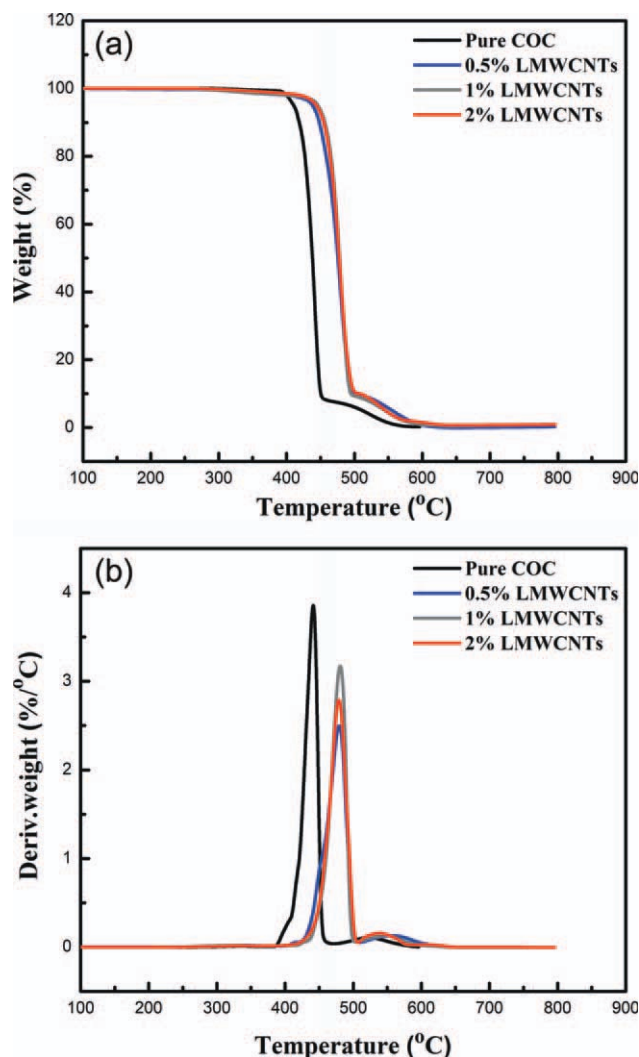


Figure 5 TGA thermograms of COC and COC/SMWCNTs nanocomposites in the air atmosphere: (a) mass loss vs. temperature, (b) derivative mass loss vs. temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



**Figure 6** TGA thermograms of COC and COC/LMWCNTs nanocomposites in the air atmosphere: (a) mass loss vs. temperature, (b) derivative mass loss vs. temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

may lead to “tortuous path,” reduce the transport of degraded products, and improve thermal stability. Such mechanism has been reported being responsible for the improved thermal stability in some study.<sup>9</sup> However, if this is the primary mechanism, the improvement in thermal stability shall also occur in the nitrogen environment, which was not observed in our experiments. CNTs may also act as radical scavengers<sup>37,38</sup> and retard polymer chain scission. Again, if this is the primary mechanism improvement of thermal stability in nitrogen atmosphere would have been observed.

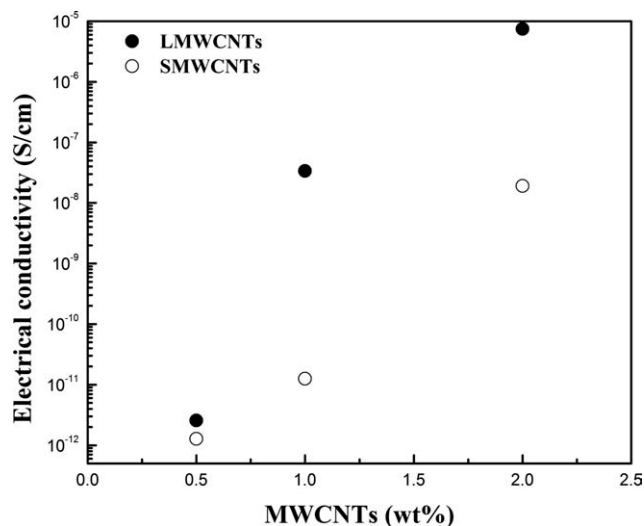
Liu et al.<sup>39</sup> studied the thermal oxidation of an in-house prepared COC and observed sample discoloration during extrusion molding. They attributed this to the thermal oxidation and generation of alkene group that was confirmed by FTIR. Yang et al.<sup>40</sup> studied the thermal degradation of COC in air using

a copolymer with slightly less norbornene content. Via detailed FTIR analysis, they revealed the oxidative degradation of COC involved dehydrogenation, ketone, and lactone formation. The primary weight loss was associated with the lactone formation and resulting polymer main chain scission. By inhibiting the formation of lactone groups from the conversion from ketone groups, the main chain scission was suppressed. It is plausible that the improvements of the nanocomposites oxidative thermal stability result from the possible stabilization effect of CNTs. The CNTs, with the large specific surface area and extensive delocalized  $\pi$  electrons, may provide substantial stabilization to the degradation intermediates (dehydrogenated polymer, ketones, etc.) by extensive  $\pi$ - $\pi$  interaction, thereby delaying the lactone formation and polymer main chain scission. This leads to the significantly improved oxidative thermal stability. As the degradation in nitrogen only involved pyrolysis and was not affected by CNTs, the abovementioned stabilization mechanisms were not present and improvement was not observed.

The secondary peak in maximum weight loss rate, which occurred at higher temperature, could be due to the charred residue formed by oxidative dehydrogenation taking place throughout the heating process in air. The delay in reaching this maximum arguably could be attributed to the fact that the carbon nanotube network enhances char formation and reduction of transport of oxygen and degraded product.<sup>36</sup>

### Electrical conductivity

The dispersion of CNTs into polymer matrices can result in substantially improved conductivities. A wide range of applications is being pursued using



**Figure 7** Electrical conductivity of COC/MWCNTs nanocomposites as a function of nanotube loading.

electrical conductive polymer/CNTs nanocomposites including electrostatic dissipation, electromagnetic interference shielding, and conductive coatings. The DC electrical conductivity of the nanocomposites was measured and the results were shown in Figure 7. The value for the neat COC was not measured in this work because its extremely low electrical conductivity ( $<10^{-16}$  S/cm) was beyond the lower limit of the electrometer. The nanocomposites showed significantly improved electrical conductivity. For example, 0.5 wt % MWCNTs nanocomposites have electrical conductivity more than four orders of magnitude higher than the pure COC. The electrical conductivity further increased tremendously with slight increase of CNTs concentration. For LMWCNT another four order of magnitude increase was achieved when the concentration increases from 0.5 to 1%, and the 2% nanocomposites had electrical conductivity  $\sim 10^{-5}$  S/cm, more than  $10^9$  times higher than that of pure COC. The aspect ratio of the CNTs had a great influence on the electrical conductivity of the nanocomposites. The nanocomposites with larger aspect ratio LMWCNTs consistently have higher electrical conductivity at the same CNTs concentration.

A number of processes and parameters would affect the nanocomposites electrical conductivity including fabrication method, dispersion state, and dimensions of the conductive particles. In the present study, good dispersion of MWCNTs was achieved in both types of nanocomposites as discussed earlier. The difference in electrical conductivity is anticipated to result from the difference of aspect ratios of the two types of CNTs, and can be understood by application of the concept of excluded volume.<sup>41</sup> The excluded volume of an object is defined as the volume around an object where the center of another similar object is not allowed to enter to avoid the overlap of these two objects. When the excluded volumes of two CNTs overlap, the nanoparticle may form a conducting link. Therefore, as the excluded volume of the CNTs increase with increasing aspect ratio, the conductive path can be obtained at lower particle loadings. At the same particles concentration, more conductive paths exist in the nanocomposites with higher aspect ratio CNTs, leading to a higher conductivity in the LMWCNT nanocomposites. It should be noted that since in the current work the higher aspect ratio was realized through the use of CNTs with similar diameter and larger length, it is less prone to the impaired efficiency as reported in the literature, where the MWNT aspect ratio was increased by a decrease in tube diameter.<sup>42</sup>

It shall be noted that further improvement in electrical conductivity by increasing CNTs loading is possible. Both TGA and DC conductivity results

showed that there is more room for improvement before the percolation threshold is reached. We are currently working on improving nanocomposite preparation that enables higher CNTs loading without scarifying dispersion. Their thermal stability and electrical conductivity will be reported in the future.

## CONCLUSIONS

In this study, COC CNTs nanocomposites were prepared by an antisolvent precipitation method using two types of MWCNTs with different aspect ratios. Good nanotube dispersion was achieved in all nanocomposites prepared herein. The glass transition temperature of the COC polymer (measured by DSC) was not affected by the presence of the CNTs. As revealed by TGA analysis, the nanocomposites showed improved thermal stability in air, which might result from the CNTs capability to stabilize the degradation intermediates. On the other hand, thermal stability of the nanocomposites in nitrogen environment was comparable to that of pure polymer. The nanocomposites showed significantly improved electrical conductivity than the pure polymer, and the improvement is substantially more prominent when CNTs with higher aspect ratio was employed.

The present study represents the first step of our comprehensive investigation of COCs carbon nanotube nanocomposites. The main focus of the current study is to develop effective process for the preparation of well-dispersed COC/MWCNTs nanocomposite and show the potential benefits from the addition of CNTs. We are currently conducting systematic investigation of the mechanical and rheological properties of COC/MWCNTs nanocomposite to further elucidate the effects of CNTs. This will be the subject of a future publication.

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