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Synthesis and Characterization of Poly(butylene Oxide) Grafted Carbon Nanofibers

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The grafting of polybutylene oxide onto purified and functionalized carbon nanofibers is reported. Grafting was possible after the insertion of 2-(formyloxy)ethyl 2-bromo-2-methylpropanoate onto the carbon nanofibers. The polymerization of tetrahydrofuran was mediated by copper(I) bromide and 1,1,4,7-pentamethyl diethylenetriamine. The polymer-grafted carbon nanofibers were characterized by Raman spectrsocopy, Transmission Electron Microscopy, and Thermogravimetric Analysis. TEM images of CNF-COOH (A), CNF-PBO (B), completely open tip of CNF-COOH, and coated tip of CNF-PBO (D) are shown in the left panel. The right panel depicts the distribution of bromine (blue), and carbon (red) atoms inside and in the vicinity of CNF-Br (as obtained by Electron Energy Loss Spectroscopy). The bottom shows the actual doped CNF. Preliminary data showed that these modified fibers have potential applications as smart (electrorheological) fluids.

Keywords: Carbon Nanofibers, Insulating Polymer, Grafting, Electrorheology.

RESEARCH ARTICLE

1. INTRODUCTION

Electrorheological (ER) fluids are typically dispersions of particles within non-conducting fluids such as silicone oil. Under the effect of an external applied electric field that exceeds a certain threshold value the dispersed particles show a reversible transition to an one-dimensional (columnar) structure. This transition is accompanied by a sudden increase of the viscosity of the fluid. Dispersions of one-dimensional structures within fluids showed potential features as electrorheological ER. Fluids as the role of the electric field is solely to align the one dimensional filler and not to trigger a transition to a columnar filling. Consequently, it is expected that the observed change in the viscosity of the dispersion will occur at lower electric fields for one-dimensional fillers than to particulate (almost three-dimensional) fillers. The static polarizability of carbon nanotubes and nanofibers and their huge aspect ratio make them particularly attractive for ER applications.[1–3] The ER features of carbon nanofibers (CNFs) dispersions in fluids are improved by increasing the concentration of CNFs. However, the electrical conductivity of CNFs limits

their maximum concentration to the percolation threshold (for dc conductivity).[4] Above the percolation threshold, the dispersion of CNTs (or CNFs) will become conducting and hence the applied electric field will no more affect efficiently the orientation of CNTs. In order to exploit the beneficial features of CNF for ER applications (high aspect ratio and large polarizability) and to reduce the limitations derived from their dc electrical conductivity, a research aiming to decrease the electrical conductivity of CNFs has been initiated. The experimental work was focused on coatings that reduce the surface conductivity of the fibers and eliminate the electrical shorting at high CNF concentrations. Preliminary results on the electrorheological capabiles of CNFs coated by insulating molecules are reported.

Coating of carbon nanotubes with insulating polymers has been reported elsewhere.[5–8] Several approaches such as *in-situ* chemical deposition of polypyrrole,[5] polyurea,[6] atom transfer radical polymerization of styrene,[7] and cationic polymerization of tetrahydrofuran[8] have been reported elsewhere. Similar techniques were used by our group in the coating of CNFs with insulating polymers.[9] Described here is the grafting of CNFs with polybutylene oxide.

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2. EXPERIMENTAL DETAILS

2.1. Materials

CNFs were obtained from Applied Sciences, Inc. All other chemicals were obtained from Aldrich Chemical Co. and were used as received unless otherwise noted. The functionalization of CNFs was supported by Raman Spectroscopy at 785 nm (Senterra, Bruker) and TGA measurements under nitrogen atmosphere by using a TGA Q500 TA instruments equipment. The morphology, structure, and composition of the chemically modified CNFs were examined by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS). Onto a carbon-coated TEM grid, a drop of the nanofibers diluted in ethanol was added and slowly evaporated for analysis on a Schottky field-emitter based FEI Tecnai TF20 (200 kV) equipped with a STEM unit, high-angle annular dark-field (HAADF) detector, and X-Twin lenses. EELS results were recorded in STEM mode with a 0.2 nm probe size in order to increase the number of counts in the detector. The convergence and collection semiangles were 3 and 10 mrad, respectively. The EELS profiles were collected with a 0.1 eV per channel dispersion, and the typical full width at half maximum (FWHM) of the zero-loss peak was approximately 1.0 eV.

Samples for rheological tests were prepared as follows: A measured amount of PBO coated carbon nanofibers (PBO-CNFs) was kept in a vial and silicone oil was added with a dropper. To obtain a homogeneous fluid, the mixture was stirred on a hot plate at 40 °C for 48 hours. The ER properties of the PBO-CNFs-silicone oil suspension were tested employing the parallel plate configuration, using a RS150 Rheometer (Thermo-Haake). DC high voltage was provided by HW10/10P & N Applied Kilovolts Ltd power supply. All measurements were performed at room temperature (24 ± 1 °C). Viscosity was determined from experimental data by using the Rheo Win pro software.

2.2. Purification and Functionalization of CNFs

2.2.1. Purification of CNFs

CNFs were purified as reported elsewhere.[10]

2.2.2. Synthesis of CNF-COOH

CNFs were refluxed in 6 M HNO_3 for 24 hours.[5] The reaction mixture was cooled to room temperature and the CNFs were collected on a 0.2 μm glass fiber filter by Millipore®. The CNFs were washed with distilled water to remove acid excess and then dried under vacuum at 100 °C overnight.

2.2.3. Synthesis of CNF-COCl

400 mg of CNF-COOH were mixed with 15 ml $SOCl_2$.[7] The mixture was heated to reflux for 24 hours and then allowed to cool to room temperature. The product was collected on a 0.2 μm glass fiber filter, washed with anhydrous THF, and dried under vacuum at room temperature for 24 hours.

2.2.4. Synthesis of CNF-OH

CNF-COCl (310 mg) were stirred for 48 hours in 20 ml ethylene glycol at 120 °C.[7] The product was collected on a 0.2 mm glass fiber filter and dried under vacuum for 24 hours.

2.2.5. Synthesis of CNF-Br

The grafted nanofibers (CNF-OH; 300 mg) were dispersed in 10 ml $CHCl_3$. The reaction was kept cool using a water/ice bath. Subsequently, 31 mg of 4-dimethyl pyridine (DMAP) and 0.4 ml triethylamine were added simultaneously. About 0.34 g of 2-bromo-2-methyl-propionyl bromide was dissolved in 5 ml $CHCl_3$ and added drop wise to the reaction mixture. This mixture was allowed to warm to room temperature under stirring for 48 hours.[7] The reaction product (290 mg of CNF-Br, or CNF grafted with 2-(formyloxy)ethyl 2-bromo-2-methylpropanoate pendant groups) was colllected on a 0.2 μm glass fiber filter, and dried under vacuum.

2.2.6. Synthesis of CNF-PBO

CNF-PBO was grafted onto the 2-(formyloxy)ethyl 2-bromo-2-methylpropanoate pendant group. 151 mg of CNF-Br were added to a 100 ml 3-neck round bottom flask and was dispersed in 13 ml of diphenyl ether. 56 mg of CuBr, 59 mg of PMDETA, and 44 mg of THF were added to the above solution. The reaction mixture was heated to 100 °C and was stirred overnight. The product was collected on 0.2 μm glass fiber filters and washed with $CHCl_3$. The product was redispersed in $CHCl_3$ and precipitated using CH_3OH. The product was collected again upon vacuum filtration and dried under vacuum for 24 hours, yielding 140 mg of polybuteneoxide-coated CNFs.

3. RESULTS AND DISCUSSION

Raman spectra of pristine and functionalized CNFs are shown in Figure 1. It is noticed that there are only minor differences between these spectra, due to the chemical functionalization of nanofibers, and in agreement with previous papers on Raman spectra of functionalized carbon nanotubes/nanofibers.[11] The Raman spectra of pristine, purified, and functionalized CNFs are dominated by the D band (located at about 1325 cm^{-1}) and the G band
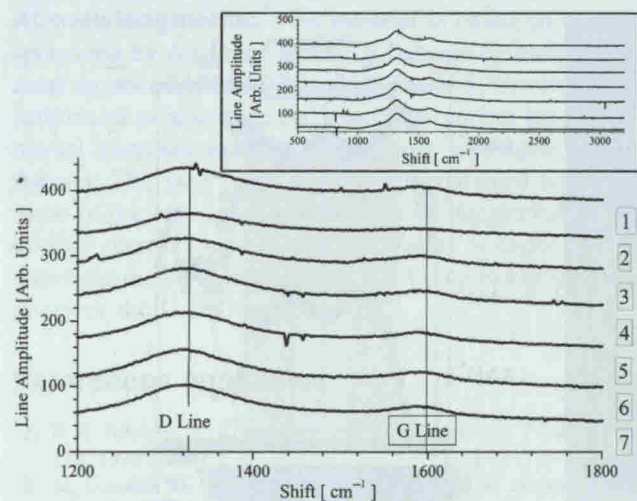
Fig. 1. Raman spectra of pristine and functionalized CNFs.

(located at 1582 cm^{-1}). The Raman line located at about 2683 cm^{-1} was observed identified as the second order Raman D line (or D*).

Details about the effect of CNF functionalization on the position of these two lines are shown in Figure 2 (top panel). Wang et al.[12] reported that the increase of the pyrolysis temperature enhances the electrical conductivity and shifts the position of the D Raman peak towards larger values. It is noticed from Figure 2 that the largest value for the D peak position has been obtained in purified CNFs and that their functionalization shifts the D peak position towards lower values (in cm^{-1}). This indicates the decrease of the electrical conductivity of CNFs and supports the formation of an insulating polymeric layer around conducting CNFs.[12,13] The bottom panel in Figure 2 shows the effect of chemical purification and functionalization on the ratio between the amplitudes of D and G lines (for
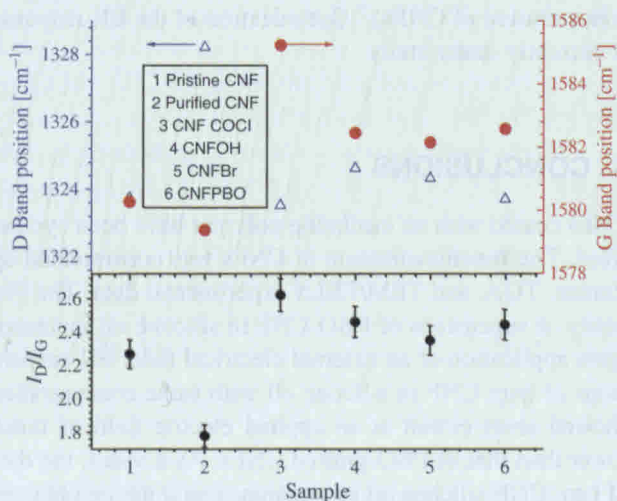

Fig. 2. The dependence of the positions of D and G Raman bands (top bottom) and of the ratio between the amplitude of D and G bands (top panel) on the chemical treatment.
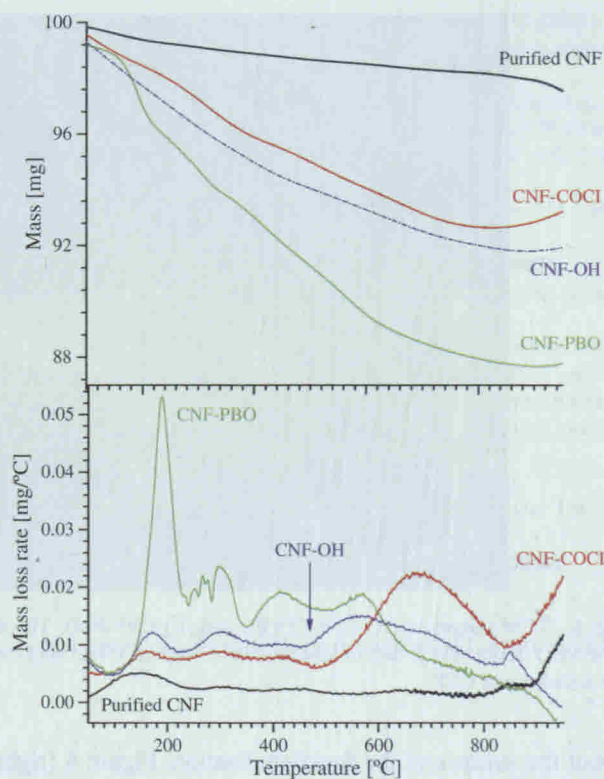

Fig. 3. TGA thermograms (dependence of the mass of functionalized carbon nanofibers on temperature (upper panel) and of the first derivative of the mass loss vs. temperature as a function of temperature (bottom panel)).

CNFs). The purification/debundling treatment of CNFs decreases the disorder of CNFs and increases the overall local conductivity of CNFs. It is noticed that the functionalization of CNFs increases the degree of (local) disorder.

TGA analysis of pristine and functionalized CNFs were performed in nitrogen atmosphere. The study aimed to confirm the functionalization of CNFs by inspecting the mass loss of these samples as a function of temperature. An ideal sample of CNFs should exhibit no mass loss in the temperature range 50 °C to about 700 °C (if the degradation is carried out in nitrogen). As can be observed in Figure 3, TGA data supports the coating of CNF by a polymeric layer, showing very small changes in the mass loss rate for the pristine CNFs in contrast with functionalized CNFs. The top panel of Figure 3 depicts the temperature evolution of the mass of the sample. The bottom panel shows the dependence of the first derivative of the sample's mass versus temperature, as a function of temperature. The coordinates of each maxim point observed on the dependencies shown in the bottom panel of Figure 3 represents the temperature at which the mass loss rate is maxim and the relative value of the mass loss rate, respectively.

The reaction steps required to obtain polybutylene oxide coated CNFs and corresponding TEM images are shown in Figure 4. TEM images (Fig. 4) confirmed the functionalization and subsequent coating of CNFs. EELS studies of brominated CNFs (CNF-Br) provided compelling evidence
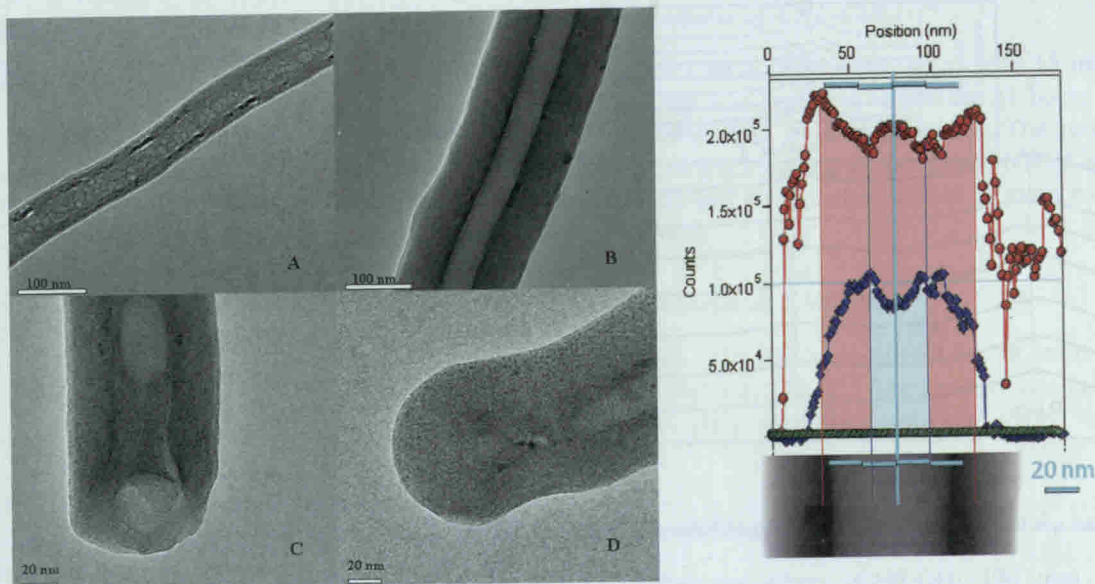
Fig. 4. TEM images of (A) CNF-COOH, and (B) CNF-PBO. The tip (C) CNF-COOH is completely open while (D) shows coating of the tip of CNF-PBO. Right: EELS data on distribution of bromine (blue), and carbon (red) atoms inside and in the vicinity of CNF-Br. The bottom panel shows the actual doped CNF.

about the success of the functionalization. Figure 4 (right) shows the distribution of bromine and carbon atoms, supporting the functionalization of CNFs. The C atom distribution includes both the atoms belonging to CNFs and the atoms belonging to the functionalized group while the Br atoms distribution substantiates the functionalization of CNFs.

Figure 5 shows the viscosity profiles of suspensions of 10% polybutylene oxide-grafted CNFs in silicone oil as a function of the intensity of the applied electrical field. As observed in Figure 5, the viscosity of the suspension increases upon the application of an external electric field. As the applied electric field was increased over 100 kV/m, the ER suspensions showed short circuit. This
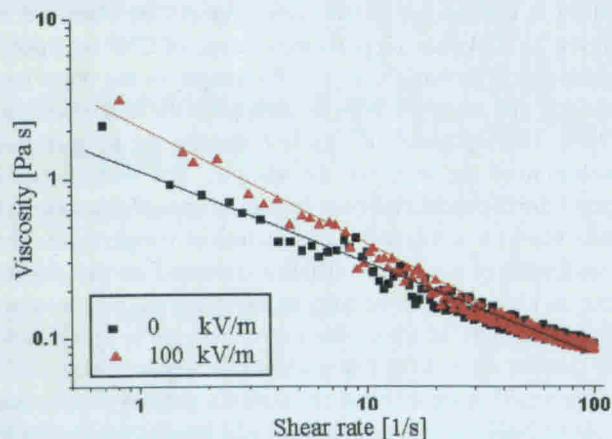
is due to the high conductivity of carbon nanofibers and to their preferential orientation perpendicular to the plates of the rheometer (along the external electric field). The distribution of CNFs along the direction of the external electric field is narrowed as the intensity of the external electric field is decreased, resulting in a dependence of the overall viscosity on the intensity of the electric field. Pristine CNF-silicone oil suspensions showed short circuit at significantly lower intensities of the electric field compared with coated CNF-silicone oil suspensions (at the same concentration of CNF). This supports the coating of CNF. Previously, ER fluid has been tried with much lower concentration of bare CNF (0.05 wt%) because of short circuiting at extremely low applied electric field (at high concentration of CNFs).[3] Optimization of the ER response is currently under study.

4. CONCLUSIONS

CNFs coated with an insulating polymer have been synthesized. The functionalization of CNFs was corroborated by Raman, TGA, and TEM/EELS experimental data. The viscosity of supensions of PBO-CNF in silicone oil increased upon application of an external electrical field. ER suspensions of bare CNF in silicone oil with same concentration showed short circuit at an applied electric field of much lower than that of PBO-grafted CNFs. As a result, the data of bare CNF-silicone oil suspensions could not be obtained at higher external electric fields. Based on this response, the PBO-grafted CNFs have potential applications as a smart ER fluid.

Fig. 5. The viscosity of Polybutylene Oxide coated CNF in silicone oil in the absence of the applied electric field and for an external electric field of 100 kV/m.

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