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Preparation and Characterization of Poly(*p*-phenylene terephthalamide)/Multiwalled Carbon Nanotube Composites via *in-situ* Polymerization

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In this study, we prepared poly(p-phenylene terephthalamide) (PPTA)/multiwalled carbon nanotube (MWCNT) composites by in-situ polymerization. The advantage of the in-situ *polymerization method for the preparation of MWCNTs-incorporated composites is that the MWCNTs can be better dispersed in the polymeric matrices. Good interfacial adhesion between the MWCNTs and polymeric matrices was also achieved by functionalizing the MWCNTs. Inherent viscosity measurements and nuclear magnetic resonance (NMR) were used to characterize the structure of the PPTA/MWCNT composites. The morphology of the composites was also observed by scanning electron microscopy (SEM). The prepared PPTA/MWCNT composites exhibited improved electrical conductivity. The mechanically ground PPTA/MWCNT particles were investigated for use as an electrorheological (ER) material. The ER fluid was prepared from the PPTA/MWCNT particles with insulating silicone oil. The ER behaviour was confirmed using an optical microscope under an applied DC electric field of 1.7 kV/mm.*

Keywords: electrorheological (ER) material; multi-walled carbon nanotube (MWCNT); poly(p-phenylene terephthalamide) (PPTA)

1. INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) is currently the most important aromatic polyamide, since it has a good chemical resistance, wear resistance and abrasion resistance. PPTA is a high-performance polymer widely used in the form of fibres or films for various

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structural applications [1–4]. Carbon nanotubes (CNTs) have become the focus of research in the field of polymeric nanocomposites, because the incorporation of CNTs into polymers can improve their mechanical and electrical properties [5–9]. For the synergistic enhancement of these composites, a high dispersivity of the CNTs is required in the polymer matrix, without their aggregation. Consequently, the in-situ polymerization process has been preferred because it allows for the good dispersion of the CNTs in the polymeric matrices [10–12]. Many different applications of CNTs have recently been developed to make use of their electrically conductive properties [13]. For example, CNT-incorporated microspheres have been fabricated by many researchers for applications such as electrorheological (ER) fluids [14]. ER fluids are a class of materials whose rheological properties are controllable through the application of an electric field. The most common type of ER fluids is a colloid of solid dielectric or conducting particles dispersed in insulating fluids [15]. Since typical ER fluids consist of suspensions of fine dielectric particles in a dielectric liquid, they undergo structural changes and form stems caused by the polarization of the particles [16]. Herein, we prepared PPTA/MWCNT particles and investigated their electrical properties. In addition, the formation of a fibrous structure caused by the ER behaviour of the PPTA/MWCNT suspensions in silicone oil was also investigated in an applied electric field.

2. EXPERIMENTAL

2.1. Materials

Terephthaloyl chloride (TCL, Aldrich, USA), *p*-phenylenediamine (PPD, Sigma, USA) and N-methyl pyrolidone (NMP, DC Chemical Co., LTD., Korea) were used as received. Calcium chloride ($CaCl_2$, Kanto Chemical Co., INC.) was finely ground and dried under a vacuum. The MWCNTs used were purchased from Iljin Nanotech Co., Korea. The purity of the pristine MWCNTs was $>95\%$.

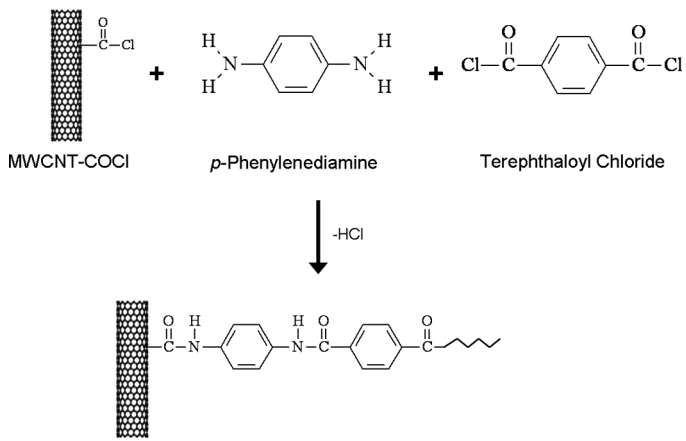
2.2. Purification and Functionalization of MWCNTs

To eliminate the impurities in the MWCNTs (such as metallic catalysts), they were treated in 3 M HNO_3 at 60°C for 12 h, followed by refluxing in 5 M HCl at 120°C for 6 h. The purity of the acid-treated MWCNTs was measured to be 99% using thermogravimetric analysis (TGA, TA instruments, Q50). These acid-treatments are known to introduce carboxylic and hydroxyl functional groups onto the surface of the MWCNTs, as well

as purify them [19,20]. The functionalized MWCNTs were filtered and washed with a large amount of water, and then vacuum-dried at room temperature overnight. The acid-treated MWCNTs were reacted with an excess quantity of $SOCl_2$ for 24 h under reflux conditions. The residual $SOCl_2$ was then removed by reduced pressure distillation in conjunction with a liquid nitrogen trap to yield the acyl chloride functionalized MWCNTs (MWCNT-COCl).

2.3. Preparation of PPTA/MWCNT Nanocomposites

NMP (80 g) was placed in a reaction vessel and cooled to 15°C. Then, finely ground dry calcium chloride (12 g) and PPD (3.65 g) were added to the NMP solution with stirring. The MWCNTs were dispersed in NMP (20 g) solution in a separate vessel by applying ultrasound using an ultrasonic generator (Kyungill Ultrasonic Co., Korea). The MWCNT-dispersed NMP solution containing TCL (6.95 g) was then added to the first reaction vessel. The polymerization reaction began immediately upon adding the MWCNT dispersion. The reaction was carried out under nitrogen purging for 1 h. During the reaction, the solution viscosity rapidly increased and the temperature rose to 30°C. The PPTA/MWCNT composites were washed thoroughly with distilled water, followed by drying in a vacuum oven for 48 h. The reaction is schematized in Scheme 1.



SCHEME 1

2.4. Characterization

The inherent viscosity of PPTA and the PTTA/MWCNT composites was measured using 0.5 g/dl of material in H_2SO_4 at 30°C using an Ubbelohde capillary viscometer (ViscoClock, Schott, Germany). The solid- state ^{13}C NMR spectra were obtained at 100 MHz on a Varian Inova 400 instrument. For the measurement of the electrical conductivity of the PPTA/MWCNT particles, they were prepared in the form of disc-type pellets with a thickness of 0.7 mm by applying a pressure of 1 ton at room temperature using a Carver laboratory press. The electrical conductivity of the composites was measured in the form of the volume conductivity (S/cm) using a 4-probe method. The ER fluid was prepared by dispersing 10 vol% of the PPTA/MWCNT particles in silicone oil by sonication. A high DC voltage source was used for applying a voltage to the sample. The gap distance between the two parallel electrodes was fixed precisely at 100 μm. The microstructure images of the ER fluid were obtained by optical microscopy (BX51, Olympus, Japan). The images were obtained in transmittance mode and captured at the same time without digital filtering.

3. RESULTS AND DISCUSSION

PPTA and PPTA/MWCNT composites were prepared by *in-situ* polymerization, and the effect of the MWCNTs on the structural changes in the composites was evaluated. The inherent viscosity of the PPTA/MWCNT composites tended to decrease compared with that of pure PPTA as shown in Figure 1.

However, the solid-state ^{13}C NMR spectra of PPTA and the PPTA/MWCNT composites were almost identical, as observed in Figure 2. The strong signal at 166.3 ppm characterizes the carbonyl carbons of PPTA, while the signals corresponding to the aromatic carbons of PPTA are observed between 140 and 110 ppm [17]. The same peaks were observed in the solid-state ^{13}C NMR spectra of both PPTA and the PPTA/MWCNT composites, and no other characteristic peaks were detected from the solid-state ^{13}C NMR spectrum of the PPTA/MWCNT composites. Therefore, it can be inferred that the MWCNTs might not significantly affect the synthesis of the PPTA.

Figure 3 shows the ground particles of the PPTA/MWCNT composites. The size of the PPTA/MWCNT particles is less than 5 μm. A lot of MWCNTs were present inside and on the surface of the PPTA/MWCNT particles. In addition, the magnified image shows that a

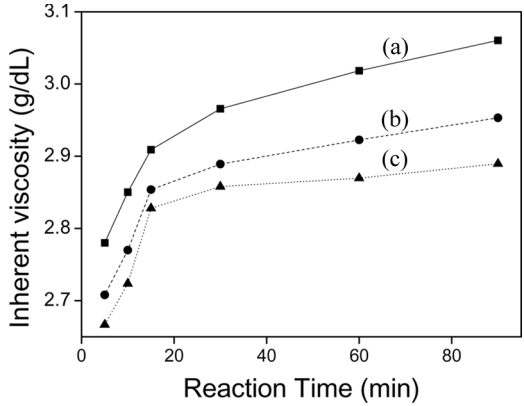


FIGURE 1 Inherent viscosity of (a) PPTA, (b) PPTA/MWCNT (1.0 wt%) and (c) PPTA/MWCNT (5.0 wt%) composites.

substantial number of MWCNTs were well dispersed and embedded in the PPTA matrix.

The electrical conductivity of the PPTA/MWCNT composites was measured by a 4-probe method at room temperature, and compared with that of PPTA in Table 1. The high dispersivity of the MWCNTs in the PPTA matrix resulted in a substantial increase in the electrical conductivity of the composites. The electrical conductivity of the

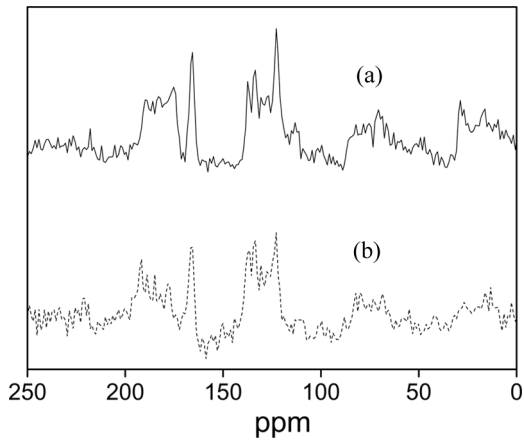


FIGURE 2 Solid-state ^{13}C NMR spectra of (a) PPTA, and (b) PPTA/MWCNT (1.0 wt%) composites.

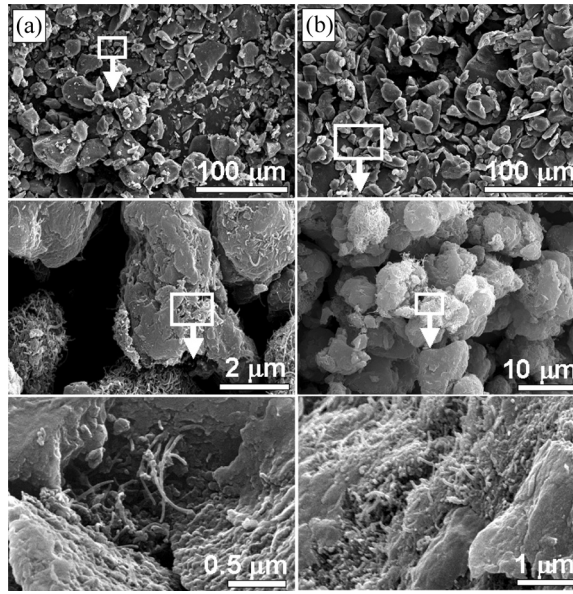


FIGURE 3 SEM images of the ground particles of PPTA/MWCNT (a) 1.0 wt% and (b) 5.0 wt%) composites.

composites increased by nine orders of magnitude from 1.01×10^{-15} to 1.50×10^{-6} S/cm, when the loading of the MWCNTs was increased from 0 to 1.0 wt%.

Figure 4 shows that the suspension of PPTA/MWCNT (1.0 wt%) particles in silicone oil (10 vol%) exhibited the typical fibrous structure of an ER fluid. The formation of particle chains (so-called fibrillation), based on the interfacial polarization of the PPTA/MWCNT particles dispersed in silicone oil, was demonstrated under an applied electric field of 1.7 kV/mm, as compared with the random distribution of the dispersed particles under no electric field. The PPTA/MWCNT particles formed thin and dense chains within one second, and their

TABLE 1 Electrical Conductivity of PPTA and PPTA/MWCNT Composites

Sample name	Electrical conductivity (S/cm)
PPTA	1.01×10^{-15}
PPTA/MWCNT (1.0 wt%)	1.50×10^{-6}
PPTA/MWCNT (5.0 wt%)	1.71×10^{-2}

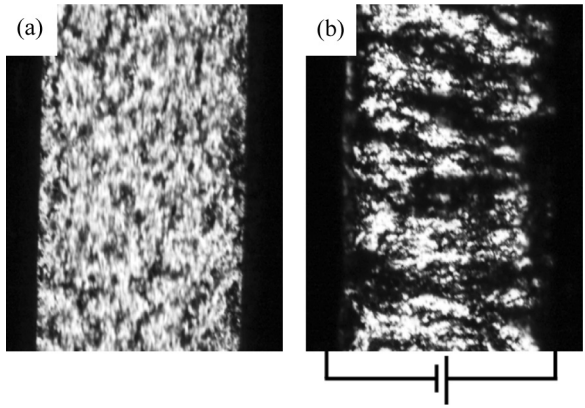


FIGURE 4 Optical microscope images of the PPTA/MWCNT (1.0 wt%) microspheres dispersed in silicone oil (10 vol%) under an electric field of (a) 0 kV/mm and (b) 1.7 kV/mm.

structure remained stable as long as the field was applied [18]. Fibrillated chains were observed and spanned the two electrodes. It is possible that the fibrillated chain structure might provide a path for the transport of the mobile carrier, and would determine the conducting behaviour of the ER fluids.

4. CONCLUSION

PPTA/MWCNT (1.0 and 5.0 wt%) composites were prepared by *in-situ* polymerization. It was found that the electrical conductivity of the PPTA/MWCNT composites was increased by the addition of the MWCNTs. The electrical conductivity of the PPTA/MWCNT (1.0 wt%) composites was about 1.50×10^{-6} S/cm. Their ER characteristics were also investigated by dispersing the PPTA/MWCNT composite particles in insulating silicone oil. The fibrillation of the particles was demonstrated under an applied electric field of 1.7 kV/mm, as compared with the random distribution of the dispersed PPTA/MWCNT composite particles at zero electric field.

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