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Dispersion of multi-walled carbon nanotubes in poly(p-phenylene) thin films and their electrical characteristics

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ABSTRACT

Dispersion of multi-walled carbon nanotubes in poly(p-phenylene) composite exposed to toluene was experimentally investigated. 3 mg of multi-walled carbon nanotubes with nominal size of 20 nm was compounded with 30 mg of poly(p-phenylene) with the presence of terpineol as binding initiator. To investigate an optimal condition for homogenizing all constituents, ultrasonication with an output power of 750 W was employed with compounding time of 3, 10, 20 and 30 min. With FTIR analyses, it could be confirmed that homogeneous composite of multi-walled carbon nanotubes and poly(p-phenylene) could be prepared. SEM analyses were also conducted to examine the dispersion of multi-walled carbon nanotubes in the polymer matrix. Then intrinsic electrical resistance of the composites after being exposed to toluene was also investigated. It was found that the composite film prepared with ultrasonication for 20 min could provide sufficiently sensitive response with respect to varied concentration of toluene.

1. Introduction

Recently smart material has drawn considerable research interest due to an abrupt increase in various applications to fulfill human needs. Polymer is recognized as versatile materials with many advantages of processing flexibility and controllable physicochemical properties. Therefore, compounding of polymer with nano-scaled particulates for preparing novel composite material has continuously been examined since the invention of conductive polymer (Zarras et al., 2003). To prepare a conductive polymer, conjugation of polymer with other novel materials would be intentionally fabricated. In recent years, polymer compounded with carbon nanotubes (CNTs) has attracted much research attention after its stimulating report of Iijima in 1991 due to its unique physical and electrical properties (Charinpanitkul, Sano, Muthakarn, & Tanthapanichakoon, 2009; Charinpanitkul, Tanthapanichakoon, & Sano, 2009; Iijima, 1991; Li et al., 2007). As a result, research attempts in synthesis and applications of CNTs have been drastically increased year by year.

Meanwhile, there are extensive reports related to utilization of composites of multi-walled carbon nanotube (MWCNT) and polymer for various applications (Kunanuruksapong & Sirivat, 2007; Yuen et al., 2008; Zhang et al., 2005; Zhu, Xie, Xu, & Xu, 2006). One promising application of such composite is fabrication of sensor for monitoring the presence of some specific chemicals. Specifically, modified electrical resistance of polymeric composite consisting of MWCNTs has been found as a useful mean for detecting some specific gases (Zhang et al., 2005; Zhu et al., 2006). Among many polymeric materials, it is well known that preparation of poly(p-phenylene) (PPP) is very simple and economical (Kunanuruksapong & Sirivat, 2007). Therefore, in this study we focus on the dispersion and use of MWCNTs within PPP composite as thin film configuration to detect toluene gas. It should be noted that performance of the fabricated thin film is closely related to its initial resistance. It was found that MWCNTs with relatively large size were difficult to disperse homogenously in molten polymer. To overcome this dispersion problem, melting polymerization, and chemical functionalization incorporated with ultrasonication was carried out. Thereby, investigation of ultrasonication effect on uniformity of MWCNTs dispersed in poly(p-phenylene) was experimentally analyzed by FTIR spectroscopy and electron microscopy. Then the intrinsic electrical resistance of MWCNT/PPP composites prepared under various conditions were examined and discussed.

2. Experiments

2.1. Materials

Poly(p-phenylene) or PPP employed in this work was synthesized in house while MWCNTs with nominal diameter of 20 nm

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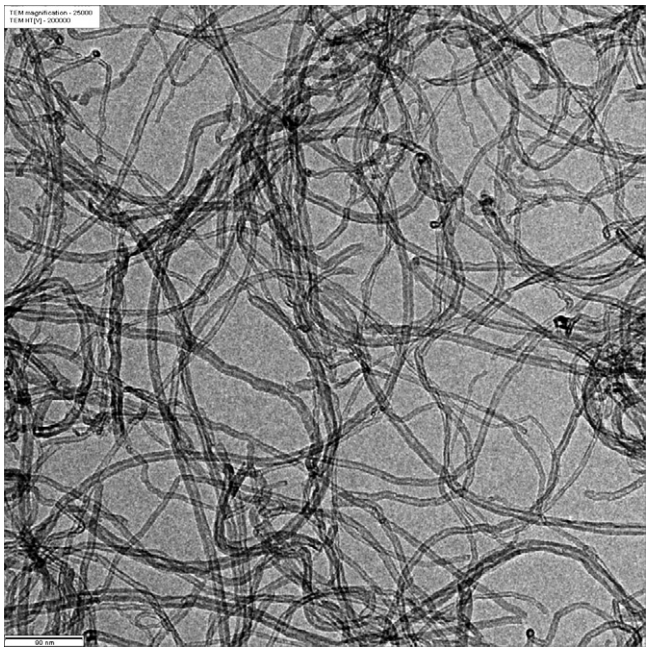

Fig. 1. Typical TEM micrograph of pristine MWCNTs employed in this work.

were supplied by Bayer Material Science, Germany. A typical TEM micrograph of the pristine MWCNTs analyzed by transmission electron microscopy (TEM; JEOL2010, JEOL) is depicted in Fig. 1. It could be clearly observed that the MWCNTs entangling with each other have a uniform diameter of 15–20 nm. Procedure for synthesizing poly(p-phenylene) was based on that reported by Kunanuruksapong and Sirivat (2007). Benzene as the monomer for synthesizing PPP was purchased from Panreac Co. Ltd., Spain. Terpineol anhydrous ($C_{10}H_{18}O$) as binding initiator was supplied by Fluka, France. A trace amount of $CuCl_2$ and Al_2O_3 as catalysts was purchased from Riedel-de Haen, Germany.

2.2. Fabrication of MWCNT/PPP composite

PPP and MWCNT with certain weight ratio were compounded by ultrasonic stimulation with the presence of terpineol of designated amount in the range of 1.5–3 mL for the purpose of examining the dependence of the composite characteristics on their preparation conditions. It should be noted that under the initial condition PPP was liquid. Terpineol was employed as the binding initiator for starting the polymerization of PPP with the presence of $CuCl_2$ and Al_2O_3 as catalysts. Compounding time was also varied for investigating its effect on the homogenization of the composite which could be achieved by employing a water bath with temperature control. After a pasty composite was prepared, a few drops of the composite were applied to coat onto a 5 mm × 15 mm alumina substrate consisting of two separate metallic electrodes printed by a sputtering method. A gap of 1 mm is intentionally designed between two metallic electrodes on which the composite film with a dimension of 5 mm × 3 mm would be coated. Therefore, the total area of the composite film to be exposed to toluene gas was 15 mm^2. Five pieces of sensors were prepared for reproducibility test. Before each confirmation test, all sensors were put into an oven for 3 h with a controlled temperature of 75 °C to ensure that excessive amount of organic constituent was removed.

2.3. Characterization methods

Immediately after its synthesis, MWCNT/PPP composite was characterized for its intrinsic chemical bonding by using Fourier transmission infrared spectroscopy (FTIR, Spectrum-I, PerkinElmer). The morphology and dispersion of MWCNT in each composite sample was analyzed using scanning electron microscopy (SEM, JSM 6400, JEOL). To monitor the electrical response of the composite film, each sensor which was prepared from the alumina substrate with copper electrodes connected to the composite was set up inside a 1000 mL glass chamber. Then the sensor was connected to a digital multi-meter (AT-9995 Automotive Meter) and measured signal was recorded by a personal computer. Toluene vapor was introduced into the measuring chamber by dropping calculated amount of toluene using a syringe.

3. Results and discussion

3.1. Effect of sonication

It has been known that addition of MWCNTs into a polymer matrix can significantly reduce electrical resistance of the polymer. The optimal amount of MWCNTs depends on the matrix and size of MWCNTs. Polystyrene, for example, with 10 wt.% of MWCNTs could exhibit a drastic improvement of its electrical resistance (Zhang et al., 2005). For polyamide, reduction of electrical resistance occurs dramatically when the content of MWCNTs is ca. 7–10 wt.% (Zhu et al., 2006). Similarly, PMMA with 4.7 wt.% of MWCNT possesses much lower electrical resistance as compared to the virgin polymer (Yuen et al., 2008). Based on many previous studies (Xie, Mai, & Zhou, 2005; Zhang et al., 2005; Zhu et al., 2006), the addition of MWCNTs will also reduce the resistance of PPP film composite. Therefore, in this study we used 10 wt.% of MWCNTs to prepare

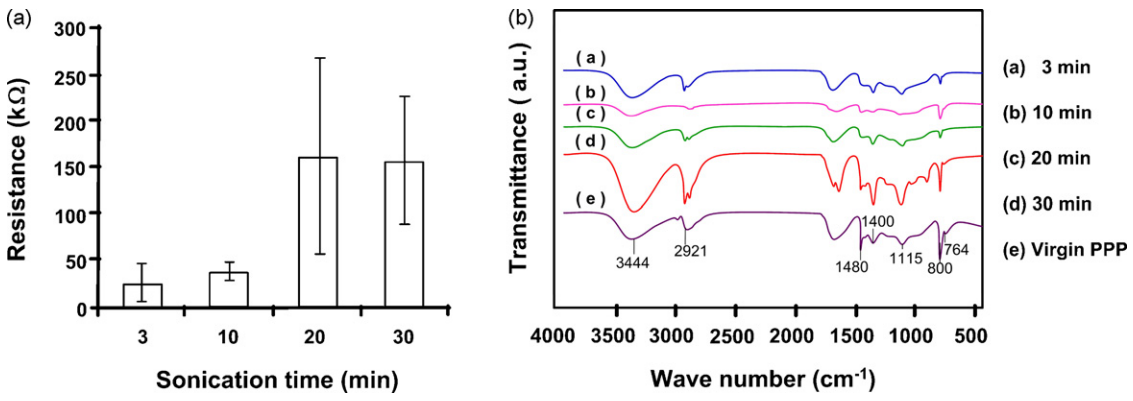

Fig. 2. Dependence of MWCNT/PPP composites properties on mixing time (a) initial resistance and (b) chemical bonding analyzed by FTIR method.