

Investigation of microstructure and electric heating behavior of hybrid polymer composite films based on thermally stable polybenzimidazole and multiwalled carbon nanotube



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ABSTRACT

Thermally stable polybenzimidazole (PBI)-based composite films filled with different pristine multiwalled carbon nanotube (MWCNT) contents of 0.0–10.0 wt% were manufactured by a facile solution casting, and their microstructural features, thermal and electrical properties were investigated as a function of the MWCNT content. Electron microscopic images and FT-IR spectra of the composite films confirmed that each MWCNT was wrapped with PBI chains by π – π interaction and thus they were well dispersed in the PBI matrix. Thus, the electrical resistivity of the composite films decreased considerably from $\sim 10^7 \Omega \text{ cm}$ to $\sim 10^{-1} \Omega \text{ cm}$ with the increment of the MWCNT content, especially at a certain percolation threshold of $\sim 0.25 \text{ wt\% MWCNT}$. The composite films containing above 0.3 wt% MWCNT contents exhibited excellent electric heating performance. For instance, the composite film with 10.0 wt% MWCNT exhibited low temperature growth/decay time constant of $\sim 1 \text{ s}$, stable maximum temperatures of 40–220 °C, and high electric power efficiency of $\sim 7.32 \text{ mW/}^\circ\text{C}$ under the relatively low applied voltages of 5–25 V. Thermogravimetric analysis revealed that the composite films were thermally stable up to $\sim 450 \text{ }^\circ\text{C}$ under air environment. It is thus reasonable to contend that PBI/MWCNT composite films can be used as high performance electric heating materials in emerging application areas.

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1. Introduction

Recently carbon nanomaterials such as carbon nanotubes (CNTs), graphene, and their derivatives have been extensively investigated for various purposes, because of their exceptionally excellent electrical conductivity, thermal conductivity, thermal stability, and mechanical performance [1–4]. Accordingly, they are considered as ideal multifunctional reinforcing fillers for polymer-based composites [5–7]. Especially, CNTs are known to be significantly effective for increasing the electrical conductivity of insulating polymer matrix [8,9]. Improvement in electrical conductivity of polymer/CNT composites has found significant applications in emerging areas of the field of sensors, actuators, electrodes, supercapacitors, electrostatic dissipation/electromagnetic interference shielding materials for electronic devices and components [10–13]. It is also conjectured that polymer composites with improved electrical conductivity can be used for electrical heating

elements [14]. Electrical heating or resistive heating converts electrical energy into thermal energy as heat. For practical applications of polymer composites as electric heating elements, a polymeric matrix with high thermal and mechanical stability is a prerequisite, in addition to the advantages of its corrosion resistance and easy processability.

Polybenzimidazoles are typical heterocyclic polymeric materials with exceptionally high thermal stability, mechanical strength, and chemical stability [15–17]. Among the family, poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) has been well developed for high performance technical fibers, coating varnishes, and membranes for fuel cells [18]. Because PBI is usually infusible up to 400 °C or higher, it is considered as an ideal polymeric matrix for electric heating polymer composites.

For the purpose of investigating polymer composites with excellent performance in electric heating and thermal stability, in this study, we have manufactured a series of PBI-based composite films reinforced with pristine multiwalled carbon nanotube (MWCNT) by using a facile solution casting, and have investigated their microstructures, thermal stability, electrical properties, and associated electric heating behavior as a function of the MWCNT

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content. A high molecular weight PBI as the polymeric matrix was synthesized via polycondensation reaction of 3,3'-diaminobenzidine and isophthalic acid in the presence of polyphosphoric acid. For achieving high electrical conductivity for the composite films, pristine MWCNT without any chemical modification and associated structural defects was adopted as a conductive nanofiller for the PBI matrix. The electric heating performance of the composite films has been analyzed systematically by taking into account temperature responsiveness, maximum temperature, and electric power efficiency achieved at different applied voltages.

2. Experimental

2.1. Materials

3,3'-Diaminobenzidine (DAB, >98.0%, TCI) and isophthalic acid (IPA, >99%, TCI) were adopted as starting monomers for the synthesis of PBI. Polyphosphoric acid (PPA, >83% P₂O₅, Sigma–Aldrich) was used for the polymerization solvent. Pristine MWCNT (CM-95, Hanwha Chemical) with 10–15 nm diameter and 10–20 μm length, produced by thermal chemical vapor deposition, was used as a reinforcing nanofiller for the PBI-based composite films. Methanesulfonic acid (MSA, >99%, Samchun Chemical) was used as a solvent for manufacturing PBI/MWCNT solutions. To measure the intrinsic viscosity of the synthesized PBI, sulfuric acid (95%, Samchun chemical) was used as a solvent. All the chemicals and materials were used as received without further purification.

2.2. Synthesis of PBI

As the polymeric matrix of the composite films, PBI was synthesized by a schematic reaction route shown in Fig. 1. First, DAB 12.00 g (56.0 mmol) was dissolved in PPA 200 g in a three-neck round flask with mechanical stirring under inert nitrogen gas flow. The mixture was heated up to 140 °C to dissolve DAB monomer in PPA solvent. Then, stoichiometrically balanced IPA 9.31 g (56.0 mmol) was added in the solution and the temperature was raised to 200 °C to synthesize a neat PBI homopolymer. During the polymerization at 200 °C for 15 h, the viscosity of the solution was progressively increased and the initial light brown solution turned to dark purple. After the polymerization, the reaction solution was poured into distilled water and the solidified reaction product was pulverized into powder. The powder sample was

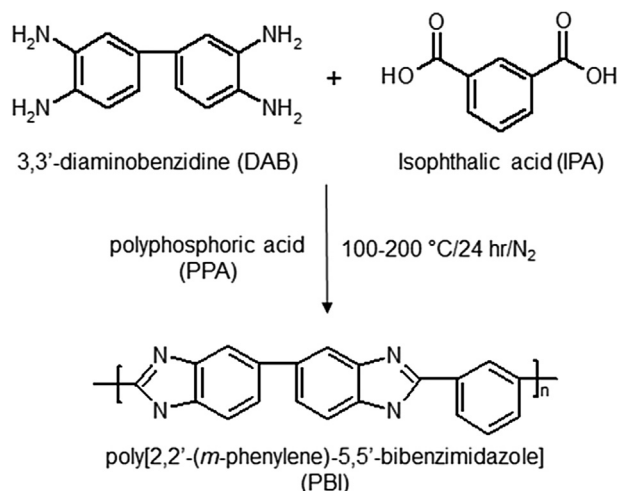


Fig. 1. Schematic reaction route to synthesize PBI homopolymer.

soaked in distilled water at 80 °C for 24 h to remove residual PPA solvent and unreacted monomers. Finally, the sample powder was dried in a vacuum oven at 150 °C for 24 h.

2.3. Preparation of PBI/MWCNT composite films

PBI-based composite films containing different pristine MWCNT contents were manufactured by an efficient solution mixing and casting. First, a predetermined amount of MWCNT was dispersed in MSA of 9.5 g by using a bath-type ultrasonicator (SK7200BT, Youngjin Corporation) for 3 h. PBI powder of 0.5 g was then added into the solution, which was heated up to 80 °C for 6 h and was ultrasonicated for 1 h. The PBI/MWCNT/MSA solution was casted on a glass petri dish and dried at 140 °C for 18 h in a ventilated hood. After evaporating the MSA solvent, the petri dish was soaked in distilled water to obtain the composites film. The composite film was further immersed in distilled water at 80 °C for 24 h to remove any remaining solvent. Finally, the composite films were dried in an oven at 150 °C for 24 h. For comparison, a neat PBI film was also prepared by the same procedure. The thickness of the films was in the range of ~50 μm. The final film samples were named as PBI/MWCNT_x, where x denotes the MWCNT content by wt% and it was controlled to be 0.1–10.0 wt% in the composite films.

2.4. Characterization

The molecular structure of the synthesized PBI as well as the interaction between PBI chains and pristine MWCNT was identified by using FT-IR spectroscopy (iS10, Thermo scientific Inc.). The intrinsic viscosity of the synthesized PBI was measured by using an Ubbelohde viscometer with 95% sulfuric acid at 30 °C and associated molecular weight was evaluated by using Mark–Houwink

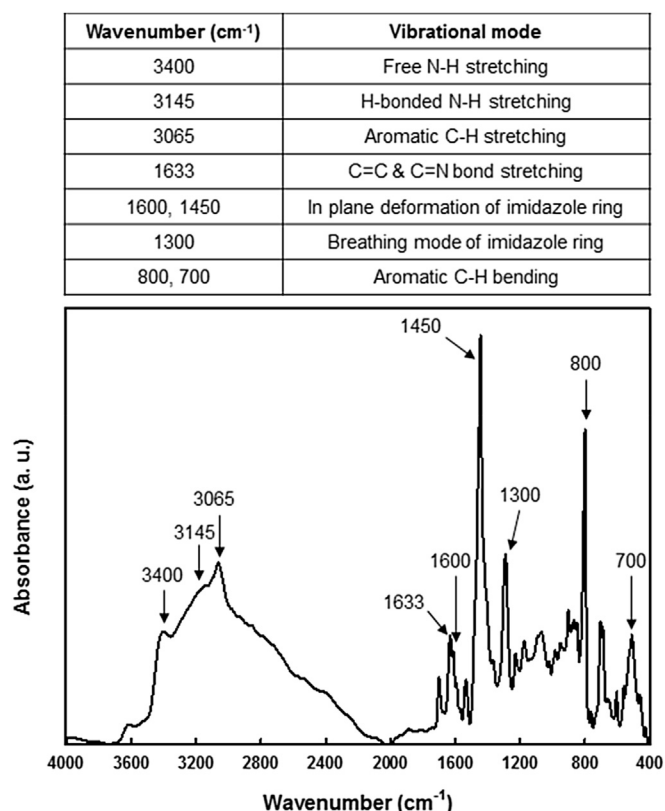


Fig. 2. FT-IR spectrum and vibrational band assignment of the synthesized PBI.

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