Preparation, structure and properties of carbon nanotube reinforced polymer nanocomposites

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A B S T R A C T

Polyetherimide (PEI) nanocomposites that contain a well-dispersed filler, multi-wall carbon nanotubes (MWCNTs), were prepared. Organic acids were covalently bonded onto the π-conjugated skeleton of surface-modified MWCNTs by treating them with carboxylic acids. Analyses of X-ray photoemission spectroscopy, Raman spectra, and Fourier transform infrared spectra of MWCNTs demonstrated that the acid-treated process increased the number defects in the graphitic layers. The acid-treated process on MWCNTs (a-MWCNTs) could improve adhesions between the organic polymer and carbon nanotubes (CNTs). The dielectric characteristics of a-MWCNTs/PEI nanocomposites with various a-MWCNTs contents were measured from 10 kHz to 1 MHz using the plate method. Two mixing rule models, the Lichtenecker logarithmic model and Yamada model, were applied to predict the dielectric constants of a-MWCNTs/PEI nanocomposites. The results indicate that the Yamada model was more effective than the Lichtenecker logarithmic model at predicting the dielectric constants of the a-MWCNTs/PEI nano-composites.

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1. Introduction

Polymer/ceramic nanocomposites are rapidly becoming important as substrates with possible applications in microwave and electronic equipment. Because they have high dielectric constants, they can be used in small embedded devices. However, to obtain the high dielectric constant, a high content of ceramic powder as a filler is required. For example, to increase the dielectric constant from 2.43 for neat polyetherimide (PEI) to $\sim$12, 60 wt% (or 29 vol%) $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O_3$ ceramic powder must be added [1]. Even when a dispersant is used, the high filler content increases the difficulty of uniformly distributing the ceramic powder in PEI. Therefore, a new filler of which can be used in low amounts to obtain a high dielectric constant, is required.

CNTs have attracted considerable attention because of their unique structural features [2,3]. CNTs, a recently discovered crystalline form of carbon, are unique nanostructured materials with remarkable physical and mechanical properties [4,5], including high tensile strength, Young's modulus [6,7] and thermal conductivity [8]. These excellent properties have inspired interest in the use of CNTs as fillers in polymer nanocomposites to improve the electrical conduction, thermal transport, and mechanical properties of their matrixes [9,10]. A few studies of the microwave properties of CNT/polymer nanocomposites were investigated. For example, some have studied the shielding effectiveness (SE) of the novel CNT polymer nanocomposites for potential use in protection against electromagnetic interference (EMI) and improvement of electromagnetic susceptibility (EMS) of optical transmitter and receiver modules [11,12]. Highstrete et al. examined CNTs that were microwave-proof at room temperature [13].

Polyimides are known for their high heat resistance, chemical resistance, strength and modulus, as well as their excellent electrical properties that remain stable over a wide range of temperatures and frequencies. However, they are difficult to process because of their stiffness and high softening temperature. In particular, PEI is an amorphous engineering thermoplastic. Its molecular structure comprises alternating aromatic imide and ether groups. The imide groups provide strength at high temperatures, while the flexible ether group linkages support relatively easy processing. PEI has some special physical, chemical, electrical, and processing characteristics [14–16]. As being compared with other reports, the dielectric constant of the PEI is higher than those of polytetrafluoroethylene (PTFE) and polyolefin elastomer (POE) [17,18]. In addition, the loss tangent of the PEI is lower than those of polyvinylidenefluoride (PVDF) and epoxy resin [19,20]. The superior features of the PEI matrix and CNTs can be combined in CNTs/PEI nanocomposites.

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CNTs/PEI nanocomposites are also expected to have favorable thermal stability, physical and electrical properties.

Few detailed studies of the relationship between the electrical properties of the MWCNTs/PEI nanocomposites without and with acid-treated process on MWCNTs (a-MWCNTs) have been performed. In this investigation, the dielectric properties of the MWCNTs/PEI nanocomposites with various contents of without and with acid-treated MWCNTs' loadings were measured using the plate method. In determining potential applications of the a-MWCNTs/PEI nanocomposites, precise prediction of their dielectric constants is very important. After the dielectric constants of the a-MWCNTs/PEI nanocomposites are measured, two mixing rule models, the Lichtenecker logarithmic model and the Yamada model, are used to calculate the dielectric constants of the a-MWCNTs. From the results, the optimization models can be determined and expected from the microstructures of the a-MWCNTs/PEI nanocomposites. The dependences of the dielectric constant (ε_r) and loss tangent (tanδ) of the a-MWCNTs/PEI nanocomposites on the frequency (1 kHz to 1 MHz) are also investigated.

2. Experimental

2.1. Surface functionalization of the MWCNTs

The surface of MWCNTs is modified by covalent attachment of organic acid to their π-conjugated skeleton by treating them with carboxylic acid. MWCNTs (95% pure, according to thermogravimetric analyzer analysis), purchased from BASF, were used as received. 63% nitric acid (HNO_3) and 98% sulfuric acid (H_2SO_4) were purchased from Merck Chemical. A 125 mL round-bottom flask that was equipped with a condenser and a stirrer was charged with CNTs (2 g), sulfuric acid (8 mL), and nitric acid (24 mL). The flask was sonicated for 30 min using an ultrasonic apparatus and chemical oxidation was carried out at 60 °C for 48 h. Following acid treatment, the MWCNTs were functionalized with carboxylic acid groups (COOH) on their surface. After it had been cooled down to room temperature, the mixture was vacuum-filtered through a 0.1 m teflon filter. The acid-treated MWCNTs (a-MWCNTs) were then washed with deionized water until the pH of the filtrate was close to 7.0 [21]. Fig. 1 schematically depicts the surface of the CNTs that were modified with carboxyl acid and hydroxyl groups.

2.2. Preparation of the n-MWCNTs/PEI and a-MWCNTs/PEI nanocomposites

The a-MWCNTs in polymer matrices might have completely different material properties from those of conventional nanocomposites. The a-MWCNTs must be separated and homogeneously distributed in the PEI matrix to exploit their high specific surface area and cause them to interact as an interphase with the PEI matrix. The neat MWCNTs (n-MWCNTs)/PEI and a-MWCNTs/PEI nanocomposites were prepared using a special methylene chloride (CH_2Cl_2) solvent mixing method. The n-MWCNTs/PEI and a-MWCNTs/PEI solutions were cast in a rotation mold at 60 °C, and the residual solvent in the homogeneous n-MWCNTs/PEI and a-MWCNTs/PEI nanocomposites were vaporized in a vacuum at 60 °C for 24 h. In this investigation, the n-MWCNTs/PEI and a-MWCNTs/PEI nanocomposites with various MWCNTs contents were thus prepared. However, a-MWCNTs were effectively dispersed in the PEI matrix using ultrasonic waves.

2.3. Characterization

The morphology of the n-MWCNTs and a-MWCNTs was observed from transmission electronic micrographs (TEM, model JEOL JEM 1200 EX). The quality of the n-MWCNTs and a-MWCNTs
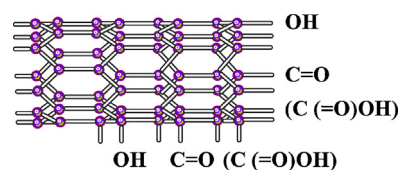

Fig. 1. Surface modification of MWCNTs.

was determined by Raman spectroscopy using the 532-nm line of a YAG laser, which was operated at a power of 500 mW. The laser, with a beam diameter of approximately 2 μm, was focused using a 1000× objective lens onto the surface of the n-MWCNTs and a-MWCNTs. Fourier transform infrared (FITR) spectra was used to identify the functional groups that were responsible for the chemical modification of the n-MWCNTs and a-MWCNTs. The atomic bonding states of the n-MWCNTs and a-MWCNTs were analyzed using X-ray photoemission spectroscopy (XPS). The glass transition temperatures (T_g) and the temperatures of the other thermal transitions of the a-MWCNTs/PEI nanocomposites were measured using a differential scanning calorimeter (DSC, TA Q100) that was equipped with a mechanical introcoller and a computer for data analysis. Unless otherwise specified, all T_g measurements were made at a scan rate of 20 °C/min during a second scanning following quenching from above the estimated T_g values. The T_g in this investigation was taken as the temperature of the onset of the transition in the DSC thermograms. The Instron–5567 universal tester was used to measure the flexural properties of the prepared samples. The dielectric constant (ε_r) and loss tangent (tanδ) of the n-MWCNTs/PEI and a-MWCNTs/PEI nanocomposites with a metal/dielectric material/metal structure were measured from 1 kHz to 1 MHz using an HP 4294 LCR meter.

3. Results and discussion

In the preparation of the MWCNTs/polymer nanocomposites, making a uniform dispersion of nanotubes in the polymer matrixes was difficult, because the inherently poor compatibility and weakness of the interactions exist between the polymer matrixes and the MWCNTs. Therefore, enhancing the physical or chemical interaction between the organic and the inorganic materials was important to distributing the MWCNTs homogeneously throughout the polymer matrixes. Ausman et al. found that the MWCNTs became soluble in amide solvents when chemically functionalized by treatment with strong mixed acid [21]. The acid-treatment on the surfaces of the MWCNTs (a-MWCNTs) with carboxyl and hydroxyl groups will strengthen interactions between the MWCNTs and the polymer matrix. The functionalization of the
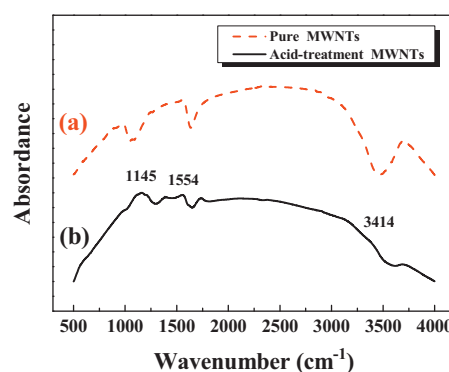

Fig. 2. FTIR analysis of (a) n-MWCNTs and (b) a-MWCNTs.