# Preparation of Polybenzimidazole/Functionalized Carbon Nanotube Nanocomposite Films for use as Protective Coatings

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Functionalized multi-walled carbon nanotubes (MWCNTs) via microwave-induced polymerization modification route, and polybenzimidazole (PBI) nanocomposite films containing 0.1-5 wt% functionalized MWCNTs were successfully synthesized. The functionalized MWCNTs were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The results verify that the polymer was successfully grafted to the MWCNTs with a polymer layer that was several nanometers thick. The TGA results showed that the quantity of the attached polymer reached approximately 9.4 wt%. The mechanical properties of the nanocomposite films were measured by tensile test and dynamic mechanical analysis (DMA). The tensile test results indicated that the Young's modulus increased by about 43.9% at 2 wt% CNT loading, and further modulus growth was observed at higher filler loading. The DMA studies indicated that the nanocomposite films had a higher storage modulus than pure PBI film in the temperature range of 30-300°C, and the storage modulus was maintained above 0.82 GPa. Simulation results confirmed that the PBI nanocomposite films had desirable mechanical properties for use as a protective coating. POLYM. ENG. SCI., 51:1525-1532, 2011. © 2011 Society of Plastics Engineers

# INTRODUCTION

Polybenzimidazole (PBI) is a material known for its remarkable thermal and chemical stability. Currently, PBI

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is widely applied to firefighter protective clothing, included in astronaut flight suits [1, 2], and used as an insulating layer for semiconductors due to its high volume resistivity. Additionally, phosphoric acid-doped PBI membranes have emerged as a suitable candidate for polymer electrolytes in high-temperature proton exchange membrane fuel cells (PEMFC) [3, 4]. Because of its chemical stability and excellent film-forming capability, PBI is a promising coating material for industrial applications. Technology development will lead to demands for PBI coatings with improved mechanical performance, which can be effectively achieved by introducing a suitable amount of inorganic reinforcement to form composite materials [5, 6].

Carbon nanotubes (CNTs) have great potential for use in high-performance composite materials and are of interest to several research groups [7-10]. Compared to conventional fillers (layered silicate [11], clay [12], metal oxide particles [13]) which have dimensions on the micro-scale. CNTs is considered to be the ultimate reinforcement fillers owing to their outstanding mechanical characteristics, extremely large interfacial contact area, high aspect ratio, and low mass density. Consequently, CNTs are used to synthesize various polymer/CNT composites [14-18]. However, there are very few reports on PBI/CNT nanocomposites [19, 20]. In our previous work, we proved that Vapor-Grown Carbon nanofibers (VGNFs) can be used as an effective reinforcement filler in PBI nanocomposites, although a few aggregation phenomena accrued in the nanocomposites at high VGNF loading [19]. The sidewall functionalization of CNTs is an effective and necessary approach to eliminating the aggregation problems [21-30]. Many techniques have been used to functionalize CNTs, including esterfication [21], layerby-layer self-assembly [22], radical polymerization [23], surfactant-aided noncovalent functionalization [24], in situ

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polymerization [25, 26], ring-opening polymerization [27], atom transfer radical polymerization [28, 29], and microwave-induced radical polymerization [30]. One of these techniques, microwave-induced radical polymerization is quite fast and efficient. Up to now, various monomers such as styrene, methyl methacrylate, acrylic acid, allyl alcohol, and acrylic amide have been grafted to the surface of CNTs [30]. The amount of the grafted polymer can be tuned by varying experiment factors such as the weight ratio of monomer and radical initiator used.

In this paper, functionalized CNTs and PBI/functionalized-CNT nanocomposite films were successfully synthesized. The functionalized CNTs were thoroughly characterized using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The mechanical properties of nanocomposite films were systematically measured by tensile test and dynamic mechanical analysis (DMA). Moreover, simulation experiments were conducted to determine the impact of the actual working environment on the mechanical properties of the nanocomposite films.

# EXPERIMENTAL

## Materials

The polymer matrix used in this study was PBI (AZ Electronic Materials, Japan K.K.) in the form of PBI matrix resin solution (PBI dissolved in DMAc at a 10% concentration). The weight-average molecular weight ( $M_w$ ) was 130,000 Da, and the number-weight molecular weight ( $M_n$ ) was 70,000 Da. Multi-walled carbon nanotubes with a diameter of 20–30 nm (Wako Pure Chemical Industries Ltd, Japan) were used as received. N,N,dimethylace-tamide (DMAc), methyl methacrylate (MMA), and benzoyl peroxide (BPO) were used without any further purification.

# Functionalization of MWCNTs via Microwave-Induced Radical Polymerization

In our experiments, the functionalization process was carried out by one-pot, microwave-induced radical polymerization according to ref [30] with some modification. Methyl methacrylate was selected as the monomer for modifying the CNTs to facilitate compatibility with the PBI matrix. 100 mg of MWCNTs was suspended in a 20 ml DMAc solution containing 2 ml MMA monomers, and 20 mg BPO in 1 ml DMAc solvent was added to the MWCNTs+MMA solution. The solution was then ultrasonicated for 5 min and irradiated with microwaves [commercial microwave oven (500 W, 2.45 GHz)] for about 15 s. This process was repeated five times for a total addition of 100 mg BPO. Upon absorbing microwave energy, benzoyl peroxide decomposed into phenyl radicals, which then served as radical initiators for polymerization of monomers in the solution. The final solution was diluted with DMAc and centrifugated at 3000 rpm for 10 min. The purpose of centrifugation was to separate the impurities and bundled MWCNTs from the solution. The supernatant solution was collected and filtered through a polytetrafluoroethylene membrane (47 mm/0.45  $\mu$ m, from Millipore) and washed with DMAc for several times. Finally, the products were dried overnight at 80°C. A pure PMMA sample for FTIR analysis was synthesized using similar methodology.

# Preparation of PBI/Functionalized CNT Nanocomposite Films

The functionalized CNTs were dispersed in DMAc solution and mixed [ultrasonic mixing (100 W, 45 KHz) and mechanical mixing] for 1 hour. The PBI matrix resin solution was then added to the CNTs solution, and the combined mixing process was continued for another 2 hours. The mixture was cast in a film-forming system at  $65^{\circ}$ C for 8 hours to evaporate the solvent and produce a uniform film. Finally, the film was compacted by aluminum sheets, put into a furnace, and held at  $120^{\circ}$ C,  $150^{\circ}$ C, and  $170^{\circ}$ C for 2 hours. The nanocomposite films were prepared with contents of 0.1, 0.2, 0.5, 1, 2, and 5 wt% of functionalized CNTs. The preparation of PBI/pristine CNT nanocomposite film was carried out by the same methodology.

## Characterization

The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken with a JEM-2010 electron microscope with an accelerating voltage of 200 kV. Infrared spectra were recorded on a Shimadzu FTIR (model IR-prestige 21) spectrometer in the region of 4000-400 cm<sup>-1</sup>. Raman spectroscopy measurements were performed on a HoloLab series 5000 Raman spectroscope (Kaiser optical systems, Inc.) furnished at 514 nm laser excitation. The thermogravimetrical analysis (TGA) was performed on a Rigaku Thermo Plus TG8120 apparatus (Rigaku Denki, Japan) under nitrogen atmosphere at 10°C/min in temperature ranging from 30°C to 550°C. X-ray photoelectron spectroscopy (XPS) analysis was used to measure the elemental composition of the samples. XPS measurements were performed on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with a standard MgK $\alpha$  (1256.6 eV) X-ray source operated at 10 mA and 15 kV. All binding energies were referenced to Au  $(4f_{7/2})$  at 84 eV. The morphologies of CNTs and nanocomposite films were observed using field emission scanning electron microscopy (FESEM, S-5000, Hitachi, Japan). Tensile properties were performed on a JIS K6251 universal testing machine



FIG. 1. (a) FESEM image of pristine CNTs; (b) FESEM and (c) high-magnification FESEM images of functionalized CNTs; (d) TEM image of pristine CNTs; (e) TEM and (f) HRTEM images of functionalized CNTs.

(RTC 1250A A&D Co. Ltd, Japan) at 1 mm/min and  $25^{\circ}$ C. Tensile specimens were cut from the nanocomposite films according ISO 527-3. Five specimens of each material were tested for reproducibility. The storage modulus of the resulting nanocomposite film was acquired with the aid of a dynamic mechanical analyzer (DVA-225, ITK Co. Ltd., Japan). The scanning ranged from  $30^{\circ}$ C to  $300^{\circ}$ C at  $5^{\circ}$ C/min.

#### **RESULTS AND DISCUSSION**

#### Characterization of Functionalized CNTs

In functionalization processes, microwave irradiation can quickly decompose benzoyl peroxide [30] and initiate the polymerization of MMA monomer as well as the grafting of oligomeric radicals onto the surface of dispersed CNTs. Therefore, effective surface modification of CNTs can be achieved in a few minutes. The amorphous impurities and unbound MMA monomer and oligomer are substantially removed after the diluting-centrifuging-filtering-washing process. Through functionalization, CNTs can be easily dispersed in ordinary organic solvents, which pave the way for promising application of CNTs as ideal reinforcement fillers.

Functionalized MWCNTs were characterized by various methods such as TEM, FESEM, FTIR, Raman, TGA, and XPS. Figure 1 represents typical FESEM and TEM images of pristine and functionalized CNTs. The FESEM image of pristine CNTs shown in Figure 1a highlights the partially bundled morphology and amorphous impurities. Comparison of functionalized CNTs (Fig. 1b) and pristine ones shows the obvious reduction of amorphous nanoparticles and bundled CNTs, as well as an increase in diameter. This phenomenon can also be observed from the TEM images of pristine (Fig. 1d) and functionalized (Fig. 1e) CNTs. Figure 1c represents a typical highmagnification FESEM image of functionalized CNTs. The functionalized CNTs have a uniform and flattened interface without particles on the CNT surface. The HRTEM image in Fig. 1f clearly reveals that the polymer is successfully grafted to the CNT surface, and the grafted polymer layer is several nanometers thick. Moreover, the grafted layer is amorphous, and the thickness of the layer can be easily regulated through the monomer and initiator concentrations.

The FTIR spectra of pristine CNTs, functionalized CNTs, and pure PMMA are shown in Fig. 2a. Most characteristic absorption peaks of the PMMA spectra are present in the functionalized CNTs, indicating that the PMMA is grafted to the nanotube surface. The peak around 1730 cm<sup>-1</sup> is attributed to C = O stretching frequency, and the peaks around 2997 and 2950 cm<sup>-1</sup> are attributed to CH<sub>2</sub> and CH<sub>3</sub> vibrations [30, 31]. All the samples have bands at 3442 and 1637 cm<sup>-1</sup>, which are assigned to O-H stretching and in-plane deforming vibrations, respectively; these are standard characteristic peaks of water. Although the chemical link between PMMA and CNTs is difficult to clarify by FTIR analysis, the difference between pristine and functionalized CNTs indicates some interaction between CNTs and PMMA.

In addition to FTIR analysis, Raman spectroscopy was employed to examine the existence of covalent bonds between the grafted PMMA polymer and CNTs. The D/G ratio is the ratio of the disorder mode (D band, 1340 cm<sup>-1</sup>) to the tangential mode (G band, 1570 cm<sup>-1</sup>). The D/G ratio is related to the amount of sp<sup>3</sup>-hybridized carbon atoms in the CNTs and thus provides direct information on the degree of sidewall functionalization, in which sp<sup>2</sup>-hybridized carbons are converted into sp<sup>3</sup>-hybridized carbons [32, 33]. According to Fig. 2b, functionalized CNTs exhibit a significant increase in the D/G ratio from 0.86 to 1.04. The observed D/G ratio decrease suggests that the outer layers of the CNTs are chemically modified.



FIG. 2. (a) FTIR spectra of pristine CNTs (1), functionalized CNTs (2), and PMMA (3); (b) Raman spectra of pristine and functionalized CNTs; (c) TGA curves of pristine and functionalized CNTs.

TGA was employed to examine the extent of polymer grafting, which can be calculated by the amount of mass reduction during measurement. Just as expected, the thermal degradation of functionalized CNTs exhibits two stages in the measured range (Fig. 2c). The first stage, up

XPS was used to determine the concentration of elements in the functionalized CNTs. Figure 3 shows a survey spectrum of the pristine and functionalized CNTs. The survey scans of the two samples identify the presence of carbon and oxygen, where the concentration of oxygen clearly increases after functionalization. The high-resolution C 1s and O 1s spectra (Figs. 3b-e) can be used to quantitatively calculate the concentration of carbon and oxygen based on the ratios of the peak areas and relative sensitivity factors. The atomic percentages for pristine CNTs are 99.54% for C 1s, 0.46% for O 1s, while functionalized CNTs are 91.35% for C 1s and 8.65% for O 1s. The increase in oxygen concentration indicates that the MMA monomer was polymerized and grafted onto the nanotube surfaces. In addition, the oxygen concentration of the functionalized CNTs is much lower than that for PMMA (about 60%), which is assumed to be a result of the polymer layer thickness being less than the scanning depth of the XPS instrument. The oxygen concentration is higher for thicker polymer layers. Overall, the TEM, FTIR, Raman, TGA, and XPS results confirm that the polymers are successfully grafted to the CNT surface.

# Morphology and Mechanical Properties of the PBI/CNT Nanocomposite Films

Figure 4 shows the morphology of the nanocomposite film filled with 5 wt% CNTs. The SEM image indicates that the functionalized CNTs are randomly oriented and uniformly dispersed throughout the PBI matrix. In addition, the CNTs form interconnecting structures.

Figure 5 illustrates the effect of CNT content on the tensile properties, including the Young's modulus and tensile strength in all of the PBI/CNT nanocomposite films. The Young's modulus increases with CNT content. Compared with the pure PBI film, the Young's modulus (see the inset of Fig. 5) increases 43.9%, from an initial value of 0.98 GPa to 1.41 GPa at 2 wt% CNTs. This increase suggests that the functionalized nanotubes are homogeneously dispersed inside the PBI matrix, and there are numerous interactions between the CNTs and the matrix. In addition, the tensile strength of the nanocomposite films also increases with the CNT content. The tensile strength for the addition of 2 wt% CNTs is 24.6% higher than that for the pure PBI film. The improvement in tensile strength of the nanocomposite films can be attributed to the load transfer from the PBI matrix to the functionalized CNTs, which is possible because the PMMA layer is highly compatible with the functionalized CNTs. Concep-



FIG. 3. XPS spectra of pristine and functionalized CNTs. (a) Survey of the spectral region from -10 to 1150 eV; narrow scan of carbon 1s region of (b) pristine CNTs and (c) functionalized CNTs; narrow scan of the oxygen 1s region of (d) pristine CNTs and (e) functionalized CNTs.

tually, the added fillers (such as layered silicate, clay, and metal oxide nanoparticles) often make composites stiff and brittle. However, uniformly dispersed functionalized CNTs, having high aspect ratios and flexible elastic behavior during loading, are different from other reinforcement fillers. After introduction of the CNTs into the PBI matrix, the ultimate strain of the nanocomposite films shows no obvious reduction, while the tensile strength clearly increases. This indicates that the synthesized PBI/ CNT composite films are mechanically robust. For comparison purposes, the PBI nanocomposite film with 2 wt% pristine CNTs was prepared and measured with respect to its mechanical properties. As shown in Fig. 5b, the enhancement of PBI nanocomposites due to the pristine CNTs is similar to that of the functionalized CNTs. However, the increase in both the tensile strength and ultimate strain is much lower, which is possibly due to the partial aggregation of the pristine CNTs in the PBI matrix and the incompatibility between the two phases.

FESEM was conducted to analyze the morphology of the fracture surface after tensile testing. The fracture sur-



FIG. 4. FESEM of PBI/CNT nanocomposite film.

face of a pure PBI film (Figs. 6a and 6b) is smooth and has many "river-like" patterns, which may be caused by the ductile deformation of the PBI polymer. The fracture



FIG. 5. (a) Stress-strain curves of pure PBI and nanocomposite films. The inset is a magnified view of the initial range (up to 0.5%) of strain from which the Young's modulus was calculated by linear regression. (b) Stress-strain curves of pure PBI, pristine CNT nanocomposite, and functionalized CNT nanocomposite films. The inset is a magnified view of the initial range of strain.



FIG. 6. FESEM images taken from fractured surface of tensile specimens. (a) Low-magnification and (b) high-magnification images of a pure PBI film. (c) Low-magnification and (d) high-magnification images of the nanocomposite film with 2 wt% CNTs.

surface of a nanocomposite film (Fig. 6c) exhibits dimple patterns with three-dimensional deformations rather than a smooth plane as in the PBI film. The deformation resistance increases due to the presence of CNTs, which increases the Young's modulus and tensile strength of the nanocomposite film. Moreover, as indicated in Fig. 6d, a number of CNTs are broken, rather than just pulled out from the PBI matrix, which demonstrates that strong interfacial bonding exists between the PBI matrix and the functionalized CNTs. In order to investigate the relationship between the storage modulus and temperature, the DMA was conducted. The corresponding storage modulus and temperature behavior are shown in Fig. 7. Addition of the CNTs increases the level of the storage modulus throughout the measured region, with the highest value observed for the filler content of 5 wt%. The storage modulus at 30°C was significantly enhanced from 3.52 GPa for pure PBI film to 5.5 GPa for the nanocomposite film containing 2 wt% functionalized CNTs. All nanocomposite films had a measured modulus greater than 0.82 GPa below 300°C.



FIG. 7. Comparison of storage modulus (10 Hz) for pure PBI films and the nanocomposite films in the  $30-300^{\circ}$ C temperature range. The inset shows the storage modulus of nanocomposite films at  $30^{\circ}$ C.



FIG. 8. Storage modulus curves of the nanocomposite films with 2 wt% CNTs at various frequencies.



FIG. 9. Percentage of remaining storage modulus (10Hz, 30°C) of nanocomposite films after exposure to the simulation solutions.

This dramatic increment in storage modulus indicates that the interactions between the PBI matrix and CNTs are strong enough to allow a very efficient load transfer to CNTs, providing high mechanical strength. The polymeric grafted PMMA along the nanotube surface can physically knot and tangle with the polymer chains of the PBI matrix, leading to very strong interactions between the CNTs and PBI matrix. The functionalized CNTs thus serve as network centers to transfer stress evenly to the other polymer chains.

In addition, the storage modulus of PBI/CNT nanocomposite films (with 2 wt% CNTs) increases with the frequency (see Fig. 8); this effect is more significant at higher frequencies. Notably, the storage modulus of the film at 30°C is greater than 15.3 GPa when the frequency is 160 Hz, suggesting that elevated film mechanical properties can be obtained at high frequencies. The reason for these properties is that the system, while at low frequencies, has more time to dissipate the external force resulting from interfacial sliding, which is similar to the relaxation behavior of typical filled-polymer composites [34].

# Effect of the Simulation Environment on the Mechanical Properties

Generally, materials are coated for use in harsh conditions in order to protect machine components. Therefore, it is important to evaluate the impact of the working environment on the mechanical properties of coating materials. To simulate the actual working environment of the coating material, nanocomposite films (with 2 wt% CNTs) were treated with different solutions (1 mol/L KOH, 1 mol/L HCl, 1 mol/L HNO<sub>3</sub>, ethanol, and machine oil) at room temperature for 1, 7, and 14 days. The storage moduli at 30°C were then measured (see Fig. 9). Clearly, all the nanocomposite films maintained the storage modulus well, even after exposure for 14 days. The films were especially resistant to ethanol and oil, with about 99% of the modulus maintained because PBI does not dissolve and is very stable in common organic solutions. The slight reduction of the modulus after treatment in acid and alkaline conditions is probably due to the doping reaction between imidazole rings in the PBI polymer chain and the acid or base, as described in several previous studies [3, 4, 35]. Past research has also indicated that doped PBI maintains excellent mechanical properties in the temperature range of 20°C–200°C [35]. Accordingly, the nanocomposite films retain their mechanical properties even in harsh conditions, and are suitable for use as protective coating materials.

# CONCLUSIONS

In this study, functionalized CNTs and polybenzimidazole nanocomposite films were successfully synthesized. FESEM, TEM, FTIR, Raman, TGA, and XPS results indicate the polymer was successfully grafted to the functionalized MWCNTs, and the quantity of the grafted polymer was about 9.4 wt%. For the PBI/CNT nanocomposites, tensile test results showed that the Young's modulus of the nanocomposite film was markedly improved in comparison to an untreated sample, with a 43.9% enhancement at 2 wt% CNT content. DMA indicated that the storage modulus increased by incorporating the CNTs, and all films maintained a storage modulus above 0.82 GPa below 300°C. The simulation experiment showed that the nanocomposite films retained their improved mechanical properties even in harsh conditions. Consequently, the synthesized PBI/CNT nanocomposite films have high potential for application as protective coating materials.

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