



## Preparation, morphology and properties of acylchloride-grafted multiwall carbon nanotubes/fluorinated polyimide composites

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### ABSTRACT

A fluorinated polyimide (PI) was synthesized by a two-step reaction from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl. A series of PI composites with various mass fractions of multi-walled carbon nanotubes (MWNTs) were prepared by either an *in situ* polymerization or blending process. To increase the chemical compatibility of carbon nanotubes with the PI matrix, MWNTs were treated with an acid mixture and sulfoxide chloride by turns. Results show that the dispersion of the MWNTs is highly improved in the PI by modification. The modified MWNTs are dispersed homogeneously in the matrix, while the structures of the PI and MWNTs are stable in the preparation process. The thermal stability of the nanocomposites is slightly lower than that of the pure PI. With incorporating MWNTs, the storage modulus and glass transition temperature of the composite films enhanced comparing to that of PI matrix. The dielectric constants of the composites increase sharply, which is favorable to their practical use in anti-static materials and embedded capacitors.

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### 1. Introduction

Polyimides (PI) are widely used as packaging materials, circuit boards, and interlayer dielectrics because of their good dielectric properties, superior thermal stability, and high strength. The thermal stability, mechanical properties, and other functional features of PI composite materials can be significantly improved compared with their pure states by introducing a small fraction of inorganic fillers, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, AlN, TiO<sub>2</sub>, and magadiite [1–7], into the matrix of the polymer. Fluorinated PIs are also high-performance polymers, particularly because of their superior thermal stability, high strength, high degree of polymerization, low color, and good film-forming ability. PIs are effectively synthesized from monomers of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), which have two trifluoromethyl groups each, and exhibit good heat resistance and feasible processability [8,9]. This kind of PI is now widely used in many fields, such as the electronics industry, telecoms, and aerospace engineering. The higher dielectric constants and electric conductivity of these composites are achieved by the construction of a percolation network for charge mitigation and electromagnetic shielding. The mechanical features of these composites are also enhanced for efficient load transfer [10–15].

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The construction of organic–inorganic composites for various applications has attracted considerable attention. Composite materials are typically formed by mixing at least two dissimilar materials to form a monolith [16]. Among the polymers, PIs possess reliable high temperature stability, good mechanical strength, and excellent chemical resistance.

The use of carbon nanotubes (CNTs) as fillers in polymeric composites is an attractive way of utilizing their superior properties [10,17–19] because of their unique structural and excellent electrical properties, high dielectric constant at room temperature, low dielectric loss, and mechanical properties [17,20–23]. Unfortunately, pure CNTs are insoluble in any organic solvent because of their intrinsic chemical structure. Also, CNTs tend to aggregate because of their extremely high surface energy, which leads to inhomogeneous dispersion in the polymer matrix and negative effects on the properties of the resulting composites. Therefore, special and more effective methods must be sought to fabricate composites with CNTs homogeneously distributed throughout the polymer matrix. To this end, several approaches have been reported [24–26], including the chemical modification of CNTs [27–31] and the *in situ* polymerization of polymers with CNTs.

In the present work, multi-walled carbon nanotubes (MWNTs) were chosen as nano-fillers for the PI matrix. The MWNTs were grafted with acylchloride to enhance their solubility in the reaction medium composed of *N,N*-dimethylacetamide (DMAc), and raise their dispersion efficiency. The PI/MWNT composite films were prepared by either *in situ* polymerization or blending

polymerization after incorporating various mass fractions of MWNTs into a diamine/dianhydride/solvent system. The morphology, structure, as well as thermal and dielectric properties of the resultant composites was also investigated. The chemical structure, mechanical properties and electrical characteristics of the composite films with various MWNT contents were analyzed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA) and the semiconductor characterization system.

## 2. Experimental

### 2.1. Materials

MWNTs produced via the chemical vapor deposition method were purchased from Nanotech Port Co., Ltd. (China). These had an outer diameter of 30–40 nm, inner diameter of 2–6 nm, and length of 2–10  $\mu\text{m}$ , and were purified to a high level (>95%). 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) were obtained from Shanghai Chemical Reagent Co. (China) and purified by vacuum sublimation. DMAc (Shanghai Chemical Reagent Co., China) was distilled over powdered calcium hydride under reduced pressure and stored over 4 Å molecular sieves prior to use.

### 2.2. Preparation of acylchloride-grafted MWNTs

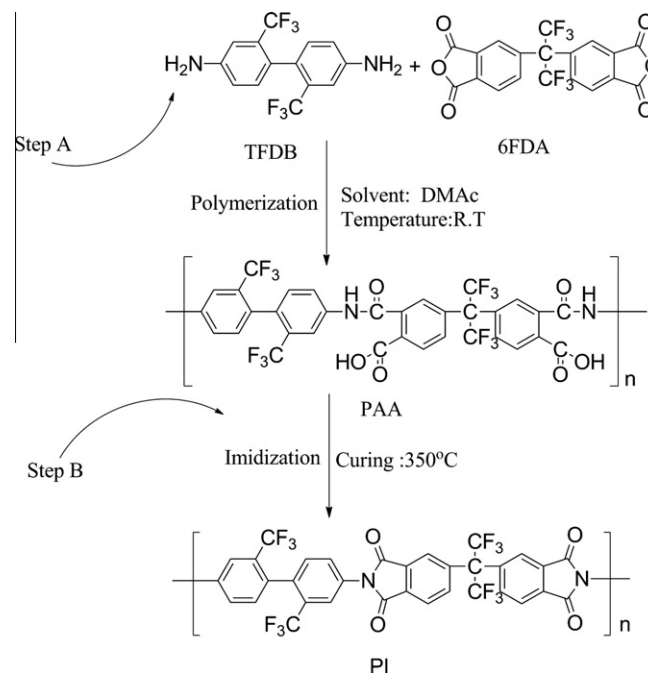
MWNTs functionalized with carboxylic acid groups (MWNT–COOH) were prepared as follows. The MWNTs were first added to an acid mix, composed of 98% sulfuric acid and 70% nitric acid (volumetric ratio, 3:1) at room temperature. The MWNTs and acids were stirred for 1 h with the aid of an ultrasonicator. After stirring, the mixture was refluxed for 4 h at 70 °C. The resultant reflux was centrifuged, washed with water, and dried under a vacuum for 24 h at 80 °C. The obtained MWNT–COOH were dissolved in dimethylformamide, followed by the addition of a certain quantity of  $\text{SOCl}_2$  and refluxing for 12 h at 70 °C. After refluxing, the excess  $\text{SOCl}_2$  and solvent were pumped. Finally, the residue was dried under a vacuum for 24 h at 100 °C.

### 2.3. Preparation of PI/MWNT nanocomposites

The pure PI (6FDA/TFDB) was synthesized according to literature [9]. The polymerization process is illustrated in Scheme 1.

The composite films were prepared by blending as follows. In a flask, 5 mL DMAc and an appropriate amount of MWNT–COCl were placed and vigorously stirred for 1 h at room temperature with an ultrasonicator until a homogenous suspension of MWNT–COCl/DMAc was obtained. Next, 0.8000 g (0.0025 mol) TFDB and 10.50 mL DMAc were placed in a flask and stirred for 30 min. Then, 1.150 g (0.0026 mol) 6FDA, in which the molar ratio of the diamine to the dianhydride was 1:1.03, was added into the suspension. The suspension was stirred overnight to prepare a 10.0% poly(amic acid) (PAA) solution. The PAA solution was then added to the prepared MWNTs/DMAc suspension. A sticky and homogenous suspension was obtained after stirring the resultant mixture for 24 h. This suspension was cast onto clean glass or stainless slides. Each slide was evaporated for 12 h at 60 °C, and then step-cured for 2 h at 100, 150, 200, 250, and 300 °C. The PI/MWNT nanocomposites were thus obtained.

In the *in situ* polymerization process, the MWNT–COCl/DMAc suspension was blended with diamine and dianhydride prior to the reactions, instead of with the PAA solution. The rest of the steps for yielding nanocomposites from *in situ* polymerization were identical to those for blending.



**Scheme 1.** Preparation of fluorinated polyimide composites (composites films prepared by means of *in situ* polymerization MWNTs–COCl were added at Step A, while blending method at Step B).

### 2.4. Characterization

FTIR spectra were obtained using a Nicolet 6700; the wavenumber range was set from 400 to 4000  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and an interval of 1  $\text{cm}^{-1}$ . The morphology of the MWNTs, MWNT–COOH, and MWNT–COCl was imaged on a transmission electron microscope (TEM, Philips Tecani 20). The phase morphology of the nanocomposites was imaged on a scanning electron microscope (SEM, FEI SIRION 200). Thermal-gravimetric analyses (TGA) were conducted using a NETZSCH DSC 200 F3 thermal analyzer under an argon atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ . Dynamic mechanical analysis (DMA) was carried out in a TA Instruments DMA Q800 apparatus at 1 Hz frequency with a heating rate of 4 °C  $\text{min}^{-1}$ , using the tensile mode. Rectangular samples were cut from the films with ca. 4 mm width and 25 mm distance between clamps. The electrical capacitance was measured on a KEITHLEY 4200-SCS semiconductor characterization system at different frequencies, while the thickness of the composite films was measured with an Alpha-Step IQ surface profiler. Each film was measured five times and their average was taken as the result. The dielectric constant was calculated from the measured capacitance data as follows:

$$\varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot S} \quad (1)$$

where  $C$  is the electrical capacitance,  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the permittivity of the free space ( $8.85 \times 10^{-12}$  MKS unit), and  $d$  and  $S$  are the film thickness and electrode area, respectively.

## 3. Results and discussion

### 3.1. Morphology of the unmodified and modified MWNTs

Fig. 1 presents the TEM images of the unmodified and modified MWNTs. In Fig. 1a and b, the unmodified MWNTs aggregate severely, indicating that the unmodified MWNTs are poorly dis-

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