Preparation and Characterization of Copolyimide/Carboxylated Multiple-walled Carbon Nanotubes Composite Films

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Abstract. The copolyimide/MWCNTs-COOH composites were synthesized by pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 4,4′-diaminodiphenyl ether (ODA) and the carboxylated multiple-walled carbon nanotubes (MWCNTs-COOH) through ultrasonic dispersion in situ polymerization. And the mechanical and thermal properties of the composite films were studied. The results showed that the carbon nanotubes were well dispersed in the polyimide composite films, the tensile properties and thermal stability were improved significantly.

1. Introduction
PI was a kind of polymer containing imide rings in the main chain. Because of its aromatic ring and heterocyclic ring structure, it exhibits a series of excellent comprehensive properties and was widely used in aerospace, microelectronics, automobile, oil and other high-tech fields [1, 2]. Carbon nanotubes (CNTs) were first discovered by Oberlin et al. [3] and aroused great interest since the rediscovery by Iijima [4]. They have been considered as excellent reinforcing fillers in polymer nanocomposites (NCs) because of their outstanding properties like high aspect ratio, nanosize in diameter, very low density, and, more importantly, excellent physical properties such as extremely high mechanical strength, high electrical, and thermal conductivity. Wu et al. [5] described a method for achieving enhanced dispersion of carbon nanotubes in the polyimide matrix by high-energy ball mill. The results showed the mechanical properties of nano-carbon incorporated PI composite films have improved significantly. Hu et al. [6] also studied amino functionalized multi-walled carbon nanotubes (MWCNTs)/polyimide nanocomposites using in situ polymerization method to disperse MWCNTs in the polyimide matrix. Rooollah moosavi Adbehgah et al. [7] doped MWCNTs-COOH with the fluorinated polyimide to obtain the nanocomposites, the mechanical properties of the composites enhanced significantly.

The thermal and mechanical properties of traditional biphenyl polyimide film are poor, which cannot meet the market’s demand at present. In order to improve the thermal and mechanical properties of polyimide films better, in this study, carboxylated carbon nanotubes were taken as reinforcing materials and polyimide/carbon nanotube composite films were prepared by copolymerization of pyromellitic dianhydride, biphenyl tetracarboxylic dianhydride and
aminobiphenyl ether and the carboxylated carbon nanotubes. What’s more their mechanical and thermal properties were also studied.

2. Experimental

2.1. Raw materials
Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) was supplied by Beijing Boyu High-tech New Materials Technology Company with carboxyl group content of 0.2wt% to 1.0wt%, the diameter of 20 to 30 nm, the length of 10 to 30 m, and purity of 95%. The 4,4'-diaminodiphenyl ether (ODA) were obtained from Nantong Huishun Chemical Co., Ltd, the 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were obtained from Shijiazhuang haili Chemical Co., Ltd and the pyromellitic dianhydride (PMDA) were obtained from Rugao Leheng Chemical Co., Ltd. The raw materials were all dried in an vacuum drying oven at 105°C for 6 h. N, N-dimethylacetamide (DMAc) were obtained from Tianjin Yongda Chemical Reagent Co., Ltd.

2.2. Preparation of the polyimide/MWCNTs-COOH nanocomposites
The DMAc and ODA were placed into a flake and vigorously stirred until the ODA was completely dissolved. Then the MWCNTs-COOH (0, 0.2wt%, 0.5wt%, 0.8wt%, 1.0wt%) was added into the system and dispersed by sonication for 1h to obtain a homogenous black solution. Moreover, BPDA and PMDA with the same molar ratio of diamine were added into the solution. Then the thick and evenly dispersed PAA/MWCNT-COOH solution with a solid content of 18 wt% was obtained successfully after 4h’s stirring in the water bath at room temperature. Finally, the suspension solution was casted onto a clean glass plate, evaporating DMAc at 70°C for 2.5h, and then curing (at each temperature of 100°C, 150°C, 200°C, and 300°C for 1h, respectively), the polyimide/MWCNTs-COOH composites films were obtained.

2.3. Characterization
Fourier transform infrared (FT-IR) spectroscopic measurements were performed to identify the structure of synthesized samples using PerkinElmer Spectrum 100. MWCNT-COOH dispersion in the polyimide matrix was observed by a scanning electron microscope (SEM). Thermal-gravimetric analyses (TGA) were performed on Waters Company TGA-Q50 in the nitrogen atmosphere with a heating rate of 20°C/min from 40°C-900°C. The glass transition temperature(Tg) was measured by DSC. Tensile properties were measured from tensile test at room temperature using a tensile tester (SANS CMT6104).

3. Result and discussion

3.1. FT-IR
Figure. 1 shows the FT-IR spectra of neat PI film and MWCNTs-COOH/PI composite film. From the spectrum of MWCNTs-COOH/PI composite film, we can see that the peak at 1773cm⁻¹ and 1707cm⁻¹ correspond to imide C=O symmetric stretching and imide C=O asymmetric stretching, respectively. And 1365cm⁻¹ corresponds to C-N stretching. And the absorption peak at 729 cm⁻¹ corresponds to bending vibration of C=O group. C–C stretching of the aromatic ring appears at 1505 cm⁻¹. A broad band at 2930cm⁻¹ can be assigned to the carboxyl groups. Comparing with the spectrum of neat polyimide film, the FT-IR spectrum of the composite film are almost the same as those of PI films, indicating that the addition of MWCNTs-COOH has no significant effect on the chemical structure of polyimide.
3.2. DSC analysis
Figure 2 shows the DSC curves of the neat PI film and MWCNTs-COOH/PI composite films. The Tg of neat PI film is 271.3 °C, when 0.2wt% MWCNTs-COOH was added to the matrix, Tg slightly change. The Tg of 0.2wt% MWCNTs-COOH/PI was 271.9 °C. When the MWCNTs-COOH content was 0.5wt% and 1.0%, Tg was increased to 278.1 °C and 283.9 °C, respectively, because of the formation of hydrogen bonds between carboxyl groups on MWCNTs-COOH and carbonyl groups of PI matrix, which limited the movement of the PI chain and reduced the free volume of the composites. Obviously, we can obtain that with the increase of MWCNTs-COOH content, the Tg of the composite film increases.

3.3. TG analysis
The thermal properties of neat PI film and MWCNTs-COOH/PI composite films were studied by means of TGA at heating rate of 20 °C/min under a nitrogen atmosphere. Figure 3 shows the decomposition temperature at 5% weight loss (T_d^5) of the neat PI was 574.3 °C. The nanocomposite film with 0.2wt% MWCNTs-COOH loading demonstrated almost the same T_d^5 as neat PI. We could observe the T_d^5 were increased with further loadings of 0.5 and 1.0wt% MWCNTs-COOH. When the loading of MWCNT-COOH was 1.0wt%, the T_d^5 was 580.4 °C. The improvement in the thermal stability of samples with MWNTs-COOH was attributed to the interfacial adhesion between
MWCNTs-COOH and PI matrix.

![TGA curves of neat PI film and the MWCNTs-COOH/PI nanocomposite films.](image)

**Figure 3.** TGA curves of neat PI film and the MWCNTs-COOH/PI nanocomposite films. (a) neat PI, (b) 0.2wt%, (c) 0.5wt%, (d) 0.8wt%, (e) 1.0wt%.

3.4. Mechanical properties

Figure 4 shows the tensile strength curves of neat PI and nanocomposites with various MWCNTs loadings. The incorporation of 0.2wt% MWCNTs into polyimide matrix resulted in the moderately increased tensile strength by 8.5%, compared with the neat PI (117MPa). With the nanocomposites containing 0.5wt%, the tensile strength experienced the most dramatic increase by 33.3% and the maximum value reached 156.3MPa. The improvement in the tensile strength can be caused by the strong interactions between polyimide matrix and MWCNTs-COOH.

![Tensile stress curves of neat PI and MWCNTs-COOH/PI nanocomposite films.](image)

**Figure 4.** Tensile stress curves of neat PI and MWCNTs-COOH/PI nanocomposite films.

4. Conclusion

MWCNTs-COOH/PI nanocomposites were successfully prepared by in situ polymerization. The results show that the MWCNTs-COOH can be dispersed in the matrix. The MWCNTs-COOH/PI composite films with only 0.5wt% MWCNTs-COOH content showed a 33% increase in tensile strength. The maximum value of the $T_d$ can reach 580°C.

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