Functionalization Multi-walled carbon nanotube and Its Bismaleimide Composites of Properties

Changwen Song, Hongxia Yan, Yi Zhang, Yusheng Tang

Department of Applied Chemistry, School of Natural of Applied Science,

Northwestern Polytechnical University, Xi'an 710072, P R China

Abstract：Carbon nanotubes (CNTs) were one of nanoparticles with unique structure and significant advantages. But the application of CNTs was limited because of the inert surface of CNTs. In this paper , fluorinating Multi-walled carbon （F-MWNTs）was synthesized by solid-phase method which taken an organic fluoride compound as the main raw material, make function carbon nanotubes. As a comparison, raw MWNTs and F- MWNTs have been characterized by using FTIR、XRD、XPS. The results showed that C–F bonds were created on the surface of carbon nanotubes, successfully synthesis fluoride carbon nanotubes. The mole contents of fluorin atom can be reached 3.59 mol%. The demonstrated C-F functionalization provides a new synthetic method and the F-MWNTs can be used as precursors for the preparation ofbismaleimide-MWNTs polymer materials.The bismaleimide (BMI)/MWNTs composites were prepared by in situ polymerization. The results showed that BMI with MWNTs fillers has extraordinary significance for the development of advanced materials with enhanced mechanical properties.

Key Words：MWNTs，Functionalization，Bismaleimide，Properties

1. Introduction

Carbon Nanotubes(CNTs) are unique nanostructured materials with remarkable physical, mechanical, chemical and electronic properties. Theses properties make them attractive for applications in many scientific and technological fields such as electronic structures, polymer composites, and biological systems[1-5]. CNTs/polymer nanocomposites have attracted considerable attention by scientists in resent years[6-9]. However, the limited ability to process and disperse in organic solvent CNTs hinders the realization of their full potential. To overcome this obstacle, surface modification of CNTs was very important in application of modified polymer [10].

In our present work, at first fluorinating multi-walled carbon nanotubes (F-MWNTs) was synthesized by solid-phase method which was a new synthetic method being differently from gas-phase method[11,12].Then the F-MWNTs can be used as precursors for the preparation of bismaleimide-MWNTs polymer materials by in situ polymerization.

2. Experimental

2.1 Materials

MWCNTs used in the paper were provided by Zhejiang University which were prepared by catalytic chemical vapor deposition method. The powder of polytetrafluoroethylene (PTEF) was supplied by HuBei Fengguang Chemicals. Bismaleimide prepolymer (BMI) was prepared by group of Rongchang Ning in Northwestern Polytechnical University (China).

2.2 Fluorinated MWNTs

Fluorinating multi-walled carbon nanotubes (F-MWNTs) was synthesized by solid-phase method which an organic fluoride (PTEF) and multi-carbon nanotubes (MWNTs) were

heated to 480-500°C for 4h in sealed vessel. The proportion of MWNTs and PTEF is 1:10. As a comparison, raw MWNTs and F-MWNTs have been characterized by using FTIR, XRD and XPS.

2.3 Properties measurements

2.3.1 Sample preparation:

At first , bismaleimide prepolymer (BMI) were melt by heating. Then F-WMNT were dispersed in acetone with ultrasonically stirring for 40 minutes at room temperature. Then the suspension was added into melted BMI at 120^{o}C and kept that temperature at stirring for 40mins. Then the mixture was poured into warm-up mould with silicone as a release layer, and the mould with the mixture was kept in a vacuum chamber and deaerated for 30 min. Following, curing:150^{o}C/1h+180^{o}C/2h +200^{o}C/2h; post-curing: 220^{o}C/4h.

2.3.2 Mechanical properties and analysis:

Composites castings were cut using a grinding wheel cutter into samples for mechanical testing in term of GB2571-1981, GB2570-1995 for determining flexural and impact strength properties, respectively. Five specimens were tested for each test and average values are reported.

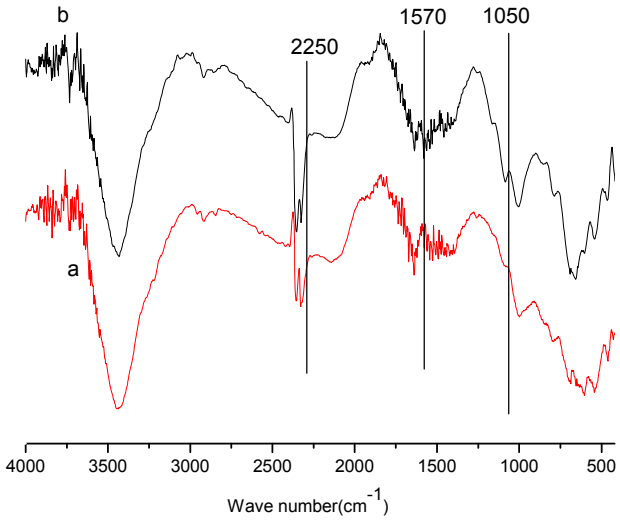
The micro morphology of the cured resin and the composites were investigated by scanning electron microscopy (SEM) on HITACHIS-570 SEM. The fracture surface of was coated with gold by vapor deposition.

3. Results and Discussion

3.1 Functionalization MWNT

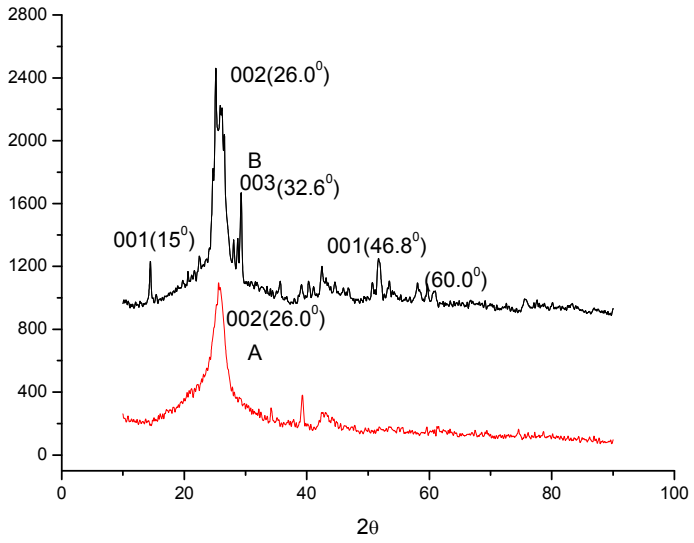
The nature of the surface groups of the F-MWNTs and the raw MWNT were investigated using FTIR spectroscopy (Fig.1). Both samples have two large peaks, one at 1570 cm^{-1}

and another at 2250cm^{-1}, which are assigned to the CNTs skeletal motions [10, 11]. Furthermore, the second-order curve displays a broad peak centered at 1050 cm^{-1} in Fig.1(b), due to the existence of C−F bonds [11]. The results of FTIR spectra confirmed the formation of new chemical bonds on the raw MWNT after treatment.



a: the raw MWNT ; b: F-MWNT

Fig. 1 FTIR spectra of the raw MWNT and F-MWNT.



a: the raw MWNT ; b: F-MWNT

Fig. 2 XRD spectra of the raw MWNT and F-MWNT

As shown in Fig. 2, the XRD results revealed the characteristic microstructure of MWNT. the XRD patterns indicate the persistence of the main reflection of the original CNT, at $2\theta \approx 26^{o}$ (Fig. 2(a)). Same results were reported in other studies [12-14]. Therefore, the structure of cylindrical concentric carbon layers is preserved. In addition, there were two characteristic peaks at $2\theta \approx 15^{o}$ and $2\theta \approx 32.6^{o}$ on the second-order curve in Fig. 2(b). Some new layered patterns (46.8^{o}, 60^{o}) in Fig. 2(b) could also be seen.

A survey XPS spectrum of a F-MWNTs sample, and for comparison, of non-fluorinated MWNTs, both are presented in Fig. 3, Fig. 4. Amount of carbon, fluorine and oxygen in the surface layer is presented in Table 1. As shown in Fig. 4 there is a new minor peak component at the binding energy of 687.8 eV corresponding to F 1*s* of the functional reaction on MWNT, which does not exist in the Fig. 3. As shown in Table 1, the carbon

C 1*s* *a*reas observed at 71125 in the raw sample is increased by 76395 to a higher binding energy after treatment, partly due to the appearance of electrophilic groups [15].

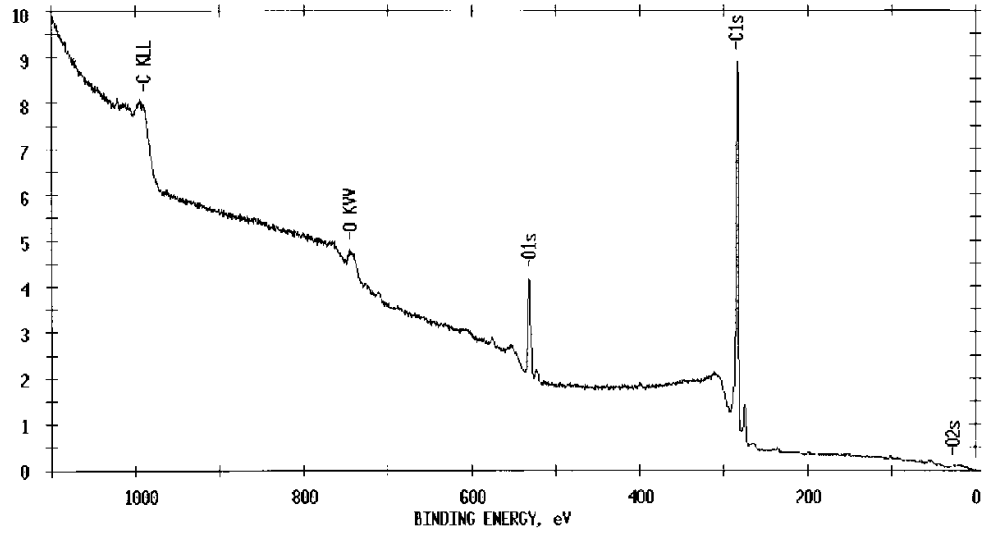


Fig. 3 XPS spectra of raw MWNT

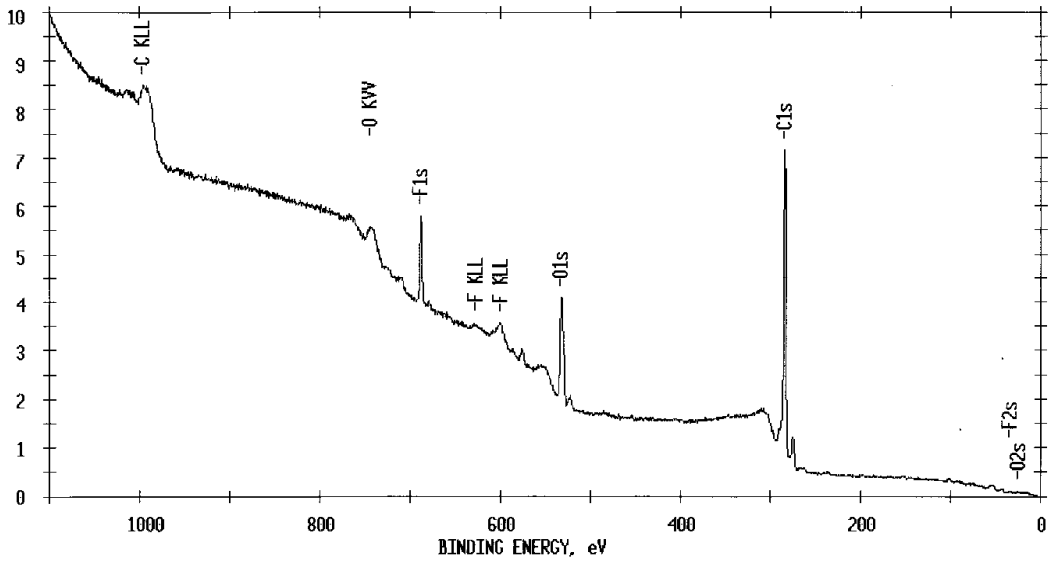


Fig. 4 XPS spectra of F-MWNT

Table 1 The result of analyzing CNTs and F-CNTs by XPS

Samples	Element	Area /cts-eV/s	Sensitivity Factor	Concentration /%
Raw MWNT	C1s	71125	0.296	88.78
	O1s	21582	0.711	11.22
	F1s	—	0	—
F-MWNT	C1s	76395	0.296	82.32
	O1s	31417	0.711	14.09
	F1s	11245	1.000	3.59

3.2 Mechanical properties

Table 2 shows the relationship between impact strength and the content of F-MWNT. From Table 2 we can see that the impact strength of BMI was improved by adding F-MWNT. First with the increase of the content of F-MWNT the impact strength of the system was enhanced and reach peak when the content is 0.6%. The impact strength was 14.68 kJ/m^2, which is much higher than the impact strength of pure BMI that was 9.48 kJ/m^2.

Tabel 2 The relationship between impact strength and the content of F-MWNT

F-MWNT (wt%)	Impact Strength (KJ/m^2)
0.0	9.48
0.2	11.98
0.4	12.79
0.6	14.68
0.8	11.15
1.0	10.82

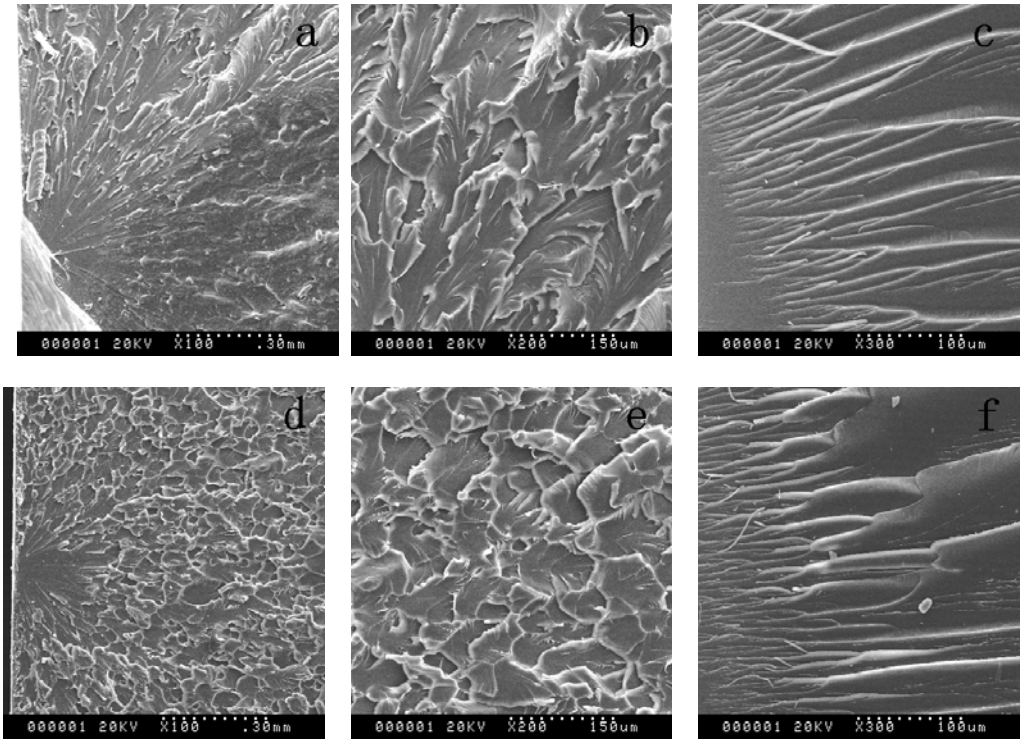


Fig. 6 SEM of fracture surfaces in the impact test of composites

a，b，c：pure BMI；　d，e，f：BMI/F-MWNT (F-MWNT:0.6%)

Fig. 6 is SEM of fracture surfaces in the impact test of samples. Photographs a, b, c are pure BMI. In these photographs, the fracture surfaces were comparatively slippery and the fracture headstream is wide. Photographs d, e, f were about BMI/F-MWNT (the content of F-MWNT was 0.6%). In contrast to pure BMI the fracture headstream of BMI / F-MWNT was small and the fine cracks were dumpy and in particular the number of toughness eddy, which was obvious bigger, is more in unit area.

4. Conclusions

A solid-phase method fluorinated MWNTs was different from the gas-phase method which usually taken strong poisonous fluorine gas as the main raw material was reported. The results in FTIR, XPS and XRD spectrums confirmed that the surface of MWNT was successfully functionalized by PTEF. Furthermore, F-MWNT was well dispersed in polar

solvents. The mechanical properties of bismaleimide resin were improved by adding F-MWNT. When the content of F-MWNT was 0.6wt%, the impact strength of BMI/F-MWNT composite could be increased 54.8%.

References

1 Chen W X, Tu J P, Wang LY, et al. Tribological application of carbon nanotubes in a metalbased composite coating and composites. Carbon, 2003, 41(2):215~22.

2 Abu Barkar Sulong, Joohyuk Park. Wear behavior of functionalized multi-walled carbon nanotube reinforced epoxy matrix. Composite Mater 2006, 40(21):1947～1960.

3 Yang Jie, Shen Zeng min, Xiong Tao. The preparation and properties of carbon nanotubes in-situ encapsulated by polyaniline. New Carbon Materials, 2003, 18(2):95～99.

4 Paiva M C, Zhou B, Fernando K A S, et al. Mechanical and morphological characterization of polymer-carbon nanocomposites from functionalized carbon nanotubes. Carbon, 2004, 42(14): 2849～285

5 D Q. Yang, J F. Rochette, E Sacher. Functionalization of multiwalled carbon nanotubes by mild aqueous sonication. Physical Chemistry B, 2005,109(16) 7788～7794

6 Mohamed Abdalla, Derrick Dean, Pamela Robinson, et al.Cure behavior of epoxy/MWCNT nanocomposites: The effect of nanotube surface modification. Polymer 2008, 49, 3310～3317.

7 F Chamssedine, D Claves. A kinetic, morphological and mechanistic approach of the fluorination of multiwall carbon nanotubes. Chemical Physics Letters, 2008, 454, 252 ~ 256.

8 Susumu Arai, Akihiro Fujimori, Masami Murai, et al. Excellent solid lubrication of electrodeposited nickel-multiwalled carbon nanotube composite films. Materials Letters, 2008, 62, 3545 ~ 3548

9 Jin shan Lu. Effect of surface modifications on the decoration of multi-walled carbon nanotubes with ruthenium nanoparticles. Carbon , 2007, 45 , 1599 ~ 1605.

10 M S P Shaffer, X Fan, A H Windle. Dispersion and packing of carbon nanotunanotubes, Carbon, 1998, 36(11), 1603 ~ 1612

11 Fadel Chamssedine, Daniel Claves. Three different modes of fluorine chemisorption at the surface of single wall carbon nanotubes. Chemical Physics Letters, 2007, 443 102 ~ 106

12 Z Gu, H Peng, R H Hauge, et al. Cutting single-wall carbon nanotubes through fluorination, Nano Letter. 2002,(2), 1009 ~ 1013.

13 W Zhao, C Song, B Zheng, J Liu, et al, Thermal recovery behavior of fluorinated single-walled carbon nanotubes. Physical Chemistry B, 2002, 106(2), 293 ~ 296.

14 S J Park, H J Jeong, C Nah. A study of oxyfluorination of multi-walled carbon nanotubes on mechanical interfacial properties of epoxymatrix nanocomposites. Materials Science and Engineering A, 2004, 385(1-2),13 ~ 16.

15 Giraudet J, Dubois M, Claves D, et al. Modifying the electronic properties of multi-wall carbon nanotubes via charge transfer by chemical doping with some inorganic fluorides.Chemical Physics Letters, 2003, 381(3-4): 306 ~ 314.

16 Okotrub A V, Yudanov N F, Chuvilin A L. Fluorinated cage multiwall carbon nanoparticles. Chemical Physics Letters, 2000, 322(3-4): 231 ~ 236.

17 Y M Shulga, TaChang Tien , ChiChen Huang, et al. XPS study of fluorinated carbon multi-walled nanotubes. Electron Spectroscopy and Related Phenomena 2007,160, 22 ~ 28.