

# EFFECT OF REACTIVE NANO-REINFORCEMENT ON MECHANICAL PROPERTIES OF PBO FIBER/EPOXY COMPOSITES

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## 1 Introduction

Poly-p-phenylene benzobisthiazole (PBO) fiber/epoxy composite is a kind of advanced material that has many promising applications in the fields of aerospace, military industry and general industry owing to the outstanding mechanical and thermal properties of PBO fiber<sup>1-2</sup>. However, the interfacial adhesion ability of PBO fiber is not good enough for practical uses. Because the surface free energy of PBO fiber is only 32.2 mJ/m<sup>2</sup>, it's difficult for the epoxy to wet the fiber<sup>3-4</sup>. Despite some aggressive researches, such as plasma treatment<sup>5-6</sup>, have been devoted to increase the surface free energy of PBO fiber<sup>7-8</sup>, the experimental results are still deficient. The improvement of performance of PBO fiber composites by increasing the wettability of epoxy is rarely reported.

As a result of their excellent mechanical, thermal, optical and electrical properties, carbon nanotubes (CNTs) have attracted worldwide attention. Unique atomic structure, very high aspect ratio, low density and extraordinary mechanical performance make them ideal reinforcing fillers in composites. Many researches have been conducted into developing high-performance CNT-filled polymer composites to fully exploit the potential of CNTs. However, it is reported that there is only marginal improvement or even decrease in mechanical properties of nanocomposites after adding commercial CNTs into epoxy matrices as a result of their aggregation and lacking of interfacial adhesion with matrices<sup>9-12</sup>. In the recent years, many progresses have been made

by researchers to improve the dispersion of CNTs and interfacial bonding with the matrices<sup>13-14</sup>. One method is the functionalization of commercial CNTs. A large number of methods for chemical functionalization of CNTs, either at the tips or sidewalls of them, have been attempted or employed<sup>15-17</sup>.

In fact, the combination of the nano-reinforcement and other traditional reinforcement will lead to the potential development of a new generation of hybrid composite materials with extraordinary behavior for both applications and fundamental science mechanisms<sup>18</sup>. In this work, the commercial MWNTs were chemically functionalized and then reactive-MWNTs (r-MWNTs) were prepared. On the basis of uniform dispersion of r-MWNTs in epoxy matrix, the three phase hybrid composites were prepared by filament winding of PBO fibers. The effects of r-MWNTs on the wettability of the epoxy matrix to PBO fiber as well as the mechanical and thermo-mechanical properties of the composites were studied in this paper.

## 2 Experimental

### 2.1 Materials

Multi-wall carbon nanotubes (MWCNTs) produced by chemical vapor deposition (CVD) method were purchased from Shenzhen Nanotech Port Co, Ltd (purity >95%). The alicyclic glycidyl ether type epoxy resin (TDE-85) was provided by Tianjin Jindong chemical

factory (epoxy value, 0.85). The curing agent, diethyl toluene diamine (DETDA, Aldrich chemical Co.) and 3'Dimethyl-4, 4' Diamino diacyclohexyl methane (DMDC, Aldrich chemical Co.) were used as received. PBO fiber was obtained from Toyobo Co., Japan.

## 2.2 Composites preparation

The amino-functionalized MWCNTs (f-MWCNTs) were obtained on the basis of the chemical grafting of the commercial MWCNTs. Then the amino-functionalized MWCNTs were mixed with the diluent, butyl glycidyl ether (BGE), and treated using a digital sonifier operating at 400 W for 2 h in an ice bath. After the f-MWCNTs reacted with BGE, the excessive solution was removed in a hot vacuum oven at 70°C until the weight ratio of MWCNTs and BGE decreased to 1:7, then the r-MWCNTs/diluents blend was obtained.

The resin matrices were made from TDE-85 epoxy resin and curing agent which was composed of DETDA and DMDC with a weight ratio of 3:1. The r-MWCNTs were dispersed into the epoxy by stirring 12 h at 60°C and then sonicating the mixture for 2 h at 60°C. The curing agent (30 wt %) was added into the obtained black mixture and agitated for 30 min at 25°C. After degassed in a vacuum oven, the mixture was used for testing of the surface energy and viscosity. The NOL rings were wound using a filament winding machine (MAW-20-LS1-6, Mikrosam Ltd) with 7N tension at 35°C. The NOL rings were cured at 80°C for 1h and 120°C for 2 h, following a post curing at 150°C for 2 h.

## 2.3 Characterizations

A Fourier Transform Infrared Spectroscopy (8700, Nicolet Ltd, USA) was applied to confirm the functionalization of the MWCNTs. The Instron 1211 machine (Instron Ltd., England) was applied to measure tensile strength and interlaminar shear strength of PBO/epoxy NOL-rings according to the ASTM D2290-00 and ASTM D2344/D2344M-00. The FE-SEM (Supra 55, Zeiss, Germany) was

applied to investigate the interfacial bonding between the PBO fiber and the nano-filled matrix through observing the structure and morphology of the fracture surface. Each sample was coated with Pt before SEM image observation.

## 3 Results and Discussion

### 3.1 The effects of reactive carbon nanotubes on wettability

The interface plays a vital role in stress transfer from one fiber to another in the matrix of a composite. An adequate wetting is required for taking advantage of the excellent mechanical properties of PBO fibers in composites. In general, the wettability of polymer matrix on the surface of a fiber could be characterized by the surface energy and the viscosity of the matrix. In practice, the wettability of the fiber reinforcement in the matrix can be improved by decreasing the surface energy and the viscosity of the uncured matrix.

The surface energy of different samples is given in Fig.1. The surface energy of all the matrices decreased with increased temperature, which indicates the wettability would be improved at a higher processing temperature. Sample without r-MWNTs had a higher surface tension compared to matrix with 0.5 wt% r-MWNTs. The surface energy demonstrated a decrease of more than 10 mJ/m<sup>2</sup> after adding 0.5 wt% r-MWNTs.

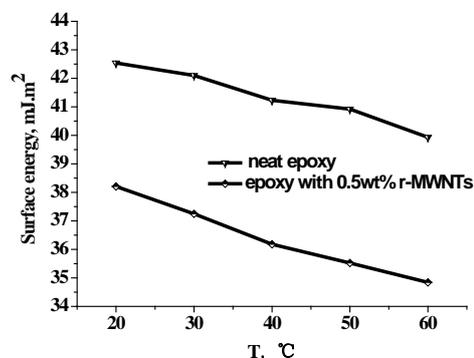


Fig.1. The surface energy of epoxy resin

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As shown in Fig.2, the viscosity of resin decreased as the rising of temperature. When the temperature was below 30 °C, the viscosity of the pure epoxy was lower than sample containing 0.5 wt% r-MWNTs. As the temperature rising, the viscosity gap between samples with or without r-MWNTs got smaller and smaller. when the temperature was higher than 30 °C, the viscosity of the two samples almost got to the same value.

As a result, the addition of r-MWNTs was effective to decrease the surface energy of epoxy while there was no obvious influence on viscosity of resin at a temperature above 30 °C. And the contact angles between the epoxy and PBO fibers became smaller by adding 0.5 wt% r-MWNTs. In general, The processing temperature of resin composites is often higher than 30 °C, and the r-MWNTs can improve the wettability of the epoxy to the PBO fiber.

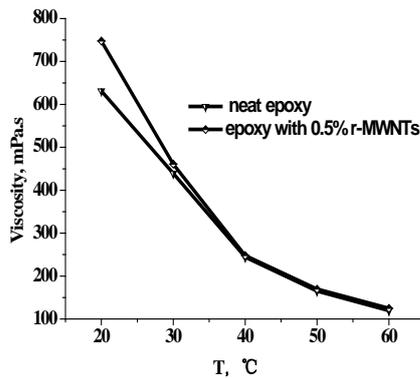


Fig.2. The viscosity of epoxy resin

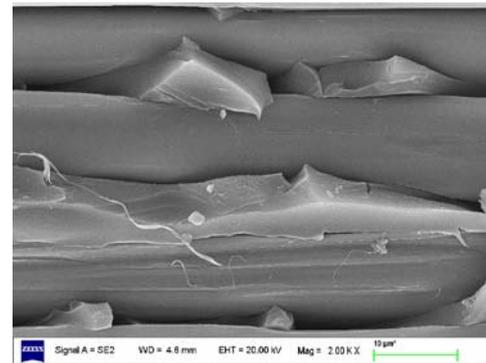
### 3.2 The effects of reactive carbon nanotubes on mechanical properties

The mechanical performances of two kinds of composites were measured, and the results are summarized in Table.1. After adding 0.5 % r-MWNTs, the tensile strength of the NOL-ring was raised by 11.02%, from 2289.7 to 2542 MPa. The tensile modulus and elongation were improved by 1.86 and 16.52%. The interfacial shear strength was improved by 61.1%, which is clear evidence of better interface adhesion between the fiber and the matrix by adding 0.5

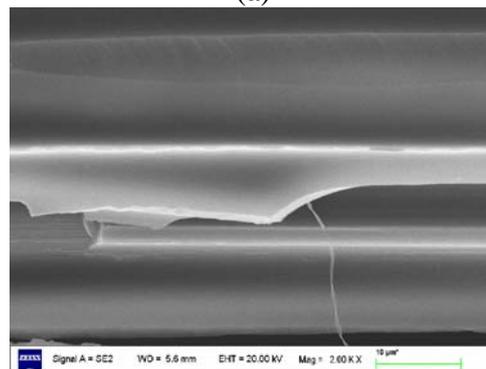
wt% r-MWNTs. And the results are also agreeable with the wettability characterization. The epoxy containing r-MWNTs wetted the fiber more fully and exhibited better interfacial bonding than that of pure epoxy.

Table 1 Mechanical properties of PBO composite NOL- rings

	Pristine epoxy	Epoxy with 0.5wt% r-MWNTs
Tensile strength (GPa)	2.29	2.54
Tensile modulus (GPa)	123.46	125.76
Elongation (%)	2.24	2.61
ILSS (MPa)	19.60	31.57



(a)



(b)

Fig.3. the microstructure of PBO/epoxy composites: (a) pristine epoxy, (b) epoxy matrix with 0.5 wt% r-MWNTs.

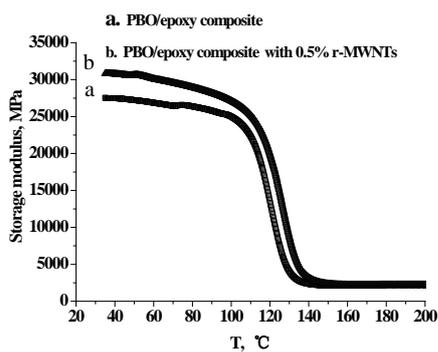
As shown in Fig.3(a) and (b), the interface adhesion between the PBO fiber and the matrix was enhanced remarkably after adding 0.5 wt% r-MWNTs. In Fig.3(a), the poor interface adhesion between the fiber and matrix was displayed, and it seems that the epoxy is blocked between the fibers. While in Fig.3(b), the epoxy wrapped the surface of the fibers, and no smooth fibers were found on the fracture surface, which may prove the strong interfacial bonding between the PBO fibers and the epoxy matrix in the composites.

### 3.3 The effects of r-MWNTs on thermo-mechanical properties

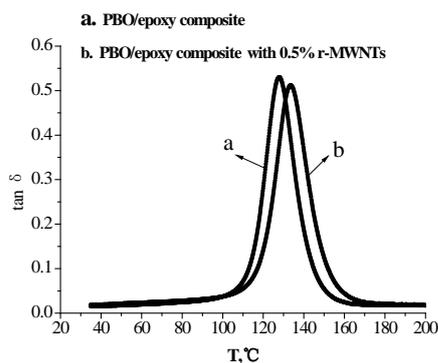
The effect of the r-MWNTs on the dynamic mechanical property of the PBO fiber/epoxy composites was analyzed by DMA in the experiment. The storage modulus ( $E'$ ) and the

loss factor ( $\tan \delta$ ) of the PBO fiber/epoxy composites were characterized as functions of temperature. As shown in Fig.4(a), an obvious increment of the storage modulus was observed in glassy region and glass transition region after adding r-MWNTs, which is consistent with the increased tensile modulus of composites. The r-MWNTs can enhance the stiffness of the epoxy matrix which induced an increment of storage modulus of the composites.

At the same time, the addition of r-MWNTs has affected the glass transition temperature ( $T_g$ ) of resulting composites (Fig.4(b)). The  $T_g$  exhibited a shift from 128.2°C to 133.5°C as a result of the addition of r-MWNTs. This phenomenon can be attributed to the stronger interfacial interaction in the composites containing r-MWNTs, which restrained the movement of polymer chains.



(a)



(b)

Fig.4. Storage modulus (a) and loss factor (b) of PBO composites

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