# Creep and Dynamic Mechanical Behavior of Natural Fiber/Functionalized Carbon Nanotubes Modified Epoxy Composites

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**Abstract**: The creep and dynamic mechanical behavior of natural fiber/epoxy composites using functionalized multiwalled carbon nanotubes (MWCNTs) modified matrix were investigated. 0.4 wt% of MWCNTs functionalized with carboxylic acid groups (MWCNTs-COOH) were dispersed in epoxy and three-phase multiscale hybrid composites were processed by hot press. Natural fiber/epoxy two-phase composites without MWCNTs were also processed by the same method for comparison. The morphologies of the two kinds of natural fiber reinforced composites were observed with the aid of Scanning Electron Microscopy (SEM). Two hours creep tests at 35°C with a constant stress level of 2 MPa and temperature scan from 55°C to 180°C at a frequency of 1 Hz were performed by a Dynamic Mechanical Analysis (DMA) instrument. The results showed that the creep resistance of natural fiber reinforced composites was greatly improved by the addition of MWCNTs. Both the dynamic mechanical analysis and morphology observations indicated the incorporation of MWCNTs restricted the movement of molecular chain of the epoxy resin and also set up bridging between natural fiber and polymer matrix, which all contributed to the improvement of the creep resistance of the composites.

**Keywords:** *Functionalized carbon nanotubes; Natural fiber; Multiscale composites; Creep; Dynamic mechanical behavior*

## 1 General Introduction

Natural fibers such as flax, hemp, sisal, ramie, jute have gained great attention as reinforcement for composites because they are low cost, low density, high specific strength and modulus and also recyclable and biodegradable compared to the traditional glass and carbon fibers[1-3]. Ramie fibers are extracted from stem bast and have an exceptional strength compared to other natural fibers[4]. Physical properties (surface topography, tensile properties, and thermal properties) of ramie fibers have been investigated[5] and the research results have shown that ramie fibers exhibit good thermal stability and high specific tensile properties. Thus, ramie fibers are considered as good reinforcing element in making polymer matrix composites.

Creep is one of the principal properties of natural fibers reinforced polymer composites and it is of great importance to understand the creep behavior for many applications such as aerospace, biomedical and civil engineering[6, 7]. Some works on the creep behavior of natural fiber reinforced polymer composites have been reported. Acha et al.[6]studied the effect of the interfacial adhesion on the creep and dynamic mechanical behavior of jute fiber reinforced PP composites. Creep behavior of bagasse fiber reinforced polymer composites has been reported by Xu et al.[8]. NUÑEZ et al.[9] analysed the creep behavior of polypropylene-woodflour composites. Several studies have also reported on the creep behavior of natural fiber reinforced polymer composites[10-12].

Carbon nanotubes (CNTs) possess excellent mechanical, electrical and thermal properties, making them an ideal candidate as reinforcing filler[13]. Small dimensions of CNTs mean they have much greater interaction with composite matrices[14]. However, a interfacial interaction between the polymer matrix and the carbon nanotubes is weak due to the inert nature of the carbon nanotubes[15]. In order to improve the interactions between the epoxy resin and the carbon nanotube, various functionalized carbon nanotubes such as amino- functionalized, fluorinated, carboxylic acid-functionalized were dispersed in the epoxy matrix to form composites[15,16]. Upon curing, functionalized multiwalled carbon nanotubes with carboxylic acid groups (MWCNTs-COOH) are connected with the epoxy matrix by cross-linking reaction[15] and MWCNTs-epoxy interface can be improved.

Traditional fiber reinforced carbon nanotubes modified matrix composites have attracted great attention in recent years[17-22]. Relevant studies have shown that the fibre-dominated properties are not significantly affected by the introduction of CNTs[23], while matrix-dominated properties are improved to some extent[15]. However, very limited work has been reported on the CNT modified natural fiber reinforced polymer composites.

In this paper, the creep and dynamic mechanical behavior of ramie fiber/epoxy composites with and without CNTs were investigated. The effects of CNTs on the creep and dynamic mechanical behavior of composites were revealed.

## 2 Experimental

### 2.1 Materials

Functionalized multiwalled carbon nanotubes with 2.56 wt% carboxylic acid groups (MWCNTs-COOH) produced by chemical vapor deposition (CVD) method were provided by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The outer diameter and length of MWCNTs-COOH are 8–15 nm and approximately 50μm, respectively. Commercial plain woven ramie fabrics purchased from Jiangxi province (China) were used as reinforcement. The epoxy resin, curing agent and accelerator used for composite preparation were Epon 862, micronized dicyandiamide (®Dyhard 100 S) and Fenuron (®Dyhard UR 300). The accelerator was used for this purpose to reduce the curing temperature due to the limited thermal stability of natural fibers during composite processing.

### 2.2 Composites preparation

The MWCNTs were first dispersed in the appropriate amount of acetone by mechanical stirring for 30 minfollowed by ultrasonication in a bath sonicator (sonic power 90W) for 4 h. The epoxy resin, diglycidyl ether of bisphenol F (EPON 862), was subsequently added to the MWCNTs suspension followed by 30 min mechanical stirring to ensure good dispersion and then the blend suspension was sonicated in ultrasonic bath for 1 h. The epoxy composites with 0.4 wt% MWCNTs -COOH (weight percentage in the cured epoxy matrix) were mixed at 60$^{o}$C with the curing agent in the ratio of 100:8 and 100:2 by weight, respectively. The ramie fabrics were dried in an oven at 120$^{o}$C for 4 h to remove moisture. The prepreg was produced by hand and the residual acetone was removed at 80$^{o}$C for 4 h and then at room temperature overnight. The composite was manufactured by hot press at 115$^{o}$C under a pressure of 2.5 MPa and then post cured at 130$^{o}$C for 2 h. Natural fiber/epoxy two-phase composites were also processed by the same method. The fiber volume content of the two-phase and three-phase composites were approximately 58%. The composites were machined into test specimens for testing.

### 2.3 Creep test

Rectangular specimens with a sizes of 56 *mm*×12 *mm*×2.5 *mm* were made for the creep tests. Dynamic Mechanical Analysis (DMA) instrument (TA Q800) was used to measure deformation as a function of time. The tests were carried out in the creep mode, using the three-point bending fixture. Two hours creep tests at 35°C with a constant stress level of 2 MPa were performed. The fracture surfaces of the two-phase and three-phase composites under flexural loading were comparatively examined and analyzed by SEM.

### 2.4 Dynamic mechanical analysis

The same equipment and sample dimensions reported in the creep test were used for the dynamic mechanical tests. Temperature scan from 55°C to 180°C at a frequency of 1 Hz was performed. The heating rate was 3°C /min. Storage modulus ($E'$), and mechanical loss factor (tan$\delta$) were measured as the function of temperature during the test.

## 3 Results

### 3.1 Creep properties

Two hours creep properties of two-phase (without CNTs) and three-phase (with 0.4 wt% CNTs) composites at 35°C were evaluated. Fig. 1 shows the effect of CNTs on the creep properties of composites. It is observed that the creep deformation of three-phase composites with 0.4 wt% CNTs decreases compared to the two-phase composites without CNTs, which shows creep resistance of the three-phase composites is better than the two-phase composites. The creep properties are especially sensitive to interfacial interactions between matrix and reinforcements and also to the properties of the polymer matrix. From previous study[15], it has been indicated the presence of MWCNTs-COOH improved the interfacial bonding between the MWCNTs and epoxy resin due to the chemical reaction of the carboxylic acid groups on the MWCNTs with the epoxy. Besides, MWCNTs -COOH was dimensionally similar to the polymer chain segments[24], which also restricts the motion

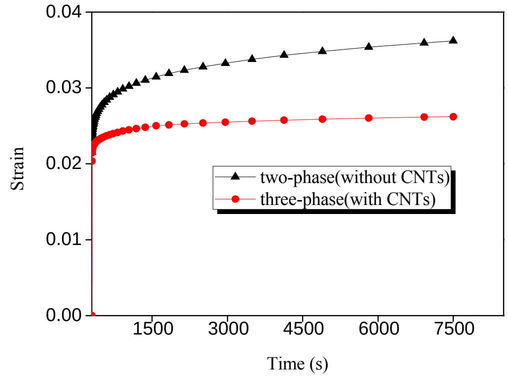


Fig. 1. Creep curves of two-phase (without CNTs) and three-phase (with 0.4wt% CNTs) composites.

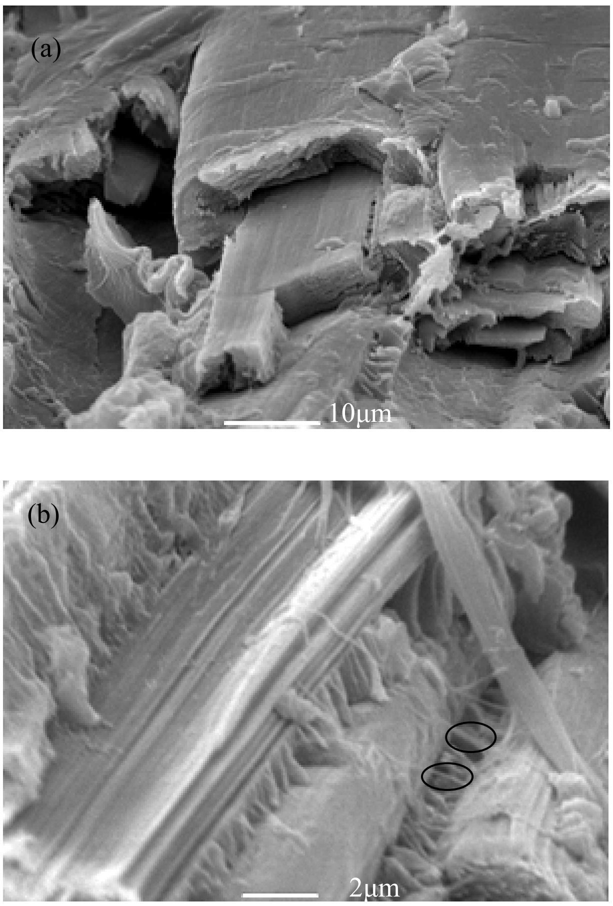


Fig. 2. (a) SEM picture of two-phase (without CNTs) sample fractured under flexural loading, (b) SEM picture of three-phase (with 0.4wt% CNTs) sample fractured under flexural loading. CNTs are present and indicated with the black ellipses.

of polymer chains and thereby improve creep resistance. SEM observation also showed that CNTs exist at the interface between ramie fiber and epoxy resin (the black ellipses in Fig. 2(b)) compared to Fig. 2 (a). Relevant research revealed that carbon nano-particles allow an infiltration between the micro-scaled fibres[23]. By adding CNTs in the matrix, a good bonding between fiber and polymer matrix can be set up, which also restrict the motion of the polymer molecules[24]. Therefore, it may also partly contribute to the improved creep resistance.

### 3.2 Dynamic mechanical analysis

The temperature (from 55°C to 180°C) dependence of storage modulus for the two-phase and three - phase composites is showed in Fig. 3. The results show that storage modulus of three-phase composites with 0.4 wt% CNTs is higher than two-phase composites.

Fig. 4 shows the change of the glass transition temperature (*T*g) of two-phase and three-phase composites. It is noticed that the glass transition temperature (*T*g) of natural fiber/epoxy composites, is 94.9°C, whereas *T*g of the three-phase composites with 0.4 wt% CNTs composites is increased by approximately 14°C. Both the increased storage modulus and *T*g indicated the restricted mobility of the resin molecules in the presence of the carbon nanotubes.

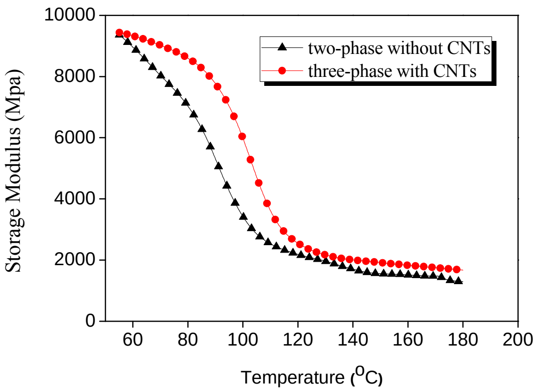


Fig.3. The variation of storage modulus of the two-phase (without CNTs) and three-phase (with 0.4 wt% CNTs) composites.

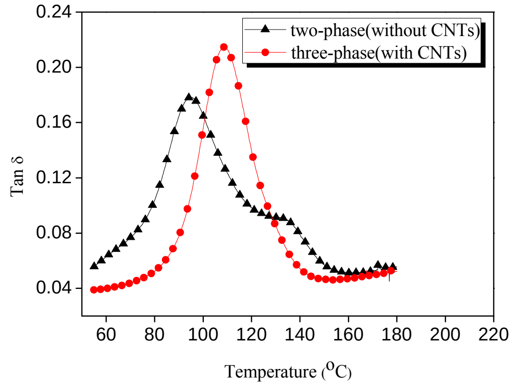


Fig. 4. The variation of tanδ of the two-phase (without CNTs) and three-phase (with 0.4 wt% CNTs) composites.

### 4 Conclusion

The creep resistance and storage modulus of the three phase composites with 0.4 wt% CNTs are higher than the natural fiber/epoxy two-phase composites without CNTs. The improved creep resistance can be explained as the restricted mobility of the molecular chains of polymer matrix due to the chemical reaction of the carboxylic acid groups on the MWCNTs with the epoxy matrix and a good bonding between ramie fiber and epoxy resin in the presence of the carbon nanotubes. The increased storage modulus and glass transition temperature of three-phase composites measured by dynamic mechanical analysis also showed consistent results with the creep tests.

### Acknowledgments

We gratefully acknowledge the support of “973” National Key Basic Research Program of China (Grants 2010CB631100).

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