

# Reinforcement of epoxy-based composites by magnetically aligned multi walled carbon nanotube

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**Abstract.** Multi walled carbon nanotubes decorated with ferrihydrous oxide nanoparticle (MWCNTs-Fe<sub>3</sub>O<sub>4</sub>) complex was used as an effective reinforcement in the polymer composites. The MWCNTs-Fe<sub>3</sub>O<sub>4</sub> with various grafting contents of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were successfully prepared by combining in situ atom transfer radical polymerization (ATRP) and coprecipitation process, which was characterized with Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscope (TEM). The MWCNTs-Fe<sub>3</sub>O<sub>4</sub> complex showed the strong magnetic response behavior, which could be easily aligned in an external magnetic field. The alignment state of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> complex could be modulated by adjusting the intensity of external magnetic field, grafting content of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and viscosity of the solvent. Moreover, with the addition of MWCNTs-Fe<sub>3</sub>O<sub>4</sub>, tensile strength and modulus of epoxy composites were enhanced by 12.3 and 10.9 %, respectively, which was due to the reinforcing effect of the aligned MWCNTs-Fe<sub>3</sub>O<sub>4</sub> within magnetic field.

## 1. Introduction

MWCNTs have been the focus of intense research and widely applied in many different fields such as composites and biotechnology due to their unique structure-dependent electrical, mechanical and optical properties. Especially in some applications where high-performance lightweight structural materials are required, and they can be developed by adding aligned MWCNTs to fiber reinforced composites. With aligned MWCNTs, the lateral mechanical performance of fiber reinforced composites can be substantially increased [1]. However, MWCNTs are easy to cluster, bundle together and entangle, causing many defects in the fiber reinforced composites, and limiting the performance of MWCNTs on polymer matrices. Besides, poor interface property resulting from weak interactions with

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the matrix also limit the efficiency of MWCNTs in fiber reinforced composites [2]. Furthermore, the alignment of MWCNTs in the fiber reinforced composites is difficult to achieve. Thus, the main challenges are to improve the dispersion, interface property and alignment of MWCNTs in the polymer matrix when preparing these nanocomposites.

There are several methods to improve the dispersion and interface property of MWCNTs in polymer matrices, such as employing optimum physical blending, in situ polymerization and chemical functionalization. Among these methods, in situ polymerization such as ATRP has been proved an efficient way to improve the dispersion and interface property of MWCNTs [3]. And the obtained MWCNTs-polymer composites exhibit excellent performance due to the MWCNTs' unique mechanical, surface and multi-functional properties, and strong interactions with the matrix. What's more, there are several techniques to achieve and characterize the alignment of MWCNTs in polymer matrices, such as employing flow field, magnetic field, electrical spinning field and orientation tensor description. Among these techniques, magnetic field is an important way because the alignment of MWCNTs can be adjusted and it can be easily applied in fiber reinforced composites by using a external magnetic field [4, 5]. Besides, the orientation tensor description provides an effective way to embody all MWCNTs- $\text{Fe}_3\text{O}_4$  directions in the selected region, which has been successfully used to describe the orientation states of short fibers. The second moments of the probability distribution function would be adopted to numerically characterize the alignment of MWCNTs, which are called orientation tensors. Via the attachment of magnetic nanoparticles onto MWCNTs, the alignment of MWCNTs can be easily achieved in weak magnetic field [6]. Recently, several methods have been reported for the attachment of magnetic nanoparticles onto MWCNTs. Miguel A. Correa-Duarte et al. obtained the coating of MWCNTs with magnetic nanoparticles by combining the polymer wrapping and layer-by-layer (LbL) assembly techniques [7]. Via the employment of polymer onto the surface of MWCNTs, the attachment between the magnetic nanoparticles and MWCNTs is stronger, and the grafting content of the magnetic nanoparticles can be much higher, meaning MWCNTs can be aligned in weak magnetic field which is more practical in industry [8]. Nevertheless, compared to ATRP, the interaction between polymer and MWCNTs by polymer wrapping process is much weaker, meaning the polymer and magnetic nanoparticles can be detached. Besides, the grafting content of the magnetic nanoparticles cannot be easily controlled.

In this contribution, we supposed to prepare MWCNTs-  $\text{Fe}_3\text{O}_4$  complex and control the alignment of MWCNTs under weak magnetic fields, based on ATRP of polymers and coprecipitation process of magnetic nanoparticles onto the surface of the MWCNTs, which were characterized by FT-IR, SEM and TEM. The method combines the ATRP and coprecipitation process techniques allowing the noncovalent attachment of nanoparticles onto MWCNTs. Via this method, the interface property, dispersion and orientation of obtained MWCNTs-  $\text{Fe}_3\text{O}_4$  complex could be largely promoted, and the  $\text{Fe}_3\text{O}_4$  nanoparticles could be efficiently grafted onto the surface of MWCNTs [9]. Furthermore, the content of  $\text{Fe}_3\text{O}_4$  nanoparticles was high and can be numerically controlled. The alignment of MWCNTs was achieved in the presence of an external magnetic field, upon grafting of magnetic nanoparticles onto the MWCNTs surface, and the alignment was numerically characterized via orientation tensor description. Based on the results, the mechanism of the alignment formation was proposed, and the effect of the intensity of magnetic field and the grafting content of magnetic particles was discussed.

## 2. Experimental section

### 2.1. Materials

MWCNTs-COOH (purity:  $\geq 95\%$ , diameter: 50-80 nm, length: 10-20  $\mu\text{m}$ ) were purchased from Chengdu Organic Chemicals Co. Ltd. (China). Glycidylmethacrylate monomer (GMA) (purity:  $\geq 97\%$ ) was obtained from SIGMA-ALDRICH Company. Silane coupling agent, KH550 (purity:  $\geq 98\%$ ), is obtained from Alfa-Aesar Company. CuBr is obtained from Alfa Aesar Company. N, N, N', N'', N''-pentmethyldiethylenetriamine (PMDETA) is obtained from TCI Shanghai Co. LTD.

2-bromo-2-methylpropionyl bromide (Bibb) is obtained from SIGMA-ALDRICH Company. Triethylamine is obtained from Beijing Tong Guang Fine Chemical Company.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was obtained from Tianjin Fuchen Chemical Reagents Factory. Tetramethylammonium hydroxide (TMAOH) (purity: ~25 %) was obtained from Tianjin Guangfu Fine Chemical Research Institute. All other chemicals and reagents were purchased from Beijing Chemical Works (China) and used directly.

### 2.2. Synthesis of MWCNTs- $\text{Fe}_3\text{O}_4$ complex

MWCNTs- $\text{NH}_2$  was prepared by mixing KH550 with MWCNT-COOH suspension under bath sonication for as following our previous works. The dried MWCNTs- $\text{NH}_2$  was dispersed in tetrahydrofuran (THF) and triethylamine by bath sonication for 0.5 h. Subsequently, Bibb mixed with THF was added into the dispersion. Then, the mixture was slowly stirred and allowed to react for 24 h at  $30^\circ\text{C}$ . The Bibb grafted MWCNTs (MWCNTs-Br) were obtained by centrifugation, washing with absolute THF several times and drying in vacuum. Then, MWCNTs-Br was dispersed in N, N-Dimethylformamide (DMF) by bath sonication for 0.5 h under nitrogen and subsequently mixed with GMA, PMDETA and CuBr. The resulting solution was further stirred for 24 h at  $30^\circ\text{C}$ . MWCNTs-PGMA was obtained by centrifugation, washing with absolute ethyl alcohol several times and drying in vacuum. The dried MWCNTs-PGMA was dispersed with de-ionized water and TMAOH by bath sonication for 1 h under nitrogen. Subsequently,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous solution was added dropwise till the pH of the final mixture is in the range of 11–13. Finally, the resultant product, MWCNTs- $\text{Fe}_3\text{O}_4$  complex, was obtained by centrifugation, washing with de-ionized water several times and drying in vacuum. The final product prepared using MWCNTs-PGMA, TMAOH,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was named as MWCNT- $\text{Fe}_3\text{O}_4$ .

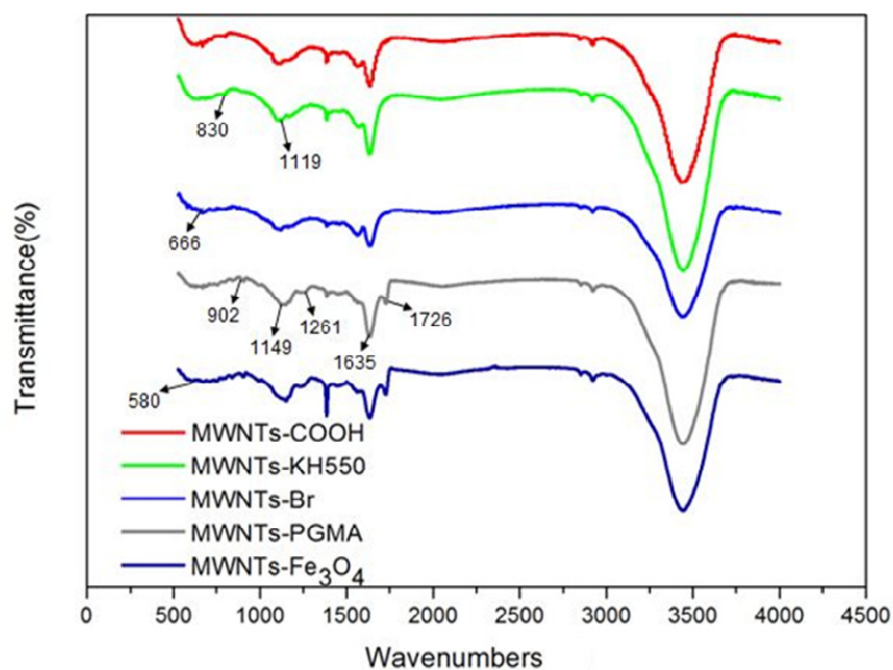
### 2.3. Characterizations

Changes of the functional groups on the surface of MWCNTs were detected with a FT-IR (Nicolet 670). Morphologies of various MWCNTs were observed by TEM (JEM100CX), respectively. The alignment of the sample was conducted by a magnet at 0.1 T. The morphology and aligned feature of as-prepared samples were also characterized using SEM (S4700) and optical microscope (IX51-21PH).

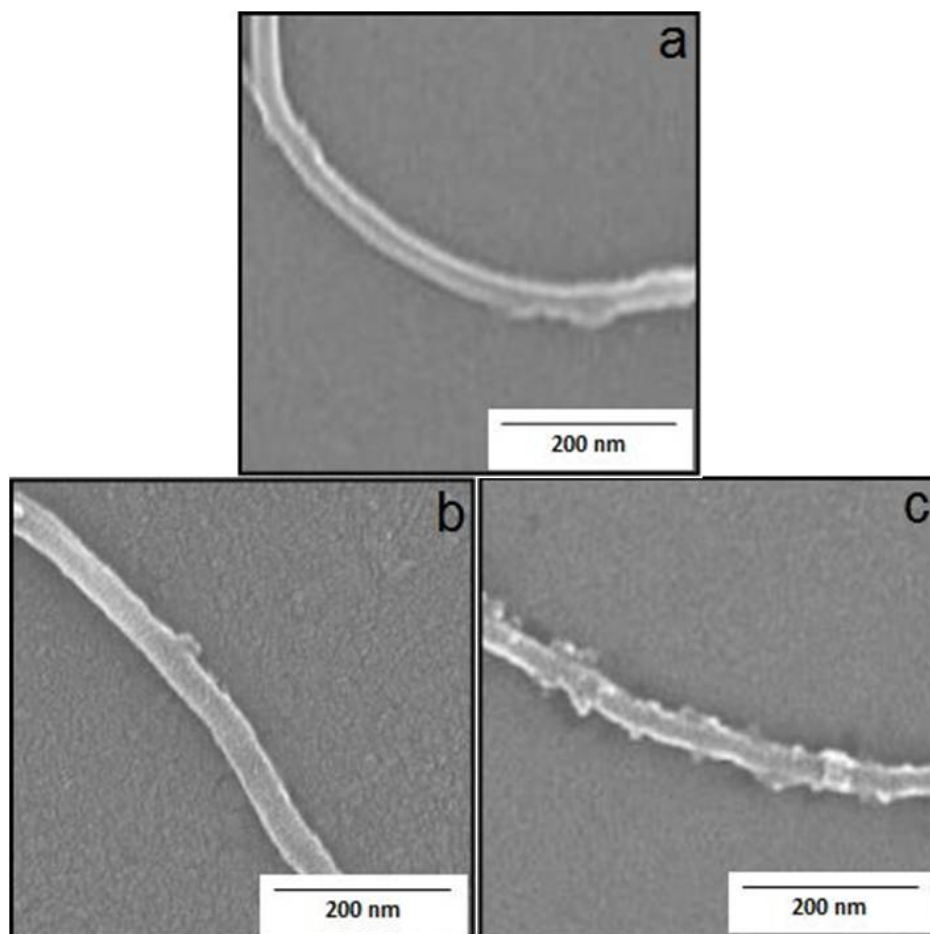
## 3. Results and discussion

### 3.1. Characterization of MWCNTs- $\text{Fe}_3\text{O}_4$ complex

Figure 1 shows the FT-IR spectra of MWCNTs-COOH, MWCNTs- $\text{NH}_2$ , MWCNTs-Br, MWCNTs-PGMA and various MWCNTs- $\text{Fe}_3\text{O}_4$ . Compared to MWCNTs-COOH, an additional peak at  $1119\text{ cm}^{-1}$  in the spectrum of MWCNTs- $\text{NH}_2$  was corresponded to Si-O-C<sub>2</sub>H<sub>5</sub> bending vibration, which meant that the coupling agent KH550 had been grafted onto MWCNT. This grafting of KH550 onto MWCNTs was further confirmed by characteristic peak of Si-C group at  $830\text{ cm}^{-1}$ . In the spectrum of MWCNTs-Br, the absorption peak at  $666\text{ cm}^{-1}$  was attributed to characteristic peak of -Br group, indicating the changes of functional groups on the surface of MWCNTs due to the bromization. The strong peaks at  $1635\text{ cm}^{-1}$  and  $1726\text{ cm}^{-1}$  appeared in the spectra of MWCNTs-PGMA, which were originated from the characteristic C=O stretching vibration of carboxylic groups and ester groups corresponding to the carbonyl groups of PGMA polymer. Noticeably, two obvious adsorption peaks at  $1149\text{ cm}^{-1}$  and  $1261\text{ cm}^{-1}$  were all originated from asymmetrical and symmetrical stretching peak of -CH<sub>3</sub> group and the absorption peak at  $902\text{ cm}^{-1}$  was ascribed to the epoxide groups from PGMA polymer. The peaks at 580 and was resulted from the stretching vibration due to the interactions of Fe-O-Fe in  $\text{Fe}_3\text{O}_4$ . These characteristic peaks in the FT-IR spectra manifested that  $\text{Fe}_3\text{O}_4$  particles were truly grafted onto the surface of MWCNTs.



**Figure 1.** FT-IR spectra of MWCNTs-COOH, MWCNTs-NH<sub>2</sub>, MWCNTs-Br, MWCNTs-PGMA, MWCNTs-Fe<sub>3</sub>O<sub>4</sub>.

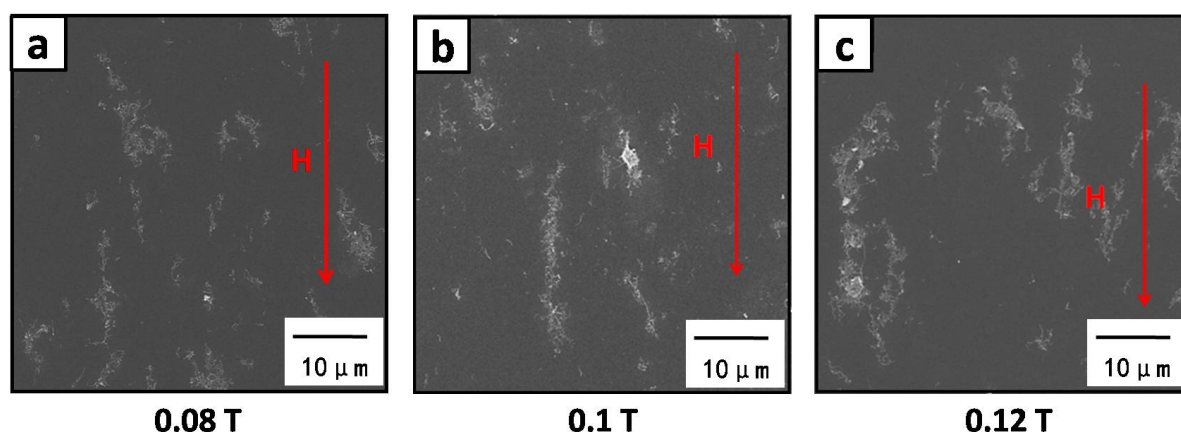


**Figure 2.** SEM of MWCNTs-COOH, MWCNTs-PGMA, MWCNTs-Fe<sub>3</sub>O<sub>4</sub>.

Figure 2 shows SEM images of MWCNTs-COOH, MWCNTs-PGMA and MWCNTs-Fe<sub>3</sub>O<sub>4</sub>. As shown in figure 2(a), the surface of the MWCNTs-COOH was very smooth, while the surface of MWCNTs-PGMA looked much rougher with a layer of the coating, confirming that PGMA was successfully grafted onto MWCNTs. For MWCNTs-Fe<sub>3</sub>O<sub>4</sub>, a large amount of nanoparticles were found to be uniformly distributed on the surface of MWCNTs as showed in figure 2(c), which indicated that the magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were deposited onto MWCNTs. The uniform distribution of Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the surface of MWCNTs was attributed to the electrostatic repulsion between the positively-charged nanoparticles as well as the impeding effect on the aggregation of nanoparticles by the introduction of TMAOH.

### 3.2. Observation of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> alignment

Figure 3 shows SEM images of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> in the magnetic field with various intensities. As showed in figure 3(a), MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was partially aligned at 0.08 T along the axis of the magnetic field instead of being randomly distributed. MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was partially stretched by the magnetic force between MWCNTs-Fe<sub>3</sub>O<sub>4</sub> complexes and magnets, but the magnetic force at the intensity of 0.08 T was not strong enough to make all the MWCNTs-Fe<sub>3</sub>O<sub>4</sub> well-aligned along the axis direction of magnetic field. When the intensity of magnetic field increased to 0.1 T, most of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was obviously aligned along the axis direction of magnetic field as showed in figure 3(b), which indicated that intensity increasing of magnetic field was beneficial to enhancing alignment degree of MWCNTs due to the increasing of the magnetic force applied on MWCNTs. However, it was unexpected that MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was found to be much less aligned at 0.12 T than at 0.1 T along the axis direction of magnetic field and started to form a number of clusters. This was because the magnetic force applied on MWCNTs was so strong that the whole MWCNTs-Fe<sub>3</sub>O<sub>4</sub> could move and pack together. Therefore, these observations revealed that the alignment state of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was sensitive to the intensity of magnetic field. Only if the intensity value of magnetic field was in a proper range to balance the moving state of MWCNTs, the optimum alignment of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> could be achieved.

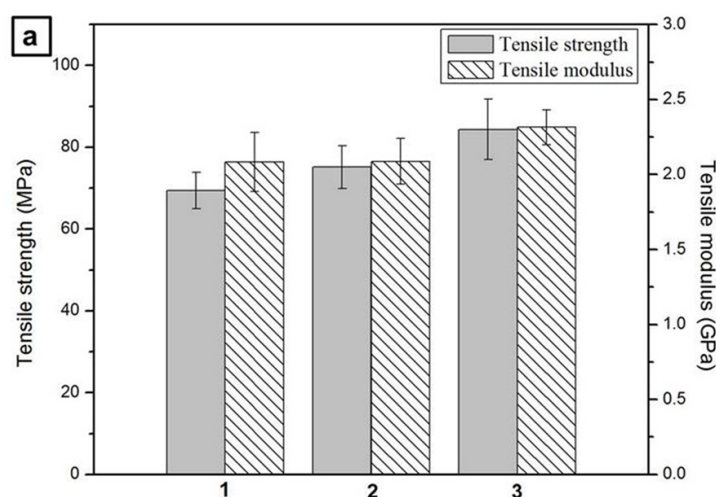


**Figure 3.** SEM images of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> in the magnetic field with various intensities.

### 3.3. Reinforcing effect of aligned MWCNTs-Fe<sub>3</sub>O<sub>4</sub> on epoxy composites

With the aim of evaluating the advantage of aligned MWCNT-Fe<sub>3</sub>O<sub>4</sub> in the application of reinforcement, MWCNT-Fe<sub>3</sub>O<sub>4</sub> was selected to prepare epoxy-based composites and their mechanical properties were tested. Figure 4 shows tensile properties of pristine epoxy and epoxy composites with 0.5 wt.% of MWCNT-Fe<sub>3</sub>O<sub>4</sub> without and with the application of external magnetic field. In comparison with the data of pristine epoxy, epoxy composites with MWCNT-Fe<sub>3</sub>O<sub>4</sub>, prepared with or without external magnetic field, apparently demonstrated higher tensile and flexural properties, showing the reinforcing effect of MWCNT. With the addition of 0.5 wt.% of MWCNT-Fe<sub>3</sub>O<sub>4</sub> into epoxy in the absence of magnetic field, the tensile strength and modulus of resulting composite

reached  $75.1 \pm 5.2$  MPa and  $2.1 \pm 0.1$  GPa, respectively. The application of magnetic field could further enhance the values by 12.3 and 10.9%, respectively. These enhancements were attributed to the directional alignment of MWCNT-Fe<sub>3</sub>O<sub>4</sub> in the epoxy matrix along the length direction of specimens since the magnetic field was set parallel to the length direction. The aligned MWCNTs were suggested able to bear more loads and subsequently enhance effective stress transfer in the composites by taking full advantage of the superior mechanical strength and modulus of CNTs themselves. This finding provided a practical possibility of applying magnetic CNTs as reinforcement for resins, in which, the CNTs could be effectively aligned by applying the proper magnetic field to achieve high performance composites.



**Figure 4.** Tensile properties of (1#) pristine epoxy and epoxy composites with 0.5 wt.% of MWCNT-Fe<sub>3</sub>O<sub>4</sub> prepared (2#) without and (3#) with the application of external magnetic field.

#### 4. Conclusions

The nanoscale complex composed of one-dimensional multiwalled carbon nanotubes and zero-dimensional ferri ferro oxide nanoparticles (MWCNTs-Fe<sub>3</sub>O<sub>4</sub>) were successfully prepared by combining atom transfer radical polymerization (ATRP) and coprecipitation process. The alignment state of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> complex could be modulated by adjusting the intensity of the external magnetic field and the grafting content of Fe<sub>3</sub>O<sub>4</sub> nanoparticles on MWCNTs. The corresponding preferential alignment degree of MWCNTs-Fe<sub>3</sub>O<sub>4</sub> was effectively and quantitatively characterized by employing an orientation tensor description in a selected region, which provided a feasible way to optimize the distribution state and exploit the whole performance of MWCNTs in various applications. Furthermore, the detailed studies to elucidate the effect of aligned MWCNTs-Fe<sub>3</sub>O<sub>4</sub> complex on properties of fiber reinforced composites were underway.

#### Acknowledgment

The authors are very pleased to acknowledge financial support from the National Natural Science Foundation of China (Grant No. U1362205, 5157031049), Natural Science Foundation of Jiangsu Province (Grant No. BK20140271), National High Technology Research and Development Program of China (Grant No. 2012AA03A203), Beijing Youth Talent Plan (Grant No. YETP0492) and 2014 Open Project of State Key Laboratory of Organic-Inorganic Composites.

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