REINFORCING EFFECT OF MAGNETICALLY ALIGNED MULTI WALL ED CARBON NANOTUBE ON EPOXY-BASED COMPOSITES

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ABSTRACT

Multi walled carbon nanotubes decorated with ferriferrous oxide nanoparticle (MWCNTs-Fe₂O₄) complex was used as an effective reinforcement in the polymer composites. The MWCNTs-Fe₂O₄ with various grafting contents of Fe₂O₄ 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-Fe₂O₄ complex showed the strong magnetic response behavior, which could be easily aligned in an external magnetic field. The alignment state of MWCNTs-Fe₂O₄ complex could be modulated by adjusting the intensity of external magnetic field, grafting content of Fe₂O₄ nanoparticles and viscosity of the solvent. Moreover, with the addition of MWCNTs-Fe₂O₄, 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-Fe₂O₄ within magnetic field. Furthermore, on the basis of the above investigation, a kind of fluorescent molecular, fluorescein isothiocyanate (FITC), was introduced into the MWCNTs-Fe₂O₄ to obtain the novel nanotubes with fluorescent imaging performance (F&M-MWCNTs). The F&M-MWCNTs showed excellent fluorescence and strong magnetic response behavior, which could be easily aligned in matrixes under an external magnetic field. The fluorescence intensity of F&M-MWCNTs could be modulated by adjusting the labeling content of FITC. The unique electromagnetic and fluorescent properties of F&M-MWCNTs made them excellent candidates and as reinforcement of composites or as tracer in various application fields.

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 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, electricspinner 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 an external magnetic field. Besides, the orientation tensor description provides an effective way to embody all MWCNTs-Fe$_3$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. 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. 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. 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-Fe$_3$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 magnetic nanoparticles onto MWCNTs. Via this method, the interface property, dispersion and orientation of obtained MWCNTs-Fe$_3$O$_4$ complex could be largely promoted, and the Fe$_3$O$_4$ nanoparticles could be efficiently grafted onto the surface of MWCNTs. Furthermore, the content of Fe$_3$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 surface of MWCNTs, 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 nanoparticles was discussed.

In addition, carbon nanotubes (CNTs) may exhibit metallic, electronic or semiconducting states, therefore, much attention has been focused on CNTs films, especially aligned films, in the field of light emitting diodes, field emission displays, and so on. The films of aligned CNTs possess outstanding electromagnetic properties and even better mechanical strength, which could broaden the applications. However, most of aligned carbon nanotube films fabricated with various methods are composed of nanotube bundles instead of individual ones in the micro-structure, which caused the difficulty in characterizing the alignment numerically. And the reported characterization approaches are unable to in-situ measure the alignment degree of such films. In this paper, we present a vacuum filter deposition method with application of an external magnetic field to prepare aligned MWCNTs films. The polymer grafted MWCNTs were labeled with fluorescein isothiocyanate (FITC) and then loaded with ferromagnetic Fe$_3$O$_4$ nanoparticles via a co-precipitation process. Finally, the magnetic and fluorescent MWCNTs (F&M-MWCNTs) were obtained and used to prepare in-plane aligned films under an external magnetic field. The alignment degree can be characterized from fluorescent morphologies of films via an orientation tensor description method.

2 EXPERIMENTAL SECTION

2.1 Materials

MWCNTs-COOH (purity: $\geq$95%, diameter:50-80nm, length:10-20μm) were purchased from Chengdu Organic Chemicals Co. Ltd.(China). 2-bromo-2-methylpropionyl bromide(Bibb), Glycidylmethacrylate monomer (GMA) (purity: $\geq$97%) and fluorescein isothiocyanate (FITC) were obtained from Sigma-Aldrich Company. Silane coupling agent, KH550(purity: $\geq$98%), and CuBr were
obtained from Alfa-Aesar Company. N, N, N’, N”-pentamethyldiethylenetriamine (PMDETA) was obtained from TCI Shanghai Co. LTD. Triethylamine, ethylenediamine(EN) (A.R.) and ethanol(A.R.) were both obtained from Beijing Tong Guang Fine Chemical Company. FeCl₃·6H₂O and FeCl₂·4H₂O were obtained from Tianjin Fuchen Chemical Reagents Factory. Tetramethylammonium hydroxide (TMAOH) (purity: ~25%) was obtained from Tianjin Guangfu Fine Chemical Research Institute. Dimethyl sulfoxide (DMSO) (A.R.) was all obtained from Beijing Chemical Works(China). All other chemicals and reagents were purchased from Beijing Chemical Works (China) and used directly.

2.2 Synthesis of MWCNTs-Fe₃O₄ complex

MWCNTs-KH550 were prepared by mixing KH550 with MWCNT-COOH suspension under bath sonication for 3 h. The dried MWCNTs-KH550 were dispersed in tetrahydrofuran (THF) and triethylamine by bath sonication for 0.5 h. Subsequently, Bibb mixed with THF were added into the dispersion. Then, the mixture was slowly stirred and allowed to react for 24 h at 30°C. The Bibb grafted MWCNTs (MWCNTs-Br) were obtained by centrifugation, washing with absolute ethyl alcohol 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°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 deionized water by bath sonication for 1 h under nitrogen. Subsequently, Fe²⁺/Fe³⁺ aqueous solution and TMAOH were added dropwise till the pH of the final mixture be in the range of 11-13. Finally, the resultant product, MWCNTs-Fe₃O₄ complex, was obtained by centrifugation, washing with deionized water several times and drying in vacuum. The final product prepared using MWCNTs-PGMA, TMAOH, FeCl₃·6H₂O and FeCl₂·4H₂O was named as MWCNT-Fe₃O₄ following our previous works.

2.3 Synthesis of F&M-MWCNTs

The MWCNTs-PGMA was dispersed in the mixture of ethanol and ethylenediamine by an ultrasonic bath for 30 min and was stirred for 24 hours. Subsequently, the amino functionalized MWCNTs (MWCNTs-NH₂) was successfully obtained. Then MWCNTs-NH₂ was redispersed by an ultrasonic bath for 30 min in the buffer solution and a solution of FITC in DMSO was added into the MWCNTs-NH₂ suspension. The mixture sustained to react at room temperature for several hours. After that, the product was rinsed and the fluorescent MWCNTs (MWCNTs-FITC) were obtained, followed by a coprecipitation for loading ferromagnetic Fe₃O₄ nanoparticles onto the MWCNTs-FITC surfaces. Thus, the final product of fluorescent and magnetic MWCNTs (F&M-MWCNTs) was obtained. The aligned F&M-MWCNTs films were fabricated via vacuum filter deposition from stable suspension under an external magnetic field.

2.4 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 both TEM (JEM100CX) and SEM (S4700), 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 and optical microscope (IX51-21PH). The scanning electron microscope fluorescence of the FITC labeled MWCNTs films was characterized via Confocal laser scanning microscope (CLSM, Leica, SP8).

3 RESULTS AND DISCUSSIONS

3.1 Characterization of MWCNTs-Fe₃O₄ complex
Fig. 1 FT-IR spectra of MWCNTs-COOH, MWCNTs-NH$_2$, MWCNTs-Br, MWCNTs-PGMA, MWCNTs-Fe$_3$O$_4$.

Fig. 1 shows the FT-IR spectra of MWCNTs-COOH, MWCNTs-NH$_2$, MWCNTs-Br, MWCNTs-PGMA and various MWCNTs-Fe$_3$O$_4$. Compared to MWCNTs-COOH, an additional peak at 1119 cm$^{-1}$ in the spectrum of MWCNTs-NH$_2$ was corresponded to Si-O-C$_2$H$_5$ bending vibration, which meant that the coupling agent KH550 had been grafted onto MWCNT. This grafting of KH550 onto MWCNTs were further confirmed by characteristic peak of Si-C group at 830 cm$^{-1}$. In the spectrum of MWCNTs-Br, the absorption peak at 666 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 cm$^{-1}$ and 1726 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 cm$^{-1}$ and 1261 cm$^{-1}$ were all originated from asymmetrical and symmetrical stretching peak of -CH$_3$ group and the absorption peak at 902 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 Fe$_3$O$_4$. These characteristic peaks in the FT-IR spectra manifested that Fe$_3$O$_4$ particles were truly grafted onto the surface of MWCNTs.

3.2 Reinforcing effect of aligned MWCNTs-Fe$_3$O$_4$ on epoxy composites

Fig. 2 Tensile properties of (1#) pristine epoxy and epoxy composites with 0.5 wt.% of MWCNT-Fe$_3$O$_4$ prepared (2#) without and (3#) with the application of external magnetic field.
With the aim of evaluating the advantage of aligned MWCNT-Fe$_3$O$_4$ in the application of reinforcement, MWCNT-Fe$_3$O$_4$ was selected to prepare epoxy-based composites and their mechanical properties were tested. Fig.4 shows tensile properties of pristine epoxy and epoxy composites with 0.5 wt.% of MWCNT-Fe$_3$O$_4$ without and with the application of external magnetic field. In comparison with the data of pristine epoxy, epoxy composites with MWCNT-Fe$_3$O$_4$, 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$_3$O$_4$ into epoxy in the absence of magnetic field, the tensile strength and modulus of resulting composite reached 75.1 ± 5.2 MPa and 2.1 ± 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$_3$O$_4$ 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.

3.3 Characterization of F&M-MWCNTs

![FT-IR spectra of MWCNTs-PGMA, MWCNTs-FITC and F&M-MWCNTs.](image)

Fig. 3 shows the FT-IR spectra of MWCNTs-PGMA, MWCNTs-FITC and F&M-MWCNTs. In the spectrum of MWCNTs-FITC, the characteristic peaks corresponding to the epoxy groups disappeared, and the vibrational peaks of -OH appeared at 1374 cm$^{-1}$, which indicated that the -NH$_2$ reacted with FITC, and FITC had successfully labeled on MWCNTs-NH$_2$. In the F&M-MWCNTs spectrum, the significant peak appeared at 584 cm$^{-1}$ was resulted from the stretching vibration due to the interactions of Fe-O-Fe in Fe$_3$O$_4$. These characteristic peaks in the FT-IR spectra manifested that Fe$_3$O$_4$ particles were truly grafted onto the surface of MWCNTs-FITC.
Morphologies of MWCNTs-FITC and F&M-MWCNTs were observed by SEM and TEM. The typical hollow, rodlike structure with rough surface was observed for MWCNTs-FITC (Fig. 4 A1), which showed a coating shell from the wrapped edge (Fig. 4 A2), confirming the successful grafting of PGMA and FITC onto MWCNTs. For F&M-MWCNTs, the mass of the nanoparticles with an diameter of less than 30 nm was found uniformly distributing on the surface of the MWCNT (Fig. 4 B1, B2), which indicated the deposition of iron oxide nanoparticles onto MWCNTs. The image in Figure B2 illustrated the characteristic electron diffraction patterns of Fe₃O₄ nanoparticles with high crystallinity. The electron diffraction (ED) patterns show a set of spotty rings derived from the random orientation of the nanoparticles, in which four rings corresponding to the (111), (220), (311) and (400) planes of the cubic Fe₃O₄ phase of inverse spinel structure can be seen[12].

As the F&M-MWCNTs were labeled with FITC, they could be observed under confocal laser scanning microscopy (CLSM) due to fluorescent performance. For aligned F&M-MWCNTs film (Fig. 5 A), the fluorescent F&M-MWCNTs tended to orderly align as green strings with regular arrangement along the direction of magnetic field[7,13]. The bright bundles of F&M-MWCNTs were almost parallel to each other and there were gaps between them, which was attributed to responses to the magnetic force[14]. The conspicuous alignment conditions of aligned F&M-MWCNTs films gave further evidence that the prepared F&M-MWCNTs were successfully labeled with FITC and loaded with magnetic nanoparticles. To quantitatively characterize the corresponding alignment state of F&M-MWCNTs films, the orientation tensor description was used to characterize the orientation states of aligned bundles. As shown in Fig. 5 A, vectors were marked in the CLSM image in accordance to the length direction of each set of F&M-MWCNTs. The alignment angle of each set of
F&M-MWCNTs was measured with Image J software. The ellipse was used to graphically describe the corresponding orientation state, and the related parameters for such ellipses were calculated on the Equation illustrated in our previous work[11]. The preferential alignment degree (PAD) could be numerically calculated. Finally, we obtained the ellipse (Fig. 5 B) of F&M-MWCNTs on the film and the calculated PAD was 69.8 %. The result confirmed the high alignment degree of F&M-MWCNTs and the effectiveness of fluorescent labeling.

4 CONCLUSIONS

The nanoscale complex composed of one-dimensional multiwalled carbon nanotubes and zero-dimensional ferriferrous oxide nanoparticles (MWCNTs-Fe$_3$O$_4$) were successfully prepared by combining atom transfer radical polymerization (ATRP) and coprecipitation process. The alignment state of MWCNTs-Fe$_3$O$_4$ complex could be modulated by adjusting the intensity of the external magnetic field and the grafting content of Fe$_3$O$_4$ nanoparticles on MWCNTs. The corresponding preferential alignment degree of MWCNTs-Fe$_3$O$_4$ 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$_3$O$_4$ complex on properties of fiber reinforced composites were underway.

MWCNTs-PGMA were successfully labelled with fluorochrome FITC and loaded with ferromagnetic Fe$_3$O$_4$ nanoparticles via a coprecipitation process to obtain fluorescent and magnetic properties. By the method of vacuum filter deposition, the aligned F&M-MWCNTs films were fabricated under an application of magnetic field respectively. The alignment possibility of F&M-MWCNTs in the presence of an external magnetic field can be affected by changing the intensity of the magnetic field. The magnetic field intensity of 30-35mT proved to be the best condition to obtain well aligned F&M-MWCNTs films. Besides, the F&M-MWCNTs were fluorescent so that the alignment degree could be characterized by the CLSM clearly.

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