Interfacial improvement of carbon fiber/polyoxymethylene composites by depositing functionalized carbon nanotubes on the fibers

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CF/POM/CNT ternary composites have been prepared by melt blending method with carbon nanotubes (CNT) as modifier, maleic anhydride (MAH) as interfacial compatibilizer and polyoxymethylene (POM) as matrix. The mechanical properties of CNT on CF/POM have been studied by temperature-controlled tensile, and scanning electron microscopy analysis. The results show that the interface properties of CF/ POM/CNT ternary composites can be improved by adding MAH, thus improving the mechanical properties of the composites. The tensile strength, bending strength and impact strength of the ternary composite at room temperature have increased, and the tensile strength of CF/POM/CNT ternary composites has improved by 12.1%.

Keywords: Carbon nanotubes, Single fiber-composite fragmentation tests, Fractographic, Wettability, Carbon fibers

1 Introduction

Electromagnetic metamaterials with negative permittivity or/and permeability have been the subject of intense research due to their unusual physical properties and exciting potential applications, such as negative refraction, optical imaging, electromagnetic cloaks, novel antenna and sensor[1]. In the past few decades, although fascinating achievements of the metamaterials have been reported, great effort is still required precisely control negative parameters as well as to achieve the desired functional properties. It is a research hotspot in this field to add toughness degradable polymer materials such as polycaprolactone (PCL) and POM to the PLA by blending method[1-3]. POM is biodegradable polyester with a flexible molecular chain and strong toughness[4]. The PLA/POM blend has the complementary effect of both properties, which not only improves the impact toughness of the PLA material, but also makes the material have good oxygen barrier properties and lower the processing temperature. It is found that the structure of PLA and POM is similar. In the PLA/POM blend system, the two are partially compatible[5-7]. When the POM content is low, the crystallization behavior of PLA is less affected. POM can effectively improve the toughness of the blend[8-10]. However, pure POM materials have poor heat resistance and low mechanical properties. Also, the thermal degradation temperature of POM is

relatively low. These shortcomings limit the further application of PLA/POM.

As a rod-shaped fiber with a certain aspect ratio, CNT has the advantages of complete biodegradability, high elastic modulus, high strength, ultra-fine structure and high transparency. It is a good biomass polymer modifier, using CNT. As a filler for biomass materials, the preparation of high biomechanical properties and low cost of fully biodegradable materials is one of the current research hotspots[11, 12].

CNT filled POM can solve the problems of poor heat resistance and low mechanical properties[13], and the problem of low cost performance and low toughness of PLA after CNT filling PLA has also been solved initially[14]. Therefore, the use of CNT as a reinforcing agent is expected to improve the mechanical properties and thermal stability of PLA/POM. There are currently no reports on CNT modified PLA/POM.

Carbon fiber (CF) reinforced thermoplastic resin composites have the advantages of low density, high strength, good toughness, short forming cycle and reusability, and are increasingly used in aviation, automotive, sports and other fields[15-18]. The thermoplastic resin matrix currently used includes polypropylene (PP), polyamide (PA), polycarbonate (PC), etc., but the composite of the above resin matrix cannot be used in a high temperature environment[19]. In recent years, nanoparticles (e.g., graphene, carbon nanotube (CNT), nanoclay, TiO_2, and Cu) have been

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coated onto fiber surfaces to enhance adhesion to a resin matrix[20-22].

Polyphenylene sulfide (PPS) is a semi-crystalline thermoplastic resin that has the advantages of high temperature resistance, corrosion resistance, and flame retardancy. As a matrix of composite materials, it can be used in more severe environments. Therefore, researchers have done a lot of research on CF/PPS thermoplastic composite materials, which has broad application prospects in the fields of military industry and aerospace. The factors affecting the properties of CF/PPS composites include CF's own properties, two-phase wettability and interfacial force. The interface as the bond between the internal matrix phase and the reinforcement phase of the composite is one of the determinants of the mechanical properties of the composite, so it is necessary to improve the mechanical properties of composites must improve the interfacial properties between CF and PPS[23]. Gao Quanxi *et al.*[9] used acetone to extract carbon fiber surface sizing agent to prepare CF/vinyl resin composite material. The infiltration property between CF and resin after acetone extraction became better, and the mechanical properties of composite materials were improved. Surface modification of CF with nitric acid solution showed that the surface roughness and oxygen-containing functional groups of CF after treatment with nitric acid solution increased, and the mechanical properties of the prepared composites were significantly improved[10].

In the CNT/PLA composite, although C-O in the PLA and POM molecules can form hydrogen bonds with the hydroxyl moiety in the cellulose, it does not form sufficient adhesion between the polyester resin material and the cellulose[11]. Therefore, cellulose-filled PLA/POM still needs to address the problem of interfacial compatibility and dispersion of CNT. In this paper, PLA/POM/CNT composites were prepared by using CNT as filler and laboratory-prepared MAH as interface compatibilizer and adding to PLA/POM composite. The effects of MAH and CNT fillers on the properties of CF/POM composites were investigated.

2 Experimental
2.1 Materials

Maleic anhydride (MAH), analytically pure, Shenyang Reagent Plant; dicumyl peroxide (DCP), analytical grade, Saan Chemical Technology (Shanghai) Co., Ltd.; PLA, 2003D, US Natureworks; POM, BioCO2TM 100, Inner Mongolia Mengxi High-tech Group Co., Ltd.; CNT, pharmaceutical grade, Qufu Tianli Pharmaceutical Excipients Co., Ltd.

Preparation of interfacial compatibilizer PLA-g-MAH: weighed 85.11% (mass fraction, the same below) and 14.89% of MAH and DCP, mixed and dissolved in an appropriate amount of solvent, after fully dissolved The solvent was distilled off, and the precipitate was dried in a vacuum drying oven and ground for use; the PLA was placed in a blast drying oven at 80 ° C for 4 hours and then used; the above MAH, DCP mixture and dried PLA (MAH: The mass ratio of DCP:PLA was 2:0.35:97.65), and it was melt-kneaded at 180 °C in a torque rheometer.

2.2 Preparation of Composite Materials

CNT (5wt%), PLA and POM were placed in torque Melt blending at 180 °C for 8 min, put the blend into a tablet press in a tablet press, and cool to room temperature to make PLA/ CC, POM/CNT composite samples; PLA, POM, CNT, PLA-g-MAH were melt blended at 180 ° C for 8 min in a torque rheometer and the blend was placed in a tablet press. Medium pressure is made into a flat material of a certain thickness; after cooling to room temperature, a sample of PLA/POM, PLA/POM/CNT, PLA/POM/CNT/PLA-g-MAH composite material is prepared.

Fourier transform infrared spectroscopy (FTIR): CF samples were measured before and after acetone treatment using a Fourier transform infrared spectrometer with a resolution of 2 cm -1 and a scanning wave number of 400 to 4 000 cm -1 .

X-ray photoelectron spectroscopy (XPS): The surface element content of CF samples before and after solvent treatment was analyzed by X-ray photoelectron spectroscopy with a depth of 10 nm.

Scanning Electron Microscopy (SEM): The surface morphology of the sample was observed by a field emission scanning electron microscope at an acceleration voltage of 20 kV.

Tensile strength: The universal material tensile test is carried out on the composite according to GB/T1040-1992 using a universal material testing machine test with a gauge length of 100 mm and a tensile speed of 10 mm/min. Each set of samples was repeated 5 times and the results were averaged.

Bending strength: A three-point bending test was performed on the composite using a universal material testing machine with a fulcrum spacing of 64 mm and a loading speed of 2 mm/min.

The bending performance is tested according to GB/T 9431-2008, and the bending rate is 2mm/min; Cantilever

beam notched impact strength according to GB/T 1843-2008 test, V-shaped notch, pendulum impact energy is 1J; SEM analysis: liquid nitrogen brittle fracture sample, section spray gold treatment, working voltage is 5kV, observed at 2000 times The microscopic appearance of the sample and photographing.

3 Results and Discussion

3.1 Surface Characteristics of CNT-deposited Carbon Fibers

Figure 1 is the SEM photograph of PLA/POM/CNT/PLA-g-MAH composites with different PLA-g-MAH content, from Fig. 1(a) it can be seen that the adhesion of the CNT to the interface of the polymer matrix at the cross section of the composite before the addition of PLA-g-MAH is poor, there is a phenomenon of fiber pull-out, and there is a clear gap between the cross-section CNT and the material. With the increase of PLA-g-MAH content, the fiber pull-out phenomenon of CNT disappeared, the gap between CNT and polymer matrix gradually became blurred, and fiber breakage occurred when PLA-g-MAH content reached 7%, but there was still polymer. The phenomenon of tight adhesion indicates that PLA-g-MAH significantly improves the interfacial compatibility between the two. It clearly shows that the changes after CNT-depositing process are negligible, which proves that the surface treatment using CNT coating introduces no damages on the carbon fibers.

As shown in Fig. 2, $1700 \sim 1760$ cm^{-1} is the stretching vibration absorption peak of C- O in -COOH, and the stretching vibration absorption of C-O-C at 1 120 cm^{-1}. With the progress of nitric acid treatment, the -CH$_2$- stretching vibration peak gradually weakens due to the long chain during the treatment. The alkyl compound is continuously reduced, and the carboxyl group peak becomes strong, indicating that the oxidation of nitric acid increases the carboxylic acid group on the surface of the carbon fiber. The increase in carboxylic acid groups facilitates the interfacial interaction between CF and POM resin. Fig 3 shows the XPS deconvolution spectra of C 1s peak.

Table 1 shows the chemical composition of the carbon nanotubes obtained from XPS measurements. Table 2 shows the C1s peak fitting results for CNTS with peal positions in parentheses. As shown in Fig. 4, multi-walled carbon nanotubes were selected as functional fillers to fabricate composite, the fillers were randomly distributed in the matrix. Additionally, the MWCNTs were enclosed by the matrix, so carbon nanotubes were hard to be observed[24].

Figures (5-7) shows the mechanical properties of CF/POM composites. It can be seen that the mechanical properties of CF/POM composites increase
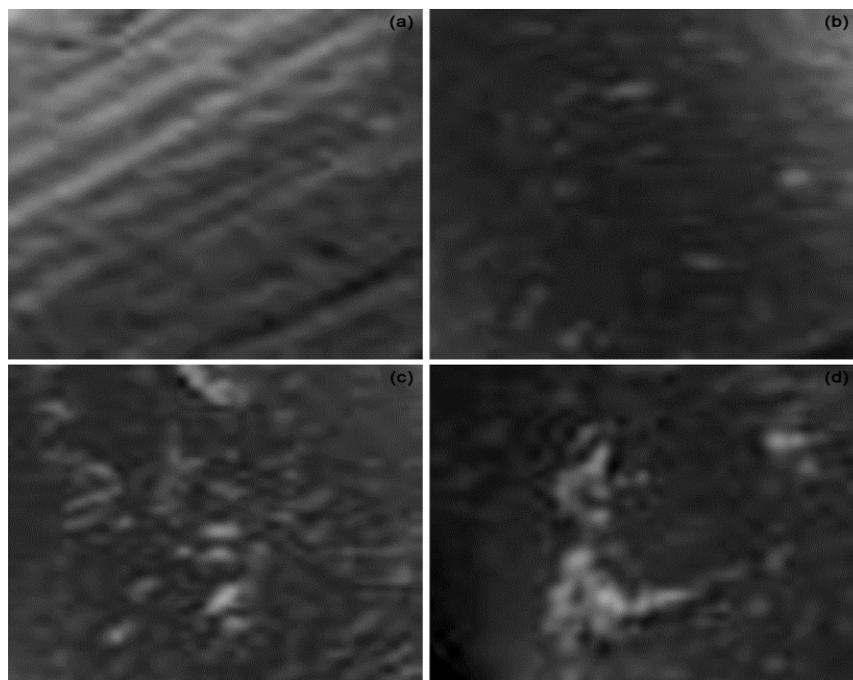
Fig. 1 — SEM images of (a) As-received carbon fiber, (b) Treated carbon fiber, (c) CNT-deposited carbon fibers without treatment and (d) CNT-deposited carbon fibers with treatment.
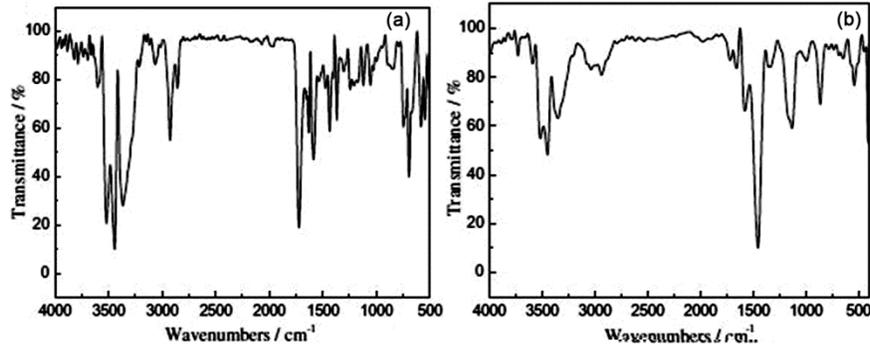
Fig. 2 — FTIR spectrum of (a) COOH–CNTs and (b) OH–CNTs.
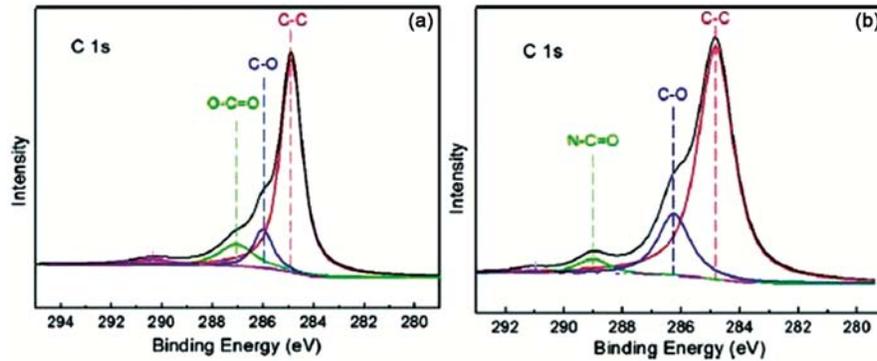
Fig. 3 — XPS deconvolution spectra of C 1s peak for (a) COOH–CNTs and (b) OH–CNTs.

Table 1 — The chemical composition of the carbon nanotubes.

CNT	C1s(%)	O1s(%)	N1s(%)
COOH-CNT	93.6	5.4	1
OH-CNT	92.7	5.5	1.8

Table 2 — C1s peak fitting results for CNTS with peal positions in parentheses.

CNT	C-C%(ev)	O-C=O%(eV)	C-O%(eV)	N-C=O%(eV)
COOH-CNT	73.1(284.9)	13(287.1)	12.8(286.0)	-
OH-CNT	77.2(284.8)	-	19.1(286.2)	4.5(289.0)

first and then decrease with the increase of CNT in CF/POM composites. When the CNT content reaches 40%, the tensile strength increases, but it is still lower than that of pure PLA. This is due to the poor dispersion of CF in POM, easy agglomeration and interface problems between CF and POM. Therefore, POM is prone to defects in PLA. In the CF/POM composites, the mechanical properties of CF/POM increased significantly with the increase of CNT content. When the content of CNT is 60%, the tensile strength and bending strength of POM/CNT are the highest, but the impact strength and elongation at break are seriously affected. However, the content of CNT of 40% has a lower influence on the impact strength and elongation at break of POM/CNT, and the tensile strength and bending strength are still significantly improved. It can be seen that with the addition of POM, there is a certain negative effect on the tensile strength and flexural strength of PLA, but the elongation at break and impact strength of PLA can be improved. When the PLA/POM mass ratio is 8:2, the tensile strength, the elastic modulus are small, and the elongation at break and the impact strength are high. This is consistent with previous studies by related scholars[17]. The tensile strength, flexural strength and impact strength were increased by 53.7%, 43.1% and 18.5%, respectively. It has little effect on the mechanical properties of the composite. This is because the addition of MAH makes the filler even dispersed in the matrix, the interfacial compatibility with the PLA phase, the POM phase, and the cellulose phase is improved, the gap between
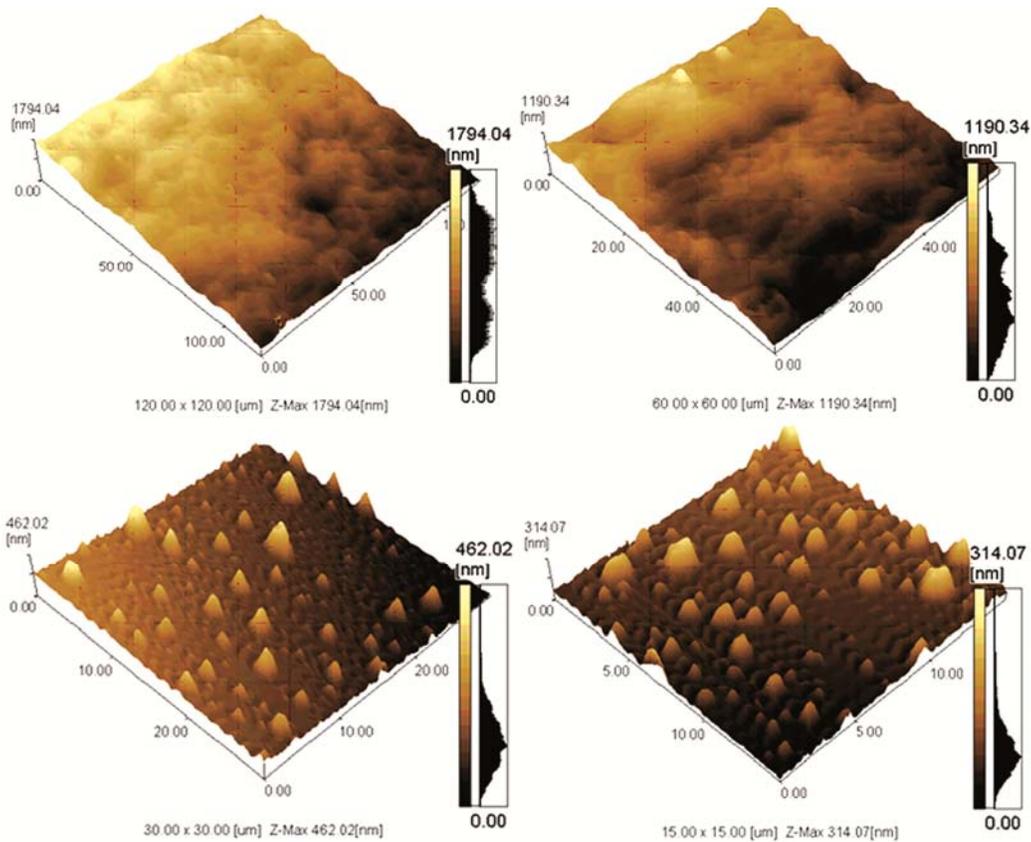
Fig. 4 — AFM topographical images of different fibers (a) As-received carbon fiber, (b) Treated carbon fiber, (c) CNT-deposited carbon fibers without treatment and (d) CNT-deposited carbon fibers with treatment.
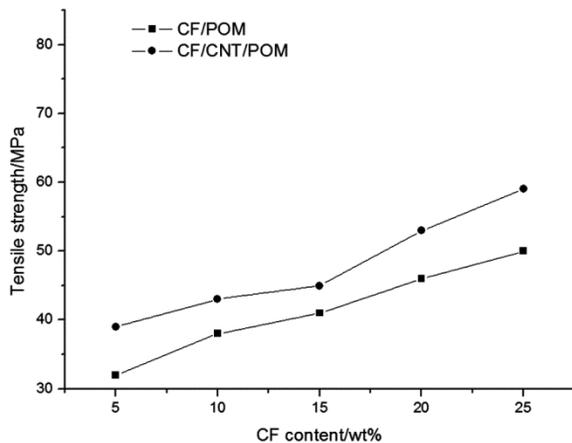
Fig. 5 — The effect of fibre loading on tensile strength of the composite.

the phases is reduced to avoid stress concentration, and the mechanical properties of the material are improved.

4 Conclusions

The addition of CNT can improve the mechanical properties, MAH can effectively improve the interfacial
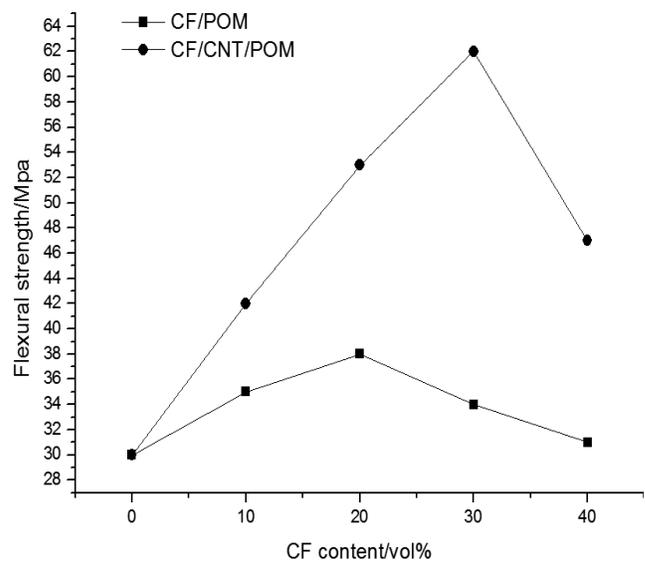
Fig. 6 — The effect of fibre loading on flexural strength of the composite.

compatibility between CNT and polymer matrix in PLA/POM/CNT composites, thus improving the mechanical properties of PLA/POM/CNT composites.
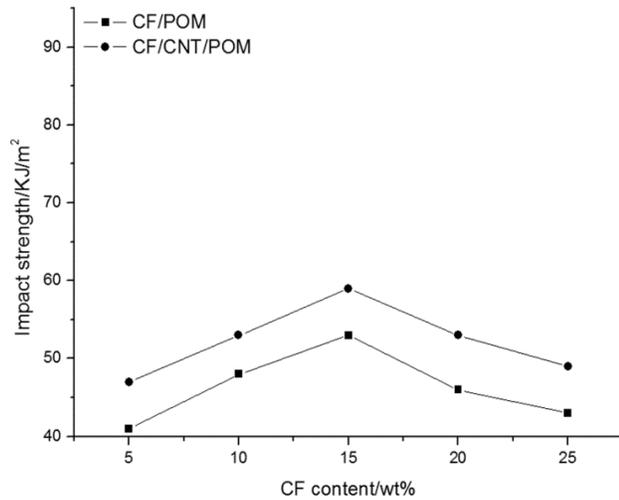
Fig. 7 — The effect of fibre loading on impact strength of the composite.

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