

Reinforcing polyamide 1212 nanocomposites with aligned carbon nanofibers



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ABSTRACT

In this study, the mechanical properties and structure orientation of pure polyamide 1212 (PA1212) were compared with those of PA1212–carbon nanofibers (CNFs) nanocomposites. The tensile strength of the composite containing 0.3 wt.% modified CNFs was improved from 328 MPa (pure PA1212) to 373 MPa after drawing. The reinforcing effect was investigated in terms of crystallization behavior, crystal morphology, alignment of CNFs, and crystal orientation degree. Spherulites developed into oriented crystals after drawing, and the CNFs aligned along the drawing direction. The heterogeneous nucleation effect of the aligned CNFs improved the crystal orientation degree, which produced the reinforcing effect. The oriented fibril structures with rigid nanofibers acting as nuclei reinforced the entire oriented crystals in the composites.

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1. Introduction

One-dimensional carbon materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are widely used in the preparation of polymer composites because of their excellent properties, such as high mechanical strength/modulus [1,2], high electrical conductivity [3], and large ratio surface area [4]. The reinforcement of polymer composites is being given particular interest [5,6]. For example, Yang et al. [7] produced polyethylene-grafted multiwalled carbon nanotubes (CNT-g-PE) which were used to reinforce polyethylene (PE). The stiffness, strength, ductility and toughness of the composites were all improved by the addition of CNT-g-PE. Zeng et al. [8] prepared polyamide 1010/CNTs composites by in situ polymerization. The results showed that the Young's modulus increased as the content of the nanotubes increased. The alignment of CNTs/CNFs and polymer chain orientation in the composites can be realized by subsequent stretching or drawing after molding [9,10]. This method is often used to improve the mechanical properties of composites [11,12]. Morioka et al. [13] reported that the high-performance PTFE films were prepared by melt-drawing. The reinforcement of the tensile strength was ascribed to polymer chain disentanglement and orientation induced crystallization. Wang et al. [14] reported an effective method to increase the strength and stiffness of the aligned

CNTs/nylon66 composites by reducing CNT waviness using a drawing and stretching approach. The tensile strength and Young's modulus of the composites were improved by 190% and 294% respectively, as the stretch ratio was increased to 7%.

High reinforcement efficiency of the composites can be completed by the alignment of CNTs/CNFs, which is beneficial for the composite to bear load along the orientation direction during the drawing process [14,15]. The draw ratio, interfacial adhesion, and dispersion state are important factors influencing CNT orientation, which significantly affect reinforcement efficiency. CNT orientation degree is improved with the increase in draw ratio because of the constraint of oriented polymer chains [14]. Strong interfacial adhesion and good dispersion state are beneficial in increasing CNT orientation degree because of great shear force during the drawing process [16].

Meanwhile, more polymer chains experience force along the load direction as the degree of polymer chain orientation increases [9,13]. Improving the degree of polymer chain orientation is another way of reinforcing the composites. The degree of polymer chain orientation is influenced by draw ratio, draw temperature, and addition of CNTs/CNFs. With the increase in draw ratio, the degree of polymer chain orientation is improved [17,18], melt-recrystallization is induced [19,20], and crystallinity is enhanced at the same time [13]. Chain disentanglement and orientation occur when a polymer is drawn at high temperatures [13]. Meanwhile, the degree of polymer chain orientation is more difficult to control. CNTs/CNFs show obvious heterogeneous nucleation effect

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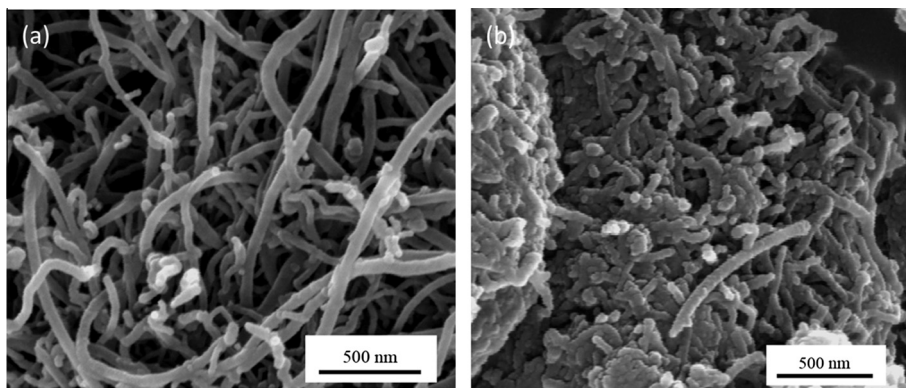


Fig. 1. SEM images of (a) pristine CNFs and (b) CNF-g-PEI.

in polymer matrix [21,22], polymer chains epitaxially crystallize on the surface of nanofibers [23,24], and then the relaxation of polymer chains is hindered [25,26].

Polyamide 1212 (PA1212) is an important plastic in engineering from the family of even–even series polyamide and it exhibits superior physical and chemical properties [27,28]. Nevertheless, PA1212 does not have sufficient mechanical properties at room temperature, which significantly restricts its application in fields of mechanics, automobile, aerospace, and petroleum [29]. In this study, PA1212 was used as matrix material, and PA1212/CNFs composites were prepared by melt blending. The oriented specimens were prepared by drawing at 170 °C (near the melting temperature of PA1212) at 380% engineering strain. The CNFs and polymer chains were aligned and oriented during the drawing process. To improve the compatibility and interfacial adhesion of CNFs in PA1212 matrix, CNFs were modified by covalent grafting of polyethyleneimine (PEI) molecules. The nanocomposites were efficiently reinforced, and the reinforcing effect was investigated in terms of microstructure, crystallization properties, and crystal morphology.

2. Experimental details

2.1. Materials

PA1212 pellets ($M_w = 16,000$ – $17,000$, $MDI = 1.4$, $MI = 3.75$ g/10 min) were purchased from Shandong Dongcheng Engineering Plastic Co. Ltd. Pristine CNFs with main diameter ranging from 50 nm to 150 nm and length ranging from 10 μm to 30 μm (>95% purity) were purchased from Beijing Dekei Daojin Nanotechnology Co. Ltd. PEI (>99% purity, $M_w = 1800$) and *N,N'*-dicyclohexylcarbodiimide (DCC) (>99% purity, $M_w = 206$) were supplied by Aladdin Chemistry Co. Ltd.

2.2. Modification of CNFs

Pristine CNFs were dispersed in concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1 v/v) solution in an ultrasonic bath (40 kHz, 200 W) for 30 min, and then mechanically stirred at 60 °C for 4 h. The dispersion solution was then diluted with large quantity of water and washed with deionized water for several times until the pH of the solution reached 7.0. The CNFs were dried at 80 °C in a vacuum environment for 24 h, resulting in CNFs modified with carboxylic acid groups (CNF-g-COOH). CNF-g-COOH (1.0 g), DCC (0.5 g), and PEI (0.5 g) were dissolved in DMF, and the solution was refluxed at 165 °C for 24 h to produce CNFs grafted with PEI molecules (CNF-g-PEI). The products were washed with ethanol to remove residual modifying agent and then dried at 80 °C for 24 h. The modified

CNFs were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA).

2.3. Preparation of PA1212/CNFs nanocomposites

Before melt blending, PA1212 pellets and CNFs were dried at 80 °C for 24 h in a vacuum oven. Composites with varying CNF contents (0.1, 0.3, 0.5, 0.7, and 1.0 wt.%) were prepared by melt blending in a Brabender mixer (40 rpm) at 205 °C for 12 min. Plate

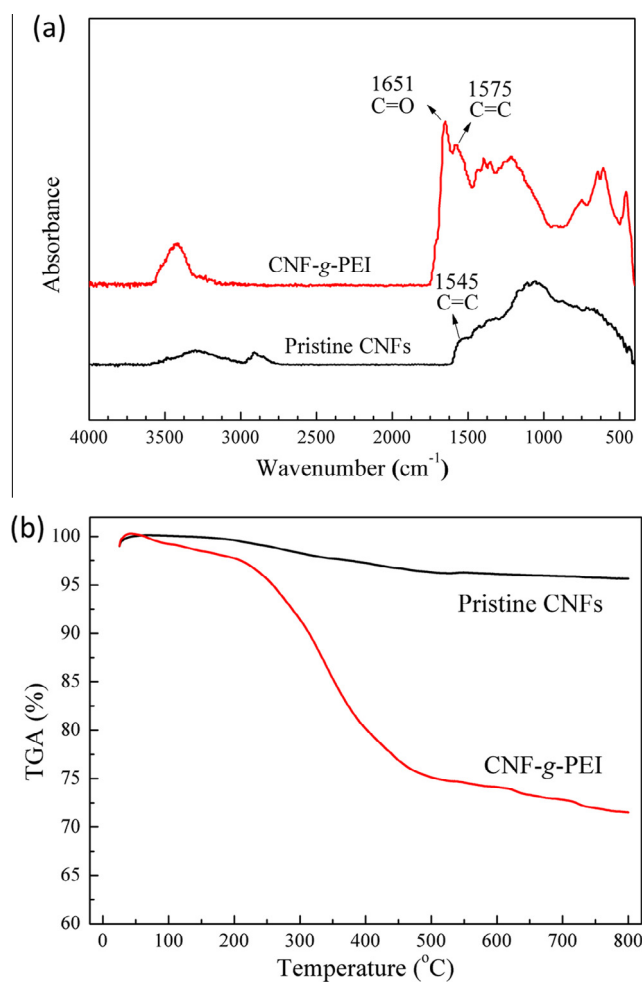


Fig. 2. (a) FTIR spectra and (b) TGA curves of pristine CNFs and CNF-g-PEI.

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