

An Environmentally Benign Fabrication Process for CNTs/PE Nanofibers from Immiscible Blends with Cellulose Acetate Butyrate

Hai-Lian Wang, Ru Xiao*

State Key Lab for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China

Abstract: Well-dispersed multiwalled carbon nanotubes (MWNTs)/polyethylene composites have been prepared from melt blending, and composite fibers were prepared via direct melt extrusion of immiscible blends with CAB and subsequent removal of CAB matrix. Scanning electron microscopy was employed to observe the distribution of the MWNTs in the composites, indicating a nanotube network formed in the matrix. SEM images also investigated that the average diameter of PE/MWNTs nanofibers can be 300-400nm. In addition, the crystalline structures of the CNTs/PE nanofibers were characterized by DSC, WAXD and POM, which show a decrease in the crystallinity of PE due to the addition of MWNTs. The thermal properties of composite fibrils were also modified. This fabrication process possesses features of controllability and is environmental friendly during the manufacture of thermoplastic nanofibers.

Keywords: Polyethylene, cellulose acetate butyrate, nanofibers, carbon nanotubes, fabrication, immiscible blends, extrusion.

1. Introduction

The development and applications of nano-structured materials have gained more and more attention because of their large surface area-to-weight ratio, showing perfect potential for uses such as high efficiency filtration and biomedical biosensors [1-3]. Nanomaterials include nanoparticles, nanotubes and nanofibers. Besides nanoparticles and nanotubes, nanofibers have much more advantages due to the inter-fiber structure and microscopic fibril surface [4]. There are many methods, such as electrospinning, melt blown, phase separation, island-in-the sea spinning and template synthesis, used to prepare polymer nanofibers [5]. Every process has its own advantages and limitations, according to different needs. Incompatibility blend-spinning, also called island-in-the sea spinning, which was developed in the 1970s by Japanese Toray Company, is a good method for producing superfine fibers [6]. When blending immiscible thermoplastic polymers, after phase separation, one polymer exists in another in various forms such as spheres, ellipsoids, fibrils, and lamellas. If the dispersed phase formed fibrils in the matrix phase, the immiscible blends are called in-situ fibrillar blends [7]. In a recent study, a novel matrix CAB was employed in immiscible blends as reusable and bio-compatible continuous phase. Dong Wang, Gang Sun successfully prepared CAB/polyolefin and CAB/polyester in situ microfibrillar blends by melt

extrusion [8]. And then iPP, HDPE, PE-co-GMA, and IPET-PEG nano-scale fibers were formed from the immiscible polymer blends with CAB and subsequent removal of matrix [9-11]. In this method, CAB was used as a sacrificial polymer to produce thermoplastic nanofibers, therefore it possesses environmental friendliness and can be exploited for bio-related applications of the thermoplastic nanofibers prepared.

Since 1991, carbon nanotubes(CNTs) have attracted much interest owing to its particular structure, superior properties and a wide range of applications. In the past few years, carbon nanotubes were also made much use of, as reinforcement for polymers and polymer/CNTs composites and have been reviewed in a lot of applications [12]. So far, a number of studies have described the preparation of polymer/CNTs composites by all kinds of methods, such as solution mixing, in situ polymerization and power ultrasonic mixing [13]. Every method has its limitation, however, only a few studies have mentioned the preparation of polymer/CNTs composites using melt blending or extrusion. Now a series of commercial polymer/CNTs composites have been prepared by melt blending using twin screw extruder and many improvements both in electrical conductivity and mechanism properties have been found [14-15].

Although there has been a significant progress in the preparation of polymer/CNTs composites, composite microfibers have not been widely reported. Dan Chen et al. [16] and Minsung Kang et al. [17] produced

*Corresponding author's email: xiaoru@dhu.edu.cn
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highly strong and tough PI/MWNTs nanofibers and silk fibroin/MWNTs nanofibers by electrospinning, respectively. In this study, MWNTs were embedded into LDPE matrix via melt blending, and then PE/MWNTs composites were mixed through twin screw extruder. After removal of CAB matrix, a moderate nano-structured fiber could be prepared. The morphology of MWNTs dispersed in PE and the micro-structure of composite fibers were investigated. The effects of MWNTs on the crystallization and thermal properties of the composite nanofibers were also discussed.

2. Experimental

2.1 Materials

The cellulose acetate butyrate (CAB) (CAB-381-0.5; butyryl content 38 wt%, acetyl content 13.5 wt% and hydroxyl content 1.3 wt%), purchased from Eastman Chemical (U.S.), was used as the matrix phase. The melting point is 130-135 °C, and the molecular weight is 30,000. Low-density polyethylene (LDPE), provided by Sinopec Shanghai Petrochemical Company Limited, with a MFR=3.1g/10min and $\rho=922\text{kg/m}^3$. The multi walled carbon nanotubes(MWNTs) were supplied by Sun Nanotech Co. Ltd, People's Republic of China, with a diameter range of 10-20nm.

2.2 Preparation of the PE/MWNTs composites

PE was melt blended with 0, 0.25, 0.5, 0.75, 1wt% MWNTs using a co-rotating twin screw extruder (EUROLAB16, D = 16mm, L/D = 40, Thermo-Haake Co.), with temperature along the barrel at 160,165,165,170,170,175,175,175,170,165 °C, screw speed was 50 rpm. Both the PE and the MWNTs were dried at 75 °C for 10hrs prior to mixing. The subsequent composites were cut to pellets via shredding machine.

2.3 Preparation of PE/MWNTs nanofibers

The CAB was mixed with the former five kinds of pellets, at the same weight ratio of 90/10. The mixtures were fed into the twin screw extruder, at a screw speed of 50 rpm and temperature along the barrel at 170, 180, 185, 185, 190, 195, 195, 190, 185, 180 °C. The blends were extruded through a strand rod die, the extrudates were hot-drawn at the die exit by a uniform draw strength and air cooled to room temperature. The CAB

was vacuum-dried at 75 °C for 24hrs prior to melt mixing.

2.4 Measurement and Characterization

PE/MWNTs and CAB/LDPE/MWNTs blends processed in the mixer were fractured in liquid nitrogen. The fracture surfaces of the blends were observed using scanning electron microscope (SEM) at an accelerating voltage of 15KV, to investigate the morphology and extent of dispersion of MWCNTs or PE in the matrix. The subsequent extrudates were immersed in acetone at room temperature for 24 hrs to remove CAB from blends. The PE and PE/MWNTs microfibrils obtained were observed using SEM. The diameter distributions and averages were gained by measuring 100 nanofibers, which was calculated using Image-Pro Plus. The number averaged diameters were calculated as follows (Eq.1).

$$D_N = \frac{\sum N_i D_i}{\sum N_i} \quad (1)$$

where D_N is the number averaged diameter, N_i is the number of microfibrils of diameter D_i .

To study the crystallinity and melting behavior of neat PE contrast to PE/MWNTs, a differential scanning calorimeter (DSC) was used and Wide angle X-ray diffraction (WAXD) was also performed using a Scintag XDS-2000 diffractometer to estimate the whole crystallinity by calculating the ratio of crystalline peak area to total areas of crystalline and amorphous regions. In addition, a polarization microscope(POM) was used to further state the modification of crystalline morphology of PE spherulites. Thermal behaviors and thermal degradation of PE and PE/MWNTs nanofibers were determined with a differential scanning calorimeter (DSC) and a thermal gravimetric analyzer (TGA) was used at a heating rate of 15 °C min⁻¹ under a nitrogen atmosphere.

3. Results and discussion

3.1 Morphology analysis

In a twin-screw extruder, the morphology development of the dispersed phase in CAB matrix is according to the combined action of shear force and later draw flow field. Fully remove the CAB phase, well-defined nanofibers were prepared from PE/CNTs/CAB (0, 0.25,