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The influence of interface and thermal conductivity of filler on the nonisothermal crystallization kinetics of polypropylene/natural protein fiber composites

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ABSTRACT

The nonisothermal crystallization kinetics of polypropylene/down feather fiber composites were investigated using a Differential Scanning Calorimeter at five different cooling rates. The Avrami and Liu models were able to satisfactorily describe the crystallization behavior of composites, which indicated the entirely unique mechanism. It was found that fiber/matrix interface and thermal conductivity of fiber had key roles for the crystallization behavior of composites and had a close relationship with the properties of the industrial product reinforced with natural protein fiber. The nucleation activity and activation energies were also calculated by different theoretical models and also proved the experimental results.

1. Introduction

Concern for the environment and shortage of oil is driving research into ways to reuse natural protein fibers, which are usually biodegradable, renewable and environmentally friendly compared with synthetic polymers. Consequently, various natural protein fibers, such as feather fiber, wool fiber and silk fiber, have been straightly applied as reinforcement to produce composites, which show better mechanical properties. Barone et al. prepare polyethylene/keratin fiber composites using Brabender mixing head set at 140–200 °C and rotating at 50, 75, or 100 rpm [1–3]. These researches prove the interaction between feather fiber and polyethylene matrix obtaining reinforcement from fibers. Loos et al. mix feather fibers and various cellulose fibers into polypropylene to compare the contributions of different kinds of fibers to the mechanical properties of composites [4]. Castanño et al. prepare poly(methyl methacrylate)/keratin biofiber composites by bulk polymerization of methylmethacrylate initiated with AIBN [5]. The keratin fibers from chicken feathers show the even distribution within and adherence to PMMA matrix, and improve the thermal stability of keratin biofiber-PMMA composites, which show increased T_g values and decomposition temperature. Lau et al. incorporate chicken feather fiber into PLA by extrusion and injection molding methods [6]. Marsano et al. compound wool fiber into biodegradable polyester using internal batch mixer at 160 °C [7]. Sun et al. mix silk fibroin fiber into poly(e-caprolactone) on a Haake Rheocord900 Rheomete, and show poor interfacial interaction between the fiber and PCL matrix [8].

Most studies of composite reinforced with natural protein fibers concentrate on interface between matrix and filler, morphologies, mechanical properties and thermal properties. It is well-know that the ultimate mechanical properties of composites are determined by interface between matrix and filler and the crystallization behavior of their matrix. Composites reinforced with natural protein fibers experienced non-isothermal crystallization other than isothermal crystallization in industrial polymer process, such as extrusion, injection molding, and film blowing. To understand the effects of complex thermal condition, the investigation of the non-isothermal crystallization kinetics is of technological and scientific importance, especially when the interface between matrix and filler is improved. There are interesting findings of nonisothermal crystallization kinetics for polypropylene composite based on inorganic particles, such as kaolin, fly ash, SiO_2, $CaCO_3$, montmorillonite, and organic cellulose fibers [10–14]. However, few studies report the nonisothermal crystallization kinetics of polypropylene composites reinforced with natural protein fiber. Furthermore, the thermal conductivity of natural protein fibers is lower than inorganic particles and cellulose fibers meaning that it is necessary to discuss the relationship between the thermal conductivity of fibers and the crystallization behavior of polymer matrix.

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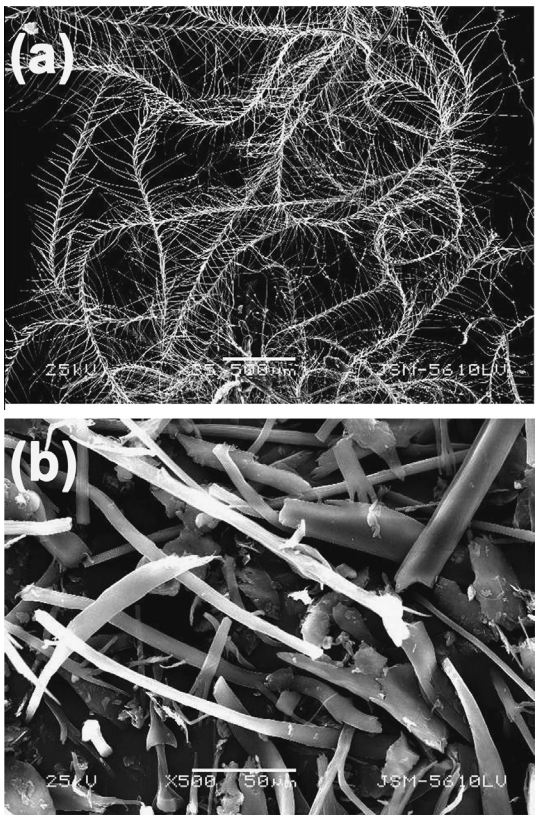

Fig. 1. SEM morphologies of down feather (a) and b down feather fiber (b).

In this context, down feather was cut into down feather fiber (DFF), which has the length to diameter ratio of 20–50 and stable structure against high temperature [9]. The main objective of this work is to study the influence of interface and thermal conductivity of filler on the nonisothermal crystallization of Polypropylene/down feather fiber composites using differential scanning calorimetry (DSC) technique. Their experimental data were analyzed based on Avrami and Liu models, respectively. The nucleation activity of down feather fiber in polypropylene (PP) matrix was calculated using Dobreva and Gutzowa method. The crystallization activation energy of all samples was evaluated using Kissinger equation and Takhor equation, respectively.

2. Experimental

2.1. Materials

Isotactic Polypropylene (Melt Flow Index = 36 g/10 min) was obtained from Panjin Co. Ltd., China. Down feather of duck was purchased from Maolong-wuzhong Down Co. Ltd., Shaoxing, China. Down feather was first grounded into down feather fiber (DFF) with length less than 300 μm on the self-made equipment, and then treated with acetone/alcohol solution to remove surface impurities. Down feather fiber was modified by stearic acid to improve the surface adhesion with polypropylene matrix, and the chemical reaction process was described previously [15]. Stearic acid, acetone and alcohol were supplied from Kedi Co. Ltd., Tianjin, China. The weight ratio of acetone and alcohol was 2:1.

2.2. Preparation of composites

Before thermal extruding, DFF and modified down feather fiber (MDFF) were dried under vacuum at 150 °C for 2 h in order to remove the moisture content, acetone or alcohol. The PP pellets were dried at 105 °C for 3 h. Pure PP, PP/DFF composite pellets

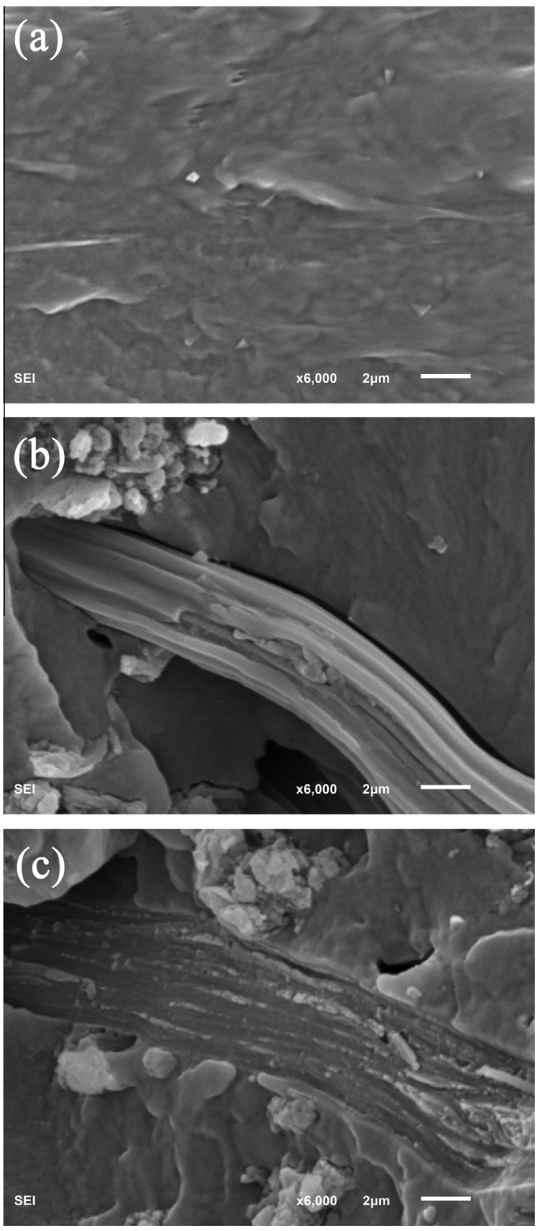

Fig. 2. SEM morphologies of cross-section: pure PP (a), PP/DFF composites (b) and PP/MDFF composites (c).

(80:20) and PP/MDFF pellets (80:20) were prepared in a twin-screw extruder (SHJ-18, China). The extruder screw speed was set at 75 rpm, and the process was carried out at six temperature zones of 120 °C, 165 °C, 170 °C, 185 °C, 185 °C and 190 °C from the metering to die zones. The strands from the extruder were cooled in water bath and palletized. After dried at 105 °C for 2 h, these pellets were respectively sandwiched between Teflon-coated compression molder and hot-pressed into thin sheets at 190 °C and 5 MPa for 5 min on the plate vulcanization machine (XLB-D350 × 350, china). Then, the sheets were removed from the molder and cooled until they reached room temperature. This resulted in foursquare sheets with around 0.5 mm in thickness and sides of 100 mm × 100 mm.

2.3. Scanning Electron Microscopy (SEM)

Morphologies of down feather and DFF were examined on a Scanning Electron Microscope (JSM-5610LV), at 25 kV after gold