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Effects of calcium sulfate whisker on the mechanical property, morphological structure and thermal degradation of poly (lactic acid) composites

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ABSTRACT

A comprehensive investigation on the fabrication and characterization of poly (lactic acid) (PLA) composites with varied mass fraction of calcium sulfate whisker (CSW) was presented. Before compounding, silanization strategy on CSW was performed by γ-(2, 3-epoxypropoxy) propytrimethoxysilane (GPTMS), and then mechanical performance, morphological structure and thermal behavior of PLA/CSW composites were explored carefully. It was found that silanization on CSW succeeded in forming well-bonded interfaces between organized CSW and PLA. Though the added CSW resulted in a moderate declination on tensile strength (less than 20%), it showed significant positive influences on the elastic modulus, elongation at break and impact toughness. The processes of glass transition and cold-crystallization were lagged at low concentration of CSW but accelerated again with further addition of whisker, as also affected the variation of actual crystallinity. However, the thermal stability was improved remarkably and kinetics analysis of thermal decomposition revealed that reaction order was hardly changed while activation energy was decreased along with increased CSW.

1. Introduction

Plastic products have been appeared everywhere in our life, and meanwhile, the significant impact of plastic wastes on the environment becoming more and more standing out. Due to the hardly degradation on the earth, how to deal with the used products derived from petroleum based polymers has been a great challenge for environmentalist in nowadays. The key point is to find an eco-friendly solution to manage the disposal of synthetic plastics. A pragmatic and effective solution should be the substitution of those synthetic plastics by biodegradable and compostable polymers, of which the representative is poly (lactic acid) (PLA). PLA is a man-made thermoplastic polymer belonged to the family of aliphatic polyesters commonly made from α-hydroxyl acids [1]. This material usually can be fabricated using renewable resources, such as cornstarch, by fermentation and it is able to be decomposed totally in the nature [2]. Thereby, it shows the splendid prospects in the packaging filed and biomedical (biocompatible and bioabsorbable) device market. Besides, PLA is characterized by high strength, high modulus and easily processed on standard plastics machine, showing a giant potential to substitute general thermoplastics, such as polypropylene (PP) and polystyrene (PS), in high volume applications. However, its inherent poor impact toughness and heat resistance is the major impediment for increasing the application window. To blend with other flexible polymer has been confirmed as a cost-effective method to improve the impact toughness, but usually accompanied with the sacrifice of strength and modulus, as is not an encouraged way in certain applications [3–9]. In order to solve this problem, inorganic fillers are added into the polymer formulations to form organic-inorganic composites, of which the positive effects of mineral fillers on the impact toughness [10–12] and heat resistance [13,14] have been demonstrated without significantly decreased mechanical properties. In those fillers, inorganic whisker is of great important due to the fine size and high aspect ratio. After all, the composites reinforced with thinner, stronger fibers could be anticipated to achieve much higher tensile strength according to the theories of short fiber composites [15].

Calcium sulfate whisker (CSW) is a kind of inexpensive filler, which could be derived from gypsum, mineral and even industrial residual (waste gypsum, waste bittern, acetylene sludge, etc.). It

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shows white color and silky smooth feel in the pure state and easy to be compounded with organic resin [16]. CSW offers excellent heat resistance, outstanding insulation properties, as well as much higher tensile strength and elastic modulus compared to polymers due to the perfect crystal structure. Such advantages allow CSW be a useful and effective reinforcement applied widely in polymers, such as increasing the mechanical properties [16–21], enhancing thermal stability [16,21–25] and crystallization process [19,24,26,27] and improving the tribological properties [17,21 and28]. Due to its non-toxic and biocompatibility, CSW is also expected as a promising reinforcement in fabricating biodegradable composites. Liu and his co-workers [18,19] used co-precipitation method to prepare polycaprolactone (PCL) composites with CSW, and they found that CSW showed giant improvements in the impact toughness and flexural properties. However, Chen et al. [24] stated that, in the absence of surface modification, CSW and PLA failed to form well-bonded interfaces under melt-blending process, and they did not investigate the evolution of mechanical property and thermal stability with varied CSW content. Thus, it should be interesting to explore the effect of CSW content on the comprehensive properties of PLA composites.

In this study, we reported the functionalization strategy to generate epoxy groups on CSW surfaces using γ-(2, 3-epoxypropoxy) propytrimethoxysilane (GPTMS) as silane agent, because expoxide surface of CSW was of great interest as it might directly react with hydroxyl groups of PLA in a ring opening process, creating secondary ether bond without any additional activation steps [29]. The CSW before and after silanizaiton were characterized to identify the variations on the crystal structures, surface elements and functional groups. Then, PLA/CSW composites were prepared by melt-blending technology. The mechanical, morphological and thermal properties of PLA/CSW composites were investigated in detail and their structure-property relationships were analyzed carefully.

2. Experimental

2.1. Materials

A commercial type poly (lactic acid) (PLA, REVODE101) was bought from Zhejiang Hisun Biomaterials Co., Ltd (China). It is pellets with the melt flow rate (MFR) of 5.5–10 g/10min and the specific gravity of 1.25 g/cm^3. Characteristics of PLA were as follows: number-average molecular weight (M_n) was 1.26 × 10^5 g/mol, weight-average molecular weight (M_w) was 2.04 × 10^5 g/mol, polydispersity index (PDI = M_w/M_n) equaled 1.62, and the content of D-lactic acid was less than 3%. Calcium sulfate whisker (CSW, industrial grade) received as white powder was kindly supplied by Wuhan Tang brothers Technology Co. Ltd (China). Its bulk density was 0.1–0.4 g/cm^3 and the length to diameter ratio of 30–70. γ-(2, 3-epoxypropoxy) propytrimethoxysilane (GPTMS, A.R. grade) was the product of Nanjing Shuguang Chemical Group Co., Ltd (China). Absolute alcohol, toluene, silicone oil and liquid paraffin were all commercial available with A.R. grade.

2.2. Sample preparation

The silanization on CSW by GPTMS was performed using the organic refluxing procedure. First, approximate 2 g CSW was suspended in 50 mL toluene with the aid of ultrasonic vibration. The suspension with 5 mL GPTMS (some drops of de-ionized water was introduced to enhance the reactivity) was sonicated for 30 min and subsequently transferred into a three-neck round bottom flask equipped with a condenser pipe. Silanization reaction was conducted in an oil bath with vigorous mechanical stirring at 120 °C. The whole procedure was under nitrogen (N_2) atmosphere and lasted up to 16 h before separating CSW from solution via precipitation and centrifugation. The collected CSW was washed using toluene, ethanol and de-ionized water successively and then dried at 90 °C in vacuum to constant weight.

PLA and CSW were mixed together in a molten state at varied blend ratio, i.e. PLA/CSW = 100/0, 95/5, 90/10, 85/15, 80/20 and 75/25 in mass ratio. Melt-compounding was performed by a twin screw extruder (SHJ-20, Nanjing Jieya Extrusion Equipment Co., Ltd, China) with the temperature profiles of 170, 180, 190, 190, 190 and 185 °C from hopper to die. The extruded composites were cooled in running water, dried by blowing air and pelletized. The standard samples were molded in a vertical injection molding machine (FT-200, Fomtec Machinery (Suzhou) Co., LTD, China), with temperature profiles of 160, 180 and 190 °C. Prior to melt-mixing, materials were dried respectively in vacuum at 60 °C for 24 h to remove the moisture.

2.3. Measurements

X-ray diffraction (XRD, XRD-6000, Shimadzu, Japan) was used to identify the surface structures of CSW before and after modification. The scanning range (2θ) was from 5 to 35° with a rate of 2°/min. A Cu target with K_α radiation (λ = 0.15418 nm) was used in the measurements.

Fourier transform infrared (FT-IR) was performed in an infrared spectrometer (Nicolet 380, Thermo Scientific, USA). About 5 mg CSW was well mixed with adequate potassium bromide (KBr), finely ground for 5 min and pressed into a pellet. The range of wave number was from 400 to 4000 cm^{-1} in the transmission mode with a solution of 4.0 cm^{-1}. Thirty-two scans were necessary to obtain spectra with good signal-to-noise ratios.

Molecular weight parameters were determined by means of gel permeation chromatography (GPC) at 25 °C using a Waters instrument (5510, Waters, USA), provided with four TSK G3000SW$_{xl}$ gel columns, using a differential refraction index detector. The mobile phase was chloroform. 200 μL of polymer solution with a concentration of 0.1 mol/L was injected at 0.5 mL/min. Average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) were calculated with reference to polyethylene oxide standards.

Morphological structure was observed by a field emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The non-conductive sample was coated by a thin Au layer via sputtering technology. The element distribution was examined by an energy-dispersive spectrometry (EDS, QUANTAX XFlash 6I100, Bruker, Germany).

Thermal analysis was conducted with a differential scanning calorimeter (DSC, Q200, TA Instrument, USA). Sample of 4.2–4.6 mg was subjected to non-isothermal melting processes from 0 to 200 °C with a heating rate of 10 °C/min under a nitrogen atmosphere (2L/min). Temperature calibration was performed with Indium as a reference, of which the melting temperature (T_m) was 156.6 °C and the heat flow was 28.5 J/g.

The study on thermal decomposition was carried out on a thermogravimetric analysis (TGA, TGA/SDTA851^e, Mettler-Toledo, USA). Approximate 10 mg sample was done from room temperature to 550 °C in a nitrogen atmosphere (60 mL/min). The heating rate was fixed at 10 °C/min. During testing, sample was measured in an alumina crucible.

Uniaxial tensile test was followed the Chinese Standards GB/T 1040.1–2006 using a computer aided universal testing machine (WDW-50, Shenzhen KQL Co., LTD, China) with a cross speed of 2 mm/min. The shape of specimen was standard dog-bone (1A type) with the gauge length of 50 mm. From the analysis of software, the stress-strain curve, tensile strength, elastic modulus, as