Materials and Design 34 (2012) 691–698

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Effect of tetra-needle-shaped zinc oxide whisker (T-ZnOw) on mechanical properties and crystallization behavior of isotactic polypropylene

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ARTICLE INFO

Article history:
Received 1 March 2011
Accepted 15 May 2011
Available online 19 May 2011

Keywords:
A. Polymer matrix composites
E. Mechanical
F. Crystalline state

ABSTRACT

Isotactic polypropylene (iPP) composites with unmodified and modified tetra-needle-shaped zinc oxide whisker (T-ZnOw) were prepared via melt blending in a twin-screw extruder. The mechanical properties, thermal properties, morphology and crystallization behavior were investigated. The mechanical properties of iPP with T-ZnOw modified by silane based coupling agent were much better than that of iPP with unmodified T-ZnOw. The reason was that the interfacial interaction between T-ZnOw and iPP matrix became stronger when T-ZnOw was modified by coupling agent. Besides, the addition of T-ZnOw improved thermal properties of iPP, including heat deflection temperature and thermal degradation temperature. Furthermore, wide angle X-ray diffraction (WAXD) results showed that T-ZnOw can be used as a novel β-nucleating agent, and the relative content of β-crystal was 0.38 when T-ZnOw content was 5 wt.%. iPP/T-ZnOw composites were found to exhibit higher crystallization temperature, smaller spherulites, and faster crystallization rate than those of pure iPP, indicating that T-ZnOw played a role of nucleating agent on the crystallization of iPP and could induce accelerated crystallization.

1. Introduction

Polypropylene (iPP) is a polymorphic material with several crystal forms, namely monoclinic (α), trigonal (β) and triclinic (γ) forms [1]. α-Crystal of iPP (α-iPP) is thermodynamically stable, and forms under conventional processing conditions. β-Crystal of iPP (β-iPP) is thermodynamically metastable and can be obtained under some special conditions, such as thermal annealing, high pressure and adding β-nucleating agent. The occurrence of γ form of iPP is extremely rare, and usually generates after crystallizing sample at high pressure. β-iPP have an important influence on the mechanical properties, because its toughness is higher than that of α-iPP at temperatures both above and below the glass transition temperature of iPP [2]. Among the techniques for preparing high content of β-iPP, adding β-nucleating agent is the most effective and accessible method. Some fillers including montmorillonite (MMT) [3], silica [4], calcium carbonate [5], zinc oxide [6,7], halloysite nanotubes [8], zeolites [9], cellulose whiskers [10] etc. have been reported to have β-nucleating activity.

Inorganic fillers have significant effect on the crystallization, mechanical, thermal and electrical properties of iPP [11–13]. Incorporating specific additives or nucleating agents, which provide foreign surfaces or nuclei, increase the nucleating and crystallization rate, as well as crystallization temperature and finer spherulites. Good adhesion between iPP matrix and additives generates the stress transfer from iPP to dispersed additives and increases the ability of iPP to absorb energy. Furthermore, the additives also can alter the polymorphism of iPP and increase crystallinity, thus improving mechanical properties of composites.

Tetra-needle-shaped zinc oxide whisker (T-ZnOw), discovered by Kitano in 1990 [14], is a special whisker with three-dimensional structure: four needles grow from one point and the angle between every two needles is 109°28′ [15]. The whiskers have many superior properties, such as semiconductivity, wear resistance, ultraviolet absorption and antibacterial effect [16]. Because it has unique structure and properties, T-ZnOw endows the polymer composites isotropic rather than anisotropic properties. T-ZnOw has been considered as an ideal reinforcement to influence the mechanical properties, crystallization behavior and conductivity of polymers [17–23]. Shi et al. [19,24] prepared T-ZnOw/PA6 composites and investigated their mechanical properties. The addition of T-ZnOw improved the composites tensile strength and impact strength greatly, because the spatial structure of T-ZnOw changed the stress distribution in the specimen. Wang et al. [16,25] studied the mechanical properties, crystallization behavior and melting behavior of nylon 11/T-ZnOw composites. T-ZnOw might act as a nucleating agent, which influenced the mechanism of non-isothermal crystallization and promoted the crystallization rate of PA11 matrix. Zhou et al. [23] summarized that the conductive mechanism

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doi:10.1016/j.matdes.2011.05.028

of polymer/ZnOw composites can be classified into tunnel effect, charge concentrating effect at the needles' tips of the whisker and conductive network.

However, only a few studies [17,26] on iPP/T-ZnOw composites have been reported in the published literature. iPP composites with T-ZnOw, which modified with different coupling agents, were prepared by Zhou et al. [26] It was found that different coupling agents have different reinforcing effects. In the present works, iPP/T-ZnOw composites were prepared via melt blending in twin-screw extruder. T-ZnOw was treated with silane coupling agent to improve the interfacial adhesion between T-ZnOw and iPP matrix. The effect of T-ZnOw on the mechanical properties and crystallization behaviors of the iPP/T-ZnOw composites were investigated.

2. Experimental

2.1. Materials

Isotactic polypropylene (iPP, T30s) with a melt flow rate (MFR) of 3.881 g × 10 min^{-1} (230 °C · 2.16 kg^{-1}) was purchased from Fujian Petrochemical Co., Ltd., Quanzhou, China. Silane coupling agent, (3-glycidoxypropyl)trimethoxysilane (KH570) was purchased from Nanjing Yudeheng fine chemical Co., Ltd. T-ZnOw was purchased from Chengdu Crystrealm Co., Ltd., China. The micrograph of T-ZnOw was shown in Fig. 1. The length and diameter of the needles of the whiskers were 10–50 μm and 0.5–5 μm, respectively. The density of T-ZnOw was 5.3 g/cm^3.

2.2. Preparation of iPP/T-ZnOw composites

2.2.1. Surface modification of T-ZnOw

The surface modification of T-ZnOw was carried out as follows: Firstly, a certain amount of KH570 coupling agent was dissolved in ethanol, and then mixed with the powder of T-ZnOw. The mixture was refluxed with stirring for 4 h at 70 °C in a two neck round bottom flask equipped with a mechanical stirrer and condenser pipe; secondly, the temperature of the mixture was increased up to the boiling point of ethanol to evaporate ethanol; lastly, the surface modified T-ZnOw was dried completely at 120 °C for 18 h. The obtained KH570 modified T-ZnOw was denoted as KH-T-ZnOw. And unmodified T-ZnOw was denoted as UN-T-ZnOw.

2.2.2. Preparation of iPP/T-ZnOw composites

iPP pellets with KH-T-ZnOw and UN-T-ZnOw were mixed and the mixture was extruded by a twin-screw extruder. The extrudate passed though a cooling water bath and were pelletized, and then dried at 75 °C for 18 h. Then the dried pellets of composites were injected into test specimens to quantitatively analyze mechanical properties.

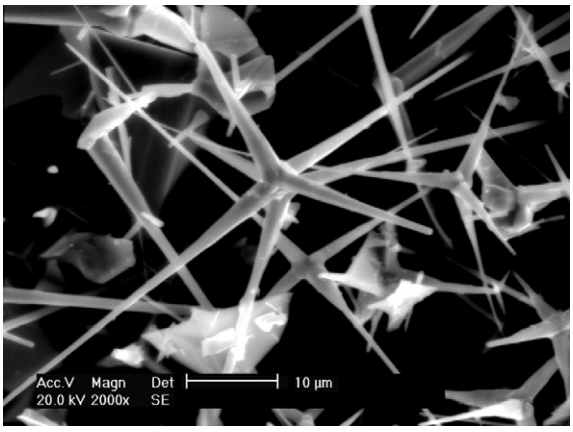

Fig. 1. SEM micrograph of T-ZnOw.

2.3. Characterization

2.3.1. Scanning electron microscopy (SEM)

The electron microscope (Philips-FEI XL30 ESEM-TMP) was employed to examine the morphology of the blends. The impact-fractured surfaces were coated with a thin layer of gold.

2.3.2. Measurement of mechanical properties

Impact strength was measured at room temperature with a XJJD impact machine using a 1.0 J hammer. The tests were conducted according to GB/T 1043-93 [27]: the samples were used with 80 mm × 10 mm × 4 mm, and V-shaped gap of 2 mm in the middle of samples. The impact-fractured surfaces of the composites were characterized via SEM.

Tensile strength was determined at room temperature using CMT-6104 testing machine according to GB/T1040-92 [28]: tensile strength was tested at a crosshead speed of 50 mm/min, using dumbbell shaped specimens with length of 120 mm, gauge length of 30 mm, width of 6 mm, and thickness of 3 mm.

2.3.3. Measurement of thermal properties

Heating deflection temperature (HDT) was measured with XRW-300HB tester according to GB/T 1634-2004 [29]. The specimens were cut with dimensions of 80 × 10 × 4 mm.

Thermogravimetric analysis (TGA) was used to determine the thermal stability and degradation of pure iPP and iPP/T-ZnOw composites. The analysis was performed on a SDT-Q600 (TA instruments) at the heating rate of 10 °C/min from room temperature to 700 °C under N_2 atmosphere.

2.3.4. Wide angle X-ray diffraction (WAXD)

Patterns of WAXD were obtained by using a Rigaku MiniFlexII X-ray diffractometer employing Cu Kα radiation (λ = 1.54 Å) and spectra were recorded in the 2θ range between 10° and 30°. The scanning speed was 2° · min^{-1}.

2.3.5. Differential scanning calorimetry (DSC)

DSC data of all samples were performed with a TA Q2000 differential scanning calorimeter under nitrogen atmosphere. DSC scanning program was set as follows: firstly, samples were rapidly heated from room temperature to 220 °C and maintained at this temperature for 5 min to eliminate the thermal history; secondly, the samples were cooled down to room temperature at the cooling rate of 10 °C min^{-1}; lastly, the samples were reheat to 200 °C at the heating rate of 10 °C · min^{-1}.

2.3.6. Polarized optical microscopy (POM)

The morphologies of the crystallites of samples were observed with a CHEMAT XP-201 Polarization optical microscope of Shanghai Caikon Optical Instrument Co., Ltd. and a CCD camera. The samples were placed between two glass slides on a hot stage and melted at 200 ± 2 °C for 10 min to erase any thermal memory, then squeezed on the top slide to form a film. Then the samples were put in the glycerin bath kept at 130 ± 2 °C for 2 h to allow crystallization. And the films were rapidly cooled to room temperature for test.