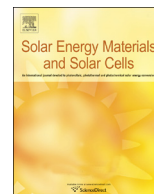




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Effect of nucleating agent on the crystallization behavior, crystal form and solar reflectance of polypropylene



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ABSTRACT

Nucleating agents of polypropylene (PP) have a function in accelerating the crystallization rate, decreasing the spherulite size and transforming the crystal form. Materials with high solar reflectance are widely used in the field for cooling purpose. In this work, three types of nucleating agents were applied to improve the optical properties: malonic acid, sorbitol, and carboxylate nucleating agent (NTC). Differential scanning calorimetry (DSC) measurement was conducted to investigate the crystallization behavior. Wide angle X-ray diffraction (WAXD) was used to study the crystal structure and the crystal form. Polarized optical morphology (POM) was chosen to observe the crystal morphology. UV–vis–NIR spectrometer was performed to record the solar reflectance from 280 to 2500 nm. It was found that nucleating agents could increase the crystallinity, decrease the spherulite size and transform the crystal form of PP, which in turn improved the solar reflectance considerably. Especially, β crystal form with high birefringence exhibited more excellent solar reflectance in comparison with neat PP, PP/malonic acid and PP/sorbitol. The order of solar reflectance is as follow: spherulites of β crystal form > small spherulites of α crystal form > large spherulites of α crystal form > disordered polymeric chain. All these types of PP have high thermal emittance more than 0.85, 1 wt% NTC even improves this value of PP to 0.90.

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1. Introduction

Solar materials have wide applications where they are used to cool an object exposed to incident irradiation from a high temperature source [1]. In normal daytime conditions, all objects on the earth facing the sky are exposed to the sun. During the day, the high-intensity solar irradiation makes the solar energy input much higher than the outgoing irradiation [2]; therefore the surface of the material does not quickly cool below ambient temperature. This accumulated heat will not only damage the material (physical aging), but will also increase the air temperature covering this material. Thus, an extra cooling system should be applied to reduce the unexpected heat, which will raise the energy cost and worsen the global warming problem [1,3–5].

In recent years, a number of researchers have focused on preparing cool materials to save energy. Levinson et al. systematically investigated solar spectral optical properties of pigments [6] and used a method for creating a non-white cool building roof by achieving high solar reflectance [7,8]. Sreeram et al. [9] prepared a cooling colorant based on rare earth metal ions. Furthermore, another researcher has studied the factors that influence on solar reflectance, and concluded that solar reflectance depended on the

size, shape, concentration of the pigment particles, thickness of the film, and the surface roughness of the material [10]. Although all the literature mentioned above investigated the solar reflectance of inorganic pigment for cooling roof coating, there are barely reports on the solar reflectance of commonly used polymeric materials.

Polypropylene (PP) is a widely used engineering commercial polymer with many applications, due to its attractive combination properties of ideal thermal stability, high heat distortion temperature, chemical resistance, mechanical property, fabrication flexibility, and low weight [11,12]. PP can be made into fiber through electrospinning technology. This kind of fiber can be fabricated into a polymeric shadow net to cover a building roof or tent for emergency situations. Moreover, because of PP's exceptional properties, it can be also made into artificial turf for football fields. There are at least four types of crystal forms existing: monoclinic α -PP, trigonal β -PP, orthorhombic γ -PP, and mesomorphic smectic forms [13]. The β crystal phase has attracted much more attention because of its excellent properties such as better elongation at break, lower density, better transparency, higher impact strength and tearing strength, etc. The regular method used to obtain β crystal form is to introduce nucleating agents into the PP matrix. When the nucleating agent is added into the polymer matrix, there must be at least three aspects to be taken into account. First of all, the thermodynamic compatibility in the nucleating agents-polymer system should be considered. The regular nucleating agents are insoluble with PP,

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while sorbitol-based nucleating agents are soluble depends on their concentration during the process. Second, the self-nucleation happens during the crystallization of a semi-crystalline polymer without nucleating agents. The purpose of introducing nucleating agents is to improve nucleation efficiency (to make the spherulite size smaller). The nucleation efficiency shows a linear increase when the concentration of nucleating agent is within a certain range. An extra content beyond the certain scope is meaningless in improving the nucleation efficiency, even if they can induce PP to crystallize into β crystals. Lately, the dispersion of nucleating agents in the PP matrix is of great importance, as the dispersion will affect the nucleation efficiency. More nucleating agents will impair their dispersion within the PP matrix. Therefore, the addition of the nucleating agents has to be less than 1 wt% in literature [12,13,16].

A number of reports focus on the solar reflectance of materials such as cool pigments, rare earth metal oxides, and factors that influence on solar reflectance [5,8,10,14]. Moreover, some researchers have studied crystallization behavior, crystal forms, and crystal morphology of PP [13,15,16]. However, the effect of crystallization behavior, crystal forms, and crystal morphology of PP on the solar reflectance have barely been investigated. In this work, three nucleating agents were added into the PP matrix so that they would improve the solar performance. Samples were prepared by melt blending. Crystallization behavior, crystal structure, crystal form, crystal morphology, and solar reflectance were examined by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), polarized optical microscopy (POM), and UV-vis-NIR spectrometer, respectively.

2. Experimental

2.1. Materials and sample preparation

Isotactic homo-polymer PP (S1004, melt flow rate=4.2 g/10 min at 230 °C and 2.16 kg) was a product from Yangzi Petrochemical Company Limited, China. Three different types of nucleating agents were employed in this investigation. Malonic acid (chemically pure reagent), sorbitol and carboxylate nucleating agent (NTC) were supplied by college of materials science and engineering, Nanjing University of Technology, China.

PP blended with or without nucleating agents was prepared with a laboratory torque rheogoniometer (Kechuang machinery XSS-300) at 180 °C and 60 rpm for 6 min. Two weight ratios of nucleating agents (0.5 and 1 wt%) were chosen to prepare the blends.

2.2. Characterization

2.2.1. UV-vis-NIR spectral measurement

The UV-vis-NIR spectral measurement was conducted using a spectrometer with an integrating sphere (Shimadzu UV-3600, Japan). The angle of the incidence applied in this investigation was 5°. The chosen spectral region used to conduct the solar reflectance and transmittance was from 280 to 2500 nm. The thickness of all samples was approximately 1 mm. Barium sulfate was applied as the white reference. The reflectance of each region in solar irradiation can be calculated by the following equation [8]:

$$R_{\lambda_0 \rightarrow \lambda_1} = \left[\int_{\lambda_0}^{\lambda_1} r(\lambda) i(\lambda) d\lambda \right] / \left[\int_{\lambda_0}^{\lambda_1} i(\lambda) d\lambda \right] \quad (1)$$

where $R_{\lambda_0 \rightarrow \lambda_1}$ is the reflected fraction of solar irradiation incident at wavelength between λ_0 and λ_1 , and $R_{\lambda_0 \rightarrow \lambda_1}$ is the irradiance-weighted average of its spectral reflectance $r(\lambda)$, $i(\lambda)$ is the solar spectral irradiance (power per unit area per unit wavelength). The irradiance-weighted average reflectance of each solar irradiation

region was calculated by this equation: UV reflectance U (280–400 nm), visible reflectance V (400–700 nm), and NIR reflectance N (700–2500 nm). The total solar reflectance S (280–2500 nm) can be calculated as the weight average of its UV, visible, and NIR reflectance, according to the aforementioned distribution of solar power yields (5% UV, 43% visible, and 52% NIR) [8]

$$S = 0.05U + 0.43V + 0.52N \quad (2)$$

2.2.2. Differential scanning calorimetry (DSC)

The effect of different nucleating agents on the crystallization behavior of isotactic PP was investigated by means of a Q200 thermal analysis apparatus (TA Instruments, America). Samples weighing about 10 mg were cut off and sealed into aluminum pans. The heating rate was 10 °C/min from 40 to 180 °C under dry nitrogen with a flux of 50 ml/min during the scanning. From the thermogram, the degree of crystallinity of PP can be calculated by the following equation [17,18]:

$$X_{DSC} = (\Delta H_f / \Delta H_f^*) \times 100\% \quad (3)$$

where ΔH_f was the enthalpy of fusion of each sample measured by DSC, and $\Delta H_f^* = 207.1$ J/g is the melting enthalpy of fusion of a 100% crystalline of PP. The subsequent crystallization process from the melt was cooled at a controlled rate of 5 °C/min to room temperature, after holding the sample at 180 °C for 3 min.

2.2.3. Wide angle X-ray diffraction measurement (WAXD)

To determine the crystal structure of each specimen, WAXD was conducted with an XRD-6000 diffractometer (Shimadzu, Japan) using nickel-filtered Cu K_α source. The scanning velocity was 5°/min ranging from 10 to 30° (40 kV, 30 mA) under ambient temperature.

The interplanar distance d and the crystal size L_{hkl} (in the direction perpendicular to (hkl) crystal plane) were calculated by the Bragg equation and the Scherrer equation, respectively, as was described in our previous investigation [19]. The overall crystallinity (X_{WAXD}) of each sample and the relative amount of β crystalline form in PP were measured based on the WAXD diffractive peaks. In the typical WAXD profile, PP has three obvious diffraction peaks of α crystal phase, at approximately $2\theta = 14.6$, 17.4 and 19.0°, which correspond to the (1 1 0), (0 4 0), (1 3 0) principal reflections [20], respectively. The diffraction peak of (3 0 0) is the principal reflection of β crystal form, which is at about 16.5° [21]. After the amorphous background was extracted, crystal peaks and the amorphous contribution were fitted by Gaussian function. This process is based on the original data without any smoothing. The crystallinity (X_{WAXD}) and the relative content in β phase of PP can be calculated according to a procedure introduced in literature [13,22], as follows:

$$X_{WAXD} = \sum A_{\text{crystallization}} / (\sum A_{\text{crystallization}} + A_{\text{amorphous}}) \quad (4)$$

$$K = A_{\beta(3\ 0\ 0)} / [A_{\beta(3\ 0\ 0)} + A_{\alpha(1\ 1\ 0)} + A_{\alpha(0\ 4\ 0)} + A_{\alpha(1\ 3\ 0)}] \quad (5)$$

in which X_{WAXD} and K value present the overall crystallinity and the relative amount of β phase with respect to α phase, respectively. $A_{\beta(3\ 0\ 0)}$, $A_{\alpha(1\ 1\ 0)}$, $A_{\alpha(0\ 4\ 0)}$ and $A_{\alpha(1\ 3\ 0)}$ are areas under each diffraction peak corresponding with each reflection of (3 0 0), (1 1 0), (0 4 0) and (1 3 0), respectively. $A_{\text{crystallization}}$ is the total fitted area of crystalline region containing all the diffraction peaks mentioned above. $A_{\text{amorphous}}$ is the fitted area of amorphous region.

2.2.4. Polarized optical microscopy (POM) observation

To observe the crystal morphology, a polarized microscope (Olympus BX 51, Japan) equipped with a temperature controller (Linkam THMS 600, England) was used under polarized light in a dark background. Extremely thin sample slices (ca. 0.02 mm) were heated to 180 °C, and held at this temperature for 3 min to eliminate

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