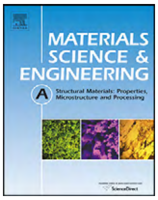
Materials Science and Engineering A 527 (2010) 6002–6011

Contents lists available at ScienceDirect

Materials Science and Engineering A

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



Nanoparticle interface driven microstructural evolution and crystalline phases of polypropylene: The effect of nanoclay content on structure and physical properties

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ARTICLE INFO

Article history:
Received 24 February 2010
Accepted 27 May 2010

Keywords:
Polypropylene
Nanoparticle effects
Spherulite
Equilibrium melting point

ABSTRACT

Significant differences in the microstructure occur when the polypropylene matrix dispersed with 4 wt.% and 8 wt.% nanoclay. In neat polypropylene, α-crystals nucleate in the low to moderate crystallization pressure range of (∼0.1–60 MPa), while γ-phase nucleates at crystallization pressure of ∼60–200 MPa. In contrast to neat polypropylene, the presence of nanoclay in the polymer matrix, promotes the formation of γ-phase at ambient crystallization pressure of 0.1 MPa. Nanoclay and pressure-induced crystallization governs phase evolution and microstructure of polypropylene and is associated with change in the thermodynamic and physical properties such as equilibrium melting point and glass transition temperature. This change in equilibrium melting point and glass transition temperature points toward thermodynamic interaction between polymer-nanoparticle and nanoparticle interface-driven microstructural evolution. The dependence of equilibrium melting point on crystallization pressure and spherulite size on undercooling delineates two distinct regimes which are ascribed to dominant α- and γ-phases of polypropylene. However, the effect of nanoparticles is less dramatic when nanoclay content is increased from 4 wt.% to 8 wt.% implying that the effect maximizes at ∼4 wt.% nanoclay.

1. Introduction

In recent years, layered silicate has been actively considered as a reinforcement mineral for polypropylene to increase physical and mechanical properties [1–4] including modulus, yield strength, flame-retardant, and heat distortion properties [1,5–7]. In this regard, nanoclay generated significant interest because it offers the possibilities of both intercalation and exfoliation.

Polypropylene (PP) is characterized by four different crystalline phases that which include monoclinic (α), hexagonal (β), orthorhombic (γ), and mesomorphic (smectic) [8–12]. The nucleation of these different polymorphs depends on the crystallization conditions. The commonly observed crystalline phase of polypropylene is α-phase (α-PP). The β-phase (β-PP) nucleates in the presence of β-nucleating agent or under specific conditions of temperature gradient and strain [13–16]. Occasionally, reinforcement minerals may act as β-nucleating agents. Typical examples are stearate-coated carbonate [15] and silica [16]. The γ-phase (γ-PP) is not nucleated at atmospheric pressure, but its crystallization has been observed to be promoted in low molecular fraction of 1000–3000 g/mol under slow cooling conditions. However, in the high molecular weight, high isotactic polypropylene, γ-phase can be obtained on crystallization at high pressure [17–21]. More recently, it was proposed that stereoirregularity or structural disorder that suppresses the chain folding of lamellae facilitates γ-phase formation [22]. In summary, the crystallization of γ-phase in high molecular weight, high isotactic polypropylene requires crystallization at high pressure or shear flow conditions [23,24]. The γ-phase is the primary phase at a high pressure of ∼200 MPa in high molecular weight polypropylene [25,26]. Polyethylene is another semi-crystalline polymer that is of significant interest in understanding the effect of pressure on structural evolution [27,28].

Given that crystallization pressure has an impact on nucleation and growth process and indicating the ultimate properties of polymeric materials, it is important to understand and elucidate the determining role of nanoparticles during pressure-induced crystallization. This need is further exacerbated by the fact that the properties of injection molded polymers can be tailored through modification of structure and that a number of processes including extrusion and injection molding involve application of high pressure.

The objective of the present study is to elucidate how nanoclay governs microstructural evolution during pressure-induced crystallization of polypropylene. The objective is achieved by inves-

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doi:10.1016/j.msea.2010.05.085

tigating two different nanoclay content of 4 wt.% and 8 wt.%. Clay has expandable layered aluminosilicate structure consisting of stacks of plate like structure of ~1–2 nm thickness separated by an interlayer distance of 1–3 nm. The platelets with aspect ratio in the range of ~50–100 nm have an extremely large surface area of ~750 m^2/g. An accompanying objective is to illustrate the possibility of nanoparticle interface-driven phase or microstructural evolution. The study is also relevant from the viewpoint of impact strength, a mechanical property that has been observed to exhibit a contrasting behavior in semi-crystalline polymers [29,30].

2. Experimental

2.1. Materials

Polypropylene (PP) from Basell Polyolefins (product name: Profax 632) was used to investigate the crystallization behavior of PP containing dispersion of nanoclay. The PP had a melt flow rate of 12 g/10 min at 230 °C/2.16 kg. In the present study nanoclay content of 4 wt.% and 8 wt.% were studied. Prior to mixing of nanoclay with polypropylene, nanoclay was dried in an oven at ~100 °C for ~24 h. First, a compatibilizer blend (masterbatch material) containing polypropylene-grafted maleic anhydride (maleic anhydride content = 1 wt.%) and nanoclay was prepared by mechanically mixing followed by melt blending in a twin screw extruder. Next virgin polypropylene and compatibilizer were mechanical mixed in a three-zone twin screw extruder such that the final product contained 4 wt.% and 8 wt.% nanoclay in the polypropylene matrix. The injection molded material was used for the crystallization experiments described below.

2.2. Pressure-induced crystallization

Neat PP and PP containing dispersion of nanoclay were crystallized in the temperature range of 130–180 °C and at different pressures of 0.1–200 MPa in an in-house designed pressure–temperature cell that provides hydrostatic condition. A typical crystallization experiment consisted of four steps: (a) elimination of prior thermal history by melting the sample at 230 °C for ~5–10 min; (b) cooling to the selected crystallization temperature and application of hydrostatic pressure on attaining thermal equilibrium; (c) isothermal crystallization at the desired pressure and temperature for adequate time (~1 h) to ensure complete crystallization; and (d) release of pressure and cooling to room temperature.

2.3. Thermodynamic and physical properties

Given the objective of the study, the thermodynamic and physical properties of interest are equilibrium melting point, glass transition temperature, and crystallinity. The effect of pressure on the equilibrium melting point ($T_m{}^\circ$) was analyzed for different combination of crystallization pressure and temperature. The equilibrium melting point ($T_m{}^\circ$) of a polymer crystal is defined as the melting point of an extended chain crystal and is an important thermodynamic property. The primary aim of determining $T_m{}^\circ$ was to make a relative comparison of structural morphology at identical or similar undercooling ($\Delta T = T_m{}^\circ - T_c$; the equilibrium melting point; $T_m{}^\circ$, increases with pressure and T_c is crystallization temperature). The equilibrium melting point ($T_m{}^\circ$) of pressure-induced crystallized samples was determined by differential scanning calorimetry (DSC) (TMA Instrument, DSC 2910). In the DSC experiments, the samples were heated from 20 °C to 200 °C at a heating rate of 10 °C/min, where the peak in the endothermic plot corresponds to the melting point (T_m). Subsequently, from the plot of melting point versus crystallization temperature, the equilibrium melting point ($T_m{}^\circ$) at particular crystallization pressure was determined by linear extrapolation of experimental melting point (T_m) to the equilibrium line ($T_m = T_c$). Using this method, a relationship between equilibrium melting point and crystallization pressure was obtained, providing an assessment of the effect of pressure on the equilibrium melting point of polypropylene in the absence and presence of nanoclay. This analysis besides providing the role of pressure, allowed us to predict the contribution of nanoclay and its content (4 wt.% and 8 wt.%) on equilibrium melting point, which has an impact on undercooling.

In the context of nanoparticles, in the present case nanoclay, an important physical property besides $T_m{}^\circ$, which is sensitive to polymer structure and mobility, is the glass transition temperature (T_g). The glass transition temperature was studied by dynamic mechanical analysis (DMA) (TA Instruments DMA 2980) in single cantilever mode. The testing frequency was 1 Hz and the heating rate was 3 °C/min.

2.4. Dispersion of nanoclay and intercalation of polypropylene

The dispersion state of nanoclay and intercalation of polypropylene between the clay layers was studied by transmission electron microscopy (TEM). Ruthenium tetroxide (RuO_4) staining method was utilized to examine the samples in TEM. The staining process involved the following steps: (a) 1 ml of 10%w/v sodium hypochlorite solution (NaClO, 13% active chlorine (Acros Organics) diluted to 10%w/v by adding deionized water) was added to 0.02 g of ruthenium (III) chloride ($RuCl_3$) in a 5 ml glass vial, mixed with a pipette, and immediately capped; (b) the trimmed specimen was stained inside this vial by fastening the sample to the vial cap with double sided tape; (c) after ~12 h, the specimen was overnight de-gassed in the fume hood prior to ultramicrotome; (d) sections of ~50–100 nm were cut using a Leica EM UC6 ultramicrotome (Leica, Austria), equipped with a diamond knife and collected in a trough filled with water and placed directly onto 400-mesh copper grids. The sections were examined by TEM using a Hitachi H-7600 at an acceleration voltage of 100 kV.

2.5. Crystallization phases and macromolecular structure

X-ray diffraction (Scintag, XDS 2000 diffractometer, USA) was used to identify phases evolved at different crystallization pressure. The X-ray diffraction was carried out at 43 kV and 21 mA using Cu Kα radiation of wavelength 1.54 Å as the X-ray source at a scan speed of 1.0 °/min in the 2θ range of 3–40°.

The macromolecular structure, in particular, spherulite size, was examined using field emission scanning electron microscopy (JEOL 6300F) (SEM). Prior to examination in SEM, the samples were chemically etched for 60 min via solution consisting of 0.07 g potassium permanganate, 4 ml concentrated sulfuric acid (95–97%) and 6.0 ml concentrated phosphoric acid (85%), while being ultrasonicated. Next, they were washed successively in 30% sulfuric acid at 2 °C, 30% aqueous hydrogen peroxide (to remove the remaining manganese dioxide), distilled water and acetone at room temperature.

3. Results and discussion

3.1. Dispersion of nanoclay and intercalation of clay

Transmission electron micrographs illustrating dispersion state of nanoclay and intercalation for the PP-4 wt.% nanoclay system is presented in Fig. 1. Fig. 1a illustrates that uniform distribution of nanoclay was achieved. In the context of the present study related to pressure-induced crystallization and associated influence on undercooling and microstructural evolution, uniform dispersion of