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Markedly improving mechanical properties for isotactic polypropylene with large-size spherulites by pressure-induced flow processing

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ABSTRACT

Mechanical property of semicrystalline polymer with large-size spherulites is rather poor, and needs to be improved by adding nucleating agent to make spherulites smaller. However, the nucleating agent causes many problems limiting its applications. In this paper, we report a method to simultaneously improve the toughness and tensile strength of isotactic polypropylene (*i*PP) with large-size spherulites by deformation of spherulites and orientation of lamellaes through pressure-induced flow processing (PIF-processing) at solid state. The initial spherulite sizes of *i*PP samples with the same crystallinity and crystal form were controlled by adding nucleating agent (NA, Talc, nano-scaled), and then the samples were subjected to PIF-processing. The resulting mechanical performance of the bulk materials, including impact and tensile strength, was simultaneously enhanced. In particular, the impact strength increases upto 8 folds higher than those obtained by conventional processing for the same bulk materials, attributing to the synergistic effect of both the orientation and the large-size spherulites. The measurements of SEM, XRD and SAXS revealed the spherulites deformation and lamellae orientation during PIF-processing, as the basis of discussing the mechanism.

1. Introduction

Isotropic polypropylene (*i*PP) [1] is replacing traditional materials in structural applications because of their relatively low cost and recyclability [2–5]. But *i*PP lacks sufficient mechanical properties for many engineering applications [6]. To promote the usage of *i*PP and other thermoplastic polymeric materials for load-bearing structures, it is important to be characterized by minimal susceptibility to mechanically induced damage (surface or bulk). So improving the mechanical properties, in particular the toughness and strength, is undoubt an important topic. The mechanical performances of *i*PP are related to spherulite sizes, that materials with large spherulites always have poor properties. So there are many studies on adding nucleating agents (NAs) to refine the spherulites in order to improve the mechanical properties. Typical organic nucleating agent for semicrystalline polymers is based on the modification of sorbitol [7–11]. Shepard et al. [7] found that dibenzylidene sorbitol (DBS) underwent self-assembly and promoted the formation of spherulites in commercially important polyolefins, such as *i*PP. Spherulite size of *i*PP has also been modified by melt mixing with various kinds of inorganic fillers, such as talc, mica, clay, whiskers, glass fiber, carbon fiber, silica nanoparticles, carbon nanotubes and calcium carbonate ($CaCO_3$) [12]. Svoboda P. et al. [13] showed that PP/PP-MA330k/clay, an intercalated three-component system containing some dispersed clay as well as the claytactoids, showed a much smaller size of spherulites and a slight increase in impact strength with increasing the clay content. Zhao L. et al. [14] illustrated that the mechanical properties of the ultrasonicated polypropylene/montmorillonite nanocomposite increased due to the improved dispersion of OMMT and diminished spherulite size. All these studies have focused on adding NA to improve the properties, which would bring other problems.

The NA includes organic and inorganic materials. The structure of organic NA is complex and sometimes NAs are with color and high cost. It is easy to separate from materials, and affects application efficiency and product quality. Meanwhile, inorganic NAs neither have good interaction with organic polymers to achieve good dispersion nor adequate adhesion [15]. The physical properties of the materials, such as surface smoothness and barrier properties, cannot be satisfied [16]. Therefore, inorganic NAs are usually not used when surface smoothness and high gloss are

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required. So adding too many NAs should be avoid in certain conditions.

Recent years, we devoted into developing a new processing method, pressure-induced-flow processing (PIF-processing), which applies pressure to materials in their solid state (at moderate temperatures). The PIF processing is similar to an approach studied previously [17] which allows free deformation only in one direction, the so-called flow direction. Previous studies showed that PIF-processing in the solid state could result in an ordered structure in some polymeric materials, and lead to markedly enhanced mechanical properties [18,19]. In this paper, we studied the mechanical properties and structures of *i*PP with large-size spherulites by deformation of spherulites and orientation of lamellaes via PIF-processing at solid state. The initial spherulite sizes of *i*PP samples were controlled by adding various contents of NA (talc, nano-scaled) and then the samples were subjected to PIF-processing. The effect of the initial spherulite size on the mechanical performances and the orientation behavior and mechanisms involved in the plastic deformation of bulk *i*PP materials by PIF-processing were investigated.

2. Experimental

2.1. Materials

Isotactic polypropylene: T300, Shanghai, M_n = 82,265 g/mol, M_w = 467,616 g/mol, PD = 5.68, T_m = 172 °C, melt flow index (MFI) = 26 g/10 min.

2.2. Sample preparation

Talc (0, 0.01, 0.025, 0.1 wt.%) was mixed together with PP pellets by a twin-screw extruder (Europ 160, Thermoelectro), the PP/talc mixture was injected into the mold of sample size 80*10*4 mm. The bars (80*10*4 mm) then were carefully machined into samples of size 20*10*4 mm for further PIF processing study.

2.3. PIF processing

The sample was deformed into a sheet in a lab-designed apparatus (Fig. 1) at the temperature of 110 °C, the pressure of 375 MPa, and kept under the condition for 5 min. In the conditions above, *i*PP materials can acquire the best mechanical properties [20]. The aim is to force the samples flow in one direction within the constraint of the two sides. LD, FD and CD represent the loading direction, flowing direction and constraint direction, respectively. After PIF-processing, the thickness of *i*PP materials is about two times of that before PIF-processing.

2.4. Measurements and characterizations

Spherulite size measurement: The spherulite size was measured under the polarizing optical microscope (POM, OLYMPUS, BX51-P), with (50*) objective. Size of spherulite is determined by average 15 individual samples.

Impact strength test: The impact tests were performed according to ISO 180 (notched Izod impact strength test): 2000 with CEAST RESIL IMPACTOR (Italy) (cantilever beam-test specimen is held as a vertical cantilevered beam and is impacted by a swinging pendulum) at room temperature. Each non-notched Izod impact strength represented the average value of 5 parallel tests, with an error bar calculated as mean square error of 5 parallel measurements. The impact direction is along the CD direction.

Tensile strength test: The tensile tests were performed according to ISO 527-1: 1993 with a (AGS-500ND) universal testing machine at room temperature and a stretching speed of 50 mm/min. Each result represented the average value from 5 parallel tests, with an error bar calculated as mean square error. The stretching direction is parallel to the FD direction.

DSC (differential scanning calorimetry): The measurement was performed using a Modulated DSC 2910 (TA Instruments Company, USA) with a heating rate of 10 °C/min from 30 to 190 °C in dry nitrogen atmosphere.

XRD (X-ray diffraction): The crystalline structure was investigated with X-ray diffracmeter (2550VPC, Rigaku-D/max, Japan). The wavelength of X-ray is 1.54 Å. The source of X-ray is Cu-kα radiation, the tube voltage is 40 kV and the electric current is 300 mA.

SEM (scanning electron microscope): SEM (JSM-5600LV, JEOL) was used to study the morphologies of samples on their fracture surface that perpendicular to the flow direction during PIF-processing. All samples were brittly fractured in liquid nitrogen and the fracture surface was sprayed with a layer of gold on the ion sputtering instrument (SC7620) for 30 s where the working current was set at 30 mA.

DMA (dynamic mechanical analysis): Using DMA (Q800, TA Instruments Company, USA) with single cantilever fixture tracks the relaxation process of samples. The frequency is 1 Hz, heating rate is 3 °C/min, amplitude is 20 μm and the sine force is exerted along the LD direction.

SAXS (small-angle X-ray scattering): Small-angle X-ray scattering (SAXS) was used for the study of the lamellar structure. SAXS profile was obtained at Beam line 16 (16B1) in Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 0.124 nm. The

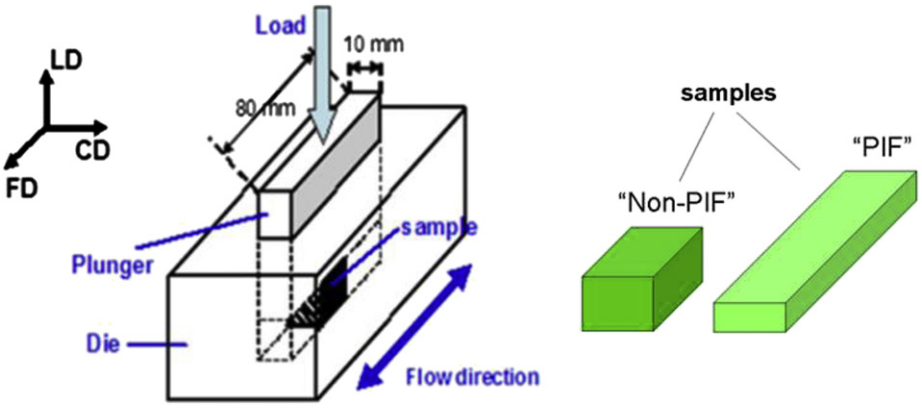

Fig. 1. Left: Scheme of PIF-processing mold, Right: Samples before and after PIF processing.