Polymer Testing 46 (2015) 41–49

Contents lists available at ScienceDirect

Polymer Testing

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

Material properties

Effects of ultrahigh molecular weight polyethylene and mould temperature on morphological evolution of isotactic polypropylene at micro-injection moulding condition

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ARTICLE INFO

Article history:
Received 25 May 2015
Accepted 30 June 2015
Available online 2 July 2015

Keywords:
Effects
Mould temperature
Oriented bundle-like β crystals
Micro-injection moulding

ABSTRACT

The effects of ultrahigh molecular weight polyethylene (UHMWPE) and mould temperature (T_{mould}) on an isotactic polypropylene (iPP) matrix moulded via micro-injection were investigated via polarized light microscopy, scanning electron microscopy, differential scanning calorimetry, wide-angle X-ray diffraction and small-angle X-ray scattering. Results showed that the complex viscosity of the system increased significantly when the UHMWPE content was more than 5%; however, this viscosity decreased when the UHMWPE content was less than 5%. In addition, the addition of UHMWPE increased the onset of crystallisation temperature and the relative crystallinity of the β-form crystals in micro-injection moulded specimens. Moreover, the UHMWPE phase induced the formation of fan-shaped β crystals in iPP/UHMWPE blends. When mould temperature was 50 °C, the degree of orientation of microparts increased and the crystalline structures were highly compact. However, the relative crystallinity of the β-phase form (K_β) was lower than those prepared at 130 °C T_{mould}. Most importantly, well-oriented, bundle-like β crystals have been discovered for the first time in 5 wt.% UHMWPE/iPP blends obtained at 130 °C T_{mould} owing to the "orientation-maintenance" and "shear-amplification" effects of UHMWPE.

1. Introduction

In recent years, there has been a growing demand for microparts and they are playing a substantial role in many fields, such as photoelectric communication, image transfer, biochemistry, medical care, information storage and precision machinery, etc [1–3]. Among the processing methods used to make polymer-based microparts, MIM is the most attractive technology due to its high efficiency, low cost and good precision, etc. Many polymeric microparts, such as micro-heat exchangers, micro-pumps, biochips, optical grating elements, etc., have been successfully fabricated by MIM [4,5]. MIM refers not only to actual reductions in the size of parts but also to the extreme processing environment involved in this process, such as extremely high shear rate, high temperature gradient, high injection pressure and high injection rate (can reach 800 mm/s or higher), etc. This can affect the crystallization behaviour of semicrystalline polymers, that is, the nucleation and growth of crystalline lamellae, resulting in a specific morphology that differs from that of macroparts prepared via conventional injection moulding [6,7].

Researches have shown that under the flow field the crystallization kinetics is accelerated, the nucleation density is increased and oriented crystalline morphologies like shish–kebab structures often develop [8–11]. Except for increasing the shear rate, prolonging the relaxation time of the system can also effectively increase the shear effect and enhance the orientation of the polymer chain. Many reports on flow-induced crystallization have verified that crystallization and orientation can be significantly enhanced by introducing a small amount of long-chain species [12–15]. For instance, two iPP samples with the same number-average (Mn) but different weight-average (Mw) and Z-average (Mz) molecular weight were used by Hsiao and co-workers to investigate the role of high molecular weight species on the evolution of oriented microstructure in iPP melt under shear flow. Their results showed that the iPP sample containing a larger amount of long chain species exhibited higher degree of crystal orientation, higher oriented crystal fraction and faster crystallization kinetics [13].

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http://dx.doi.org/10.1016/j.polymertesting.2015.06.018
0142-9418/

Shear amplification is an important concept that was first proposed by Cakmak et al. to explain the enhanced orientation of injection moulded nylon 6/clay nanocomposite [16]. Considering much higher orientation for the composites than that for pure iPP, Fu et al. verified once again that shear amplification indeed existed in iPP/clay nanocomposites [17]. Li et al. observed an amplification effect of shear on the shear-induced row nuclei and orientation of isotactic polypropylene crystals under the existence of shear flow and nanoparticles [18,19]. Xu et al. [20] found that rich self-reinforced shish-kebab structure could be produced because of shear amplification effect of UHMWPE phase, which significantly facilitated enhancement of mechanical properties of oscillatory shear injection moulded high-density polyethylene blends.

The process of micro-injection moulding is very complex and there are many factors which influence this process, such as: injection speed, injection pressure, melt temperature, mould temperature, etc [21,22]. Different process parameters can affect the crystallization behaviour of semicrystalline polymers, that is, the nucleation and growth of crystalline lamellae, resulting in a specific morphology. Among the main process parameters, mould temperature have much influence on the final micro features of parts [23]. In this study, two different mould temperatures (50 °C and 130 °C) were chosen to study the effect of the mould temperature on the crystalline and oriented morphologies of microparts. Results show that, compared with those obtained at 130 °C T_{mould}, the samples obtained at 50 °C T_{mould} possess higher degree of orientation and more compact crystalline structures, but relatively lower K_β. In addition, in 5 wt.% UHMWPE/iPP blends obtained at 130 °C T_{mould}, well-oriented, bundle-like β crystals have been discovered for the first time.

2. Experimental section

2.1. Materials

A commercially available iPP (tradename T30S, from Dushanzi Petroleum Chemical Co., China) was used. Its weight-averaged molecular mass (Mw) and melt flow index (MFI) are 39.9×10^4 g mol^{-1} and 2.6 g/10 min, respectively. UHMWPE, tradename M-II, Mw = 2.5×10^6 g/cm^3, was provided by Second Auxiliary Factory, Beijing, China.

2.2. Sample preparation

Solution-mixed blends were carried out by dissolving the composition of iPP and UHMWPE in xylene according to the procedure described in Ref. [24]. In brief, the mixture was heated slowly to 140 °C with continuous stirring until the polymer was totally dispersed into the xylene (the solution became transparent). The solution was kept at this temperature for 2 h and then poured into iced methanol. The precipitate was then filtered, washed and dried under vacuum at 770 °C 48 h. The same procedure was also applied to prepare a pure iPP sample.

The dried iPP/UHMWPE granules were melted and injection moulded using a micro-injection moulding machine (Micropower5, Battenfeld Co., Austria) to produce the samples (length 8 mm, width 4 mm, thickness 0.3 mm). The injection speed was 250 mm/s, the holding pressure was 80 MPa and the holding time was 10 s. For comparison, the mould temperature was set to 50 °C and 130 °C, respectively.

Table 1 gives the detailed designations and compositions of samples of pure iPP and the blends. The preparation of specimen for analyses is illustrated in Fig. 1.

Table 1
Interpretation of sample code for the samples of pure iPP and the blends.

Code	Composition
PP0	iPP
PP1	99 wt.% iPP + 1 wt.% UHMWPE
PP3	97 wt.% iPP + 3 wt.% UHMWPE
PP5	95 wt.% iPP + 5 wt.% UHMWPE
PP10	90 wt.% iPP + 10 wt.% UHMWPE

2.3. Dynamic rheology measurements

The dynamic rheology properties of the samples were examined by a rotational rheometer (Malvern Instruments, Bohlin Gemini 200, UK). Disks with a diameter of 25 mm and a thickness of 1.2 mm were prepared by compression molding of the dried pellets at 200 °C and 10 kN for 5 min. A dynamic frequency sweep mode was applied at a shear rate of 0.01–100 s^{-1} at 200 °C.

2.4. Differential scanning calorimetry

The crystallization and melting behaviours of the samples were determined on a TA Q20 differential scanning calorimeter (DSC) in a nitrogen atmosphere. A sample of about 5 mg–8 mg was first heated to 200 °C and held for 5 min with the melting curves recorded. Then, it was cooled to 40 °C at a rate of 10 °C/min to investigate the crystallization behaviour of the sample.

2.5. Polarized light microscopy

Thin slices cut by means of a microtome were used for optical morphology observations by polarized light microscopy (PLM). The sampling zones were located in the middle of samples along the flow direction, as shown in Fig. 1. Morphology observations were conducted using a DX-1 (Jiang Xi Phoenix Optical Co., China) microscope connected to a Nikon 500D digital camera.

2.6. Scanning electronic microscopy

For the scanning electronic microscopy (SEM) observation, the samples were etched for a certain time in a 1.5% w/v solution of potassium permanganate dissolved in mixed sulphuric and phosphoric acids, and then washed with 30% hydrogen peroxide and distilled water. The sampling zone was located in the middle of sample, as shown in Fig. 1. The specimen was gold sputtered before observation.

2.7. Synchrotron two-dimensional wide-angle X-ray diffraction and small-angle X-ray scattering

The synchrotron Two-dimensional Wide-angle X-ray diffraction (2D-WAXD) and Two-dimensional small-angle X-ray scattering (2D-SAXS) experiments were carried out on the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China. The wavelength was 0.124 nm. The two-dimensional diffraction patterns were recorded every 120 s by a Mar CCD 165 X-ray detector system in transmission mode at room temperature. The backgrounds of all the WAXD and SAXS patterns had been extracted. Mar165-CCD was set at 137 mm and 1873 mm sample-detector distance in the direction of the beam for WAXD and SAXS data collections, respectively. The orientation level of various planes could be calculated by the orientation parameter P_2, which was calculated as shown by Equations (1) and (2) [25]: