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Hierarchical structure and unique impact behavior of polypropylene/ethylene-octene copolymer blends as obtained via dynamic packing injection molding

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ABSTRACT

Controlling the hierarchical structure of melt-processed polymers is vital to "structuring" processing and tailoring properties of the product. In this work, polypropylene (PP)/octene-ethylene copolymer (POE) blends were injection-molded using so-called dynamic packing injection technique, which imposed oscillatory shear on the gradually cooled melt during the packing solidification stage. In this way, samples with highly oriented PP matrix and elongated POE particles were obtained. Most interestingly, it was found for the first time that the elongated POE particles could not improve any impact toughness of oriented PP, which is completely different from that for the isotropic ones. Polarized optical microscope, scanning electron microscope, micro-Fourier transform infrared spectroscopy and differential scanning calorimetry were used to characterize the microstructures along sample thickness. The crack-initiation term, impact fractured surface and cross-section of the impact surface were inspected to understand the difference in impact behavior between the oriented PP/POE blends and their isotropic counterparts. The results show that massive crazing or plastic flow of the matrix could not be effectively initiated in the oriented blends. Our work provides a good example for better understanding structure–property relationship of polymers via well controlling their internal hierarchical structure.

1. Introduction

As is well-known, molten-state processing, such as extrusion, injection molding, hot compression and melt spinning, is the most widely-utilized strategy to fabricate polymer-based materials and composites. Controlling of the internal structure of the products is one of the main tasks for polymer processing. Considering the viscoelastic nature of polymer melt, processing temperature and stress field are considered to be two intrinsic factors in determining the structures of material. Much work [1–5] has been done to survey the processing-structure-performance relations with varying processing temperature [1,2,4] or stress field [3,5], and the results are well understood. But in practical, the situation is usually more complex: the coupling of various external fields will significantly affect the formation and evolution of structure/morphology, resulting in a macroscopic hierarchical structure with multi-scale anisotropy frozen in the products [4,6–9]. From a structure-dominating performance point of view, the hierarchical structure with significant variables like chain configuration, crystalline polymorphism, orientation, phase separation behavior should play a vital role in determining the ultimate properties of polymer products, and controlling the hierarchical structure seems key to "structuring" processing and tailoring the properties of polymer-based products.

In order to control the hierarchical structure in processed polymer products, plenty of work [9–12] on polymer processing is correlated to the influences of externally applied fields. By in-situ monitoring the evolution of morphology/structure during processing or precisely revealing the microstructure change along special directions, the roles of processing variables like temperature gradient, shear velocity, stress gradient, strain rate on hierarchical structure can be ascertained and demonstrated clearly [9–12]. The rules concluded from the relevance provide guidance for us to optimize the processing parameters, thus make the hierarchical structure adjustable. However, only qualitative correlations between processing variables and hierarchical structure feature can be established, products dominated by desired microstructures could still hardly be successfully prepared.

Thanks to the fast progress of mechanical technique, a variety of new techniques such as shear controlled orientation injection molding (SCORIM) [13,14], dynamic packing injection molding

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(DPIM) [7,15–17], vibration-assisted injection molding (VAIM) [18], ultrahigh-speed shear processing [19–21], co-extrusion technique [22–26], die/roller-draw [27,28] and solid-state shear pulverization (SSSP) [29–31] technique have been developed, and various external fields such as shear [7,13–17,19–21], extension [27,28], ultrasonic [32] and supercritical fluid field [33,34] can also be nicely introduced into polymer processing to control the hierarchical structure or tailor the microstructures/properties of the materials. On the one hand, special structures and morphologies could be introduced into the materials by directly processing with a specific new technique: Banded spherulites of HDPE could be obtained by gas-assisted injection molding [8]; shish-kebab could be found in polyolefin by SCORIM [13,14] or DPIM [7,17,35]; Interfacial crystallization (hybrid shish-kebab, transcrystalline and shish-calabash) and epitaxial morphology could also be ascertained in some polymer blends [15,16] or fibrous filler strengthened composites [17]. The properties of the above-mentioned materials were reported to be improved significantly. On the other hand, the hierarchical structure could be somehow tailored, namely, the thickness or percentage of a specific layer could be well controlled, or articles dominated by desired microstructures could be prepared. Co-extrusion technique, which enables the fabrication of materials with defined numbers of alternating layers of different compositions [22,23], shows the feasibility. Not only the number of layers, but also the particular flow field and nanoscale confinement crystallization are reported to play an important role on the structures and properties of the material [24–26]. Another good example is a novel bamboo-like bionic structure using iPP containing β-nucleating agent via DPIM [7]. By a combination of oscillatory shear field and the addition of β-nucleating agent, the crystalline morphology changed dramatically in different layers of the DPIM bar. More importantly, the thickness of various layers could be controlled and PP with balanced mechanical properties could be obtained. So controlling the hierarchical structure provides a new pathway to better understand the structure–property relations of polymer-based materials, and, to some extent, represents the advance trend in the polymer processing area.

In this work, DPIM was adopted again to control the internal hierarchical structure of a model PP/POE blend, a typical elastomer-toughened thermoplastic system [36–39]. The main feature of DPIM is that the melt is forced to move repeatedly in a chamber by two pistons moving reversibly with the same frequency after it was injected into the mold. In this way, samples dominated by highly oriented PP matrix and highly elongated POE particles were obtained and investigated comparatively with the isotropic ones. Most interestingly, the elongated POE particles could not improve the impact toughness of oriented PP, while toughness enhancement with a brittle-to-ductile (B–D) transition is found in the isotropic ones. This phenomenon is reported for the first time to the best of our knowledge, and microstructures of both matrix and the rubber domain were systematically investigated and related to the properties. This work provides a good example for better understanding structure–property relationship and toughening mechanism of polymers via well controlling their hierarchical structure.

2. Experimental

2.1. Materials

Isotactic polypropylene (iPP) T30S, with the density of 0.91 g/cm^3 and melt flow index (MFI) of 2.1 g/10 min (200 °C, 2.16 kg), was a commercial product of Dushanzi Co. Ltd, China and adopted as basal resin. Two kinds of POE with different octene contents and roughly the same molecular weight were purchased from Dow Chemical and used as toughening elastomers. Further details on properties and designations of PP and POE are provided in Table 1.

Table 1
Properties and designations of the materials used.

Mark name	Density (g/cm^3)	Octene content	*Mn*	*Mw*/*Mn*	MFI[a] (g/10 min)	Tm (°C)[b]
T30S	0.91	0%	390,000	4.6	2.1	168
8450	0.902	12%	44,400	2	4	98
8400	0.87	24%	43,800	1.96	35	60

[a] MFI of both PP and POE were tested at 200 °C (2.16 kg).
[b] DSC. Measurements were performed at a heating rate of 10 °C/min.

2.2. Sample preparation

Various binary blends were prepared by varying the POE content in iPP matrix, with the POE contents of 0%, 10%, 20%, 30%, 40% and 50%, respectively. Melt blending a pair of polymers was conducted using TSSJ-25 co-rotating twin-screw extruder with the barrel temperature of 200 °C and the screw speed of 110 rpm. To prepare the oriented samples, the blends were molded by dynamic packing injection molding (DPIM), in which oscillatory shear (10 S^{-1}) was imposed on the gradually cooled melt during the packing solidification stage. The detailed experiment procedure has been described in Ref. [35]. For comparison, injection molding under static packing was also carried out by using the same processing parameters but without shear. The processing parameters are listed in Table 2.

The samples obtained by DPIM are called dynamic samples (D), while the samples obtained by static packing injection molding are called static samples (S). The as-obtained blends are labeled according to the POE mark name, weight content of POE and molding condition. For example, 8400-30-D represents the blended sample with 30 wt% 8400 molded by DPIM.

2.3. Characterization and testing

2.3.1. Mechanical tests

The Izod notched impact strength of the specimens was measured with a VJ-40 Izod machine according to ASTM D256-04. The fracture direction is vertical to the flow direction.

2.3.2. Optical microscope (OM) observation

To examine the hierarchical structure of the injection-molded bars, a Leica RM2245 microtome was used to cut a 30-μm slice from the injection-molded bars vertical to the flow direction. The sample slice was placed between two glass slices and then inspected on a Leica DMIP microscope equipped with crossed polarizer. The pictures were recorded with a Canon Power-Shot 550 digital camera.

In order to examine the crack initiation stage, an arrested crack in the specimen was produced with an Izod impact tester. In detail, the pendulum was raised at an angle of 60° from the vertical and then released to hit the specimen. With appropriately chosen

Table 2
Processing parameters in dynamic packing injection molding.

Parameters	Values
Injection pressure	90 MPa
Injection speed	80 cm^3/s
Oscillating packing pressure	4 MPa
Oscillating frequency	1.0 Hz
Holding time	~4 min
Melt temperature	200 °C
Hold temperature	Room temperature (about 25 °C)