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Shear-induced change of phase morphology and tensile property in injection-molded bars of high-density polyethylene/polyoxymethylene blends

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ABSTRACT

It is feasible to control the phase morphology and phase inversion for immiscible polymer blends to manipulate their properties. In this work, the blend of high-density polyethylene (HDPE)/polyoxymethylene (POM) was used as an example, to demonstrate the effect of shear on the phase morphology and resultant mechanical properties in immiscible polymer blends. To do so, a well defined "in-process morphology control" process during injection molding was conducted. That was: after making the blends via melt mixing, the injection-molded bars were prepared via a so-called dynamic packing injection molding equipment to impose a prolonged shearing on the melts during the solidification stage. Phase morphologies and crystal structures of the blends were estimated mainly through scanning electron microscopy, differential scanning calorimetry and 2D wide-angle X-ray scattering, respectively. For in-process morphology controlled samples, co-continuous structures, especially subinclusions inside another continuous phase induced by shear, were observed when the HDPE content was between 30 wt% and 50 wt%, leading to much early occurrence of phase inversion and also the lowest degree of orientation for both HDPE and POM. However, for samples obtained via conventional injection molding, a droplet morphology was always observed with HDPE dispersed in POM as the content of HDPE was up to 30 wt%, but with POM dispersed in HDPE as the content of HDPE was 50 wt%. The performances of injection-molded bars were mainly respect to the phase morphologies for samples obtained via conventional injection molding in which tensile properties continuously decreased with increasing of HDPE content up to 30 wt% and then increased with further increasing of HDPE content. For the in-process morphology controlled samples, the tensile properties depended not only on the phase morphology, but more importantly on the degree of orientation. One observed only a slight decrease of tensile property as the content of HDPE was less than 15 wt%, while an abrupt decrease when the content of HDPE was between 30 wt% and 50 wt%, probably due to the lowest degree of orientation in this composition range.

1. Introduction

Large-scale application of polyoxymethylene (POM) in the automotive and electronic industries has aroused extensive research interest because of great practical and theoretical interest. Researches focus mainly on the thermal degradation [1,2], wear behaviors [3–5] and toughening [6–8] of polyoxymethylene and its blends with other polymers. There are also some in-depth studies on the crystallization behavior and/or phase morphologies of POM as well as its blends [9–11]. As far as polyethylene (PE)/POM blends are concerned, researchers tend to resolve the problems related to the subjects mentioned

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above. Although PE may improve some properties [12–14] (anti-wear and electrical property) and reduce the cost to some extent, the poor miscibility will limit the efficiency and lead to a decrease of other properties. Morphology and crystalline structures of PE/POM blends were seldom reported [15,16], and little direct information was available.

In recent years, the concept of "in-process morphology control" or "melt manipulation" during injection molding has been proposed and intensively developed. A detailed description about that strategy can be seen in a review by Kikuchi et al. [17]. In general, to realize "in-process morphology control", the prolonged oscillating shear field was imposed on the polymer melt during the packing stage of injection molding, resulting in a high orientation of molecular chains and anisotropic morphology. Several advanced injection molding techniques were developed to bring in proper force fields [18–20]. As expected, the structural feature and mechanical properties of the molded bars prepared via "in-process morphology control" processing were rather different from that of those bars via conventional injection molding. Kalay and Kalay [21] observed an interlocking shish-kebab superstructure in the oriented bars of polybutene, while a synergistic increase of toughness and stiffness was achieved in the oriented bars of PP [22].

We have performed extensive experimental work on the controlling of phase morphology of polyolefin blends, such as PP/LLDPE [23], PP/HDPE [24], PP/EPDM [25,26], HDPE/EVA [27] and PP/clay nanocomposites [28], PP/PS [29], HDPE/LLDPE [30], HDPE/inorganic whisker [31], by using the concept of "in-process morphology control", which is realized by our dynamic packing injection molding (DPIM) technique. The super polyolefin blends with high modulus and tensile strength as well as high impact strength has been obtained [23,24,27]. By introducing shear during packing stage of injection molding of HDPE/inorganic whisker composites, a hybrid shish-kebab, with inorganic whisker served as shish and HDPE as kebab was found for the first time in an injection-molded product [31].

In this work, our attention was mainly devoted to investigate the change of phase morphology and resultant tensile properties of the blends of two immiscible polymers, HDPE and POM, under the effect of shear field. For this reason, the samples of HDPE/POM blends were prepared with the aid of dynamic packing injection molding (DPIM), in which the melt was firstly injected into the mold and then forced to move repeatedly in a chamber by two pistons which moved reversibly with the same frequency as the solidification progressively occurred from the skin to the core part in the mold cavity. The complicated phase morphology was analyzed with scanning electron microscopy; the tensile properties were examined by Instron, and the oriented structure was characterized by 2d-WAXD experiment. Our purposes are 2-folds, one is to further investigate the change of phase morphology of immiscible polymer blends under the effect of external shear stress, and the other is to better understand the relationship between the phase morphology and the mechanical properties in immiscible polymer blends of HDPE and POM.

2. Experimental

2.1. Materials

A commercially available HDPE (trade marked as 2911) with melt flow index (MFI) of 20.5 g/10 min (190 °C, 2.16 kg), was supplied by Lanzhou Petrol. Corp., China. The molecular weight (M_w) was 1.2×10^5 g/mol and the density (ρ) was 0.96 g/cm^3, respectively. POM (M90) was a commercial product of Yuntian Chemical Co. Ltd., China. MFI = 9.0 g/10 min (190 °C, 2.16 kg), $M_w = 1.3 \times 10^5$ g/mol, and $\rho = 1.41$ g/cm^3.

2.2. Samples preparation

HDPE and POM were melt compounded together using a TSSJ-25 co-rotating twin-screw extruder with a barrel temperature of 160–195 °C. After pelleting and drying, HDPE/POM blends were injected into a mold with the aid of an SZ100g injection-molding machine with barrel temperature of 190 °C, and then the DPIM technology was applied, whose main feature was to introduce repeated shearing to the cooling melt during the packing stage (for about 3 min) by two pistons that moved reversibly with a same frequency (0.3 Hz). The melt temperature in the hot runner was 195 °C and that in the mold was about 25 °C (ambient temperature). The schematic representation of DIPM can be found elsewhere [32]. The as-obtained samples were labeled according to the weight content of HDPE and molding condition (DPIM was used or not). For example, D30 represents the sample with 30 wt% HDPE molded by DPIM and S30 means the one with 30 wt% HDPE obtained by traditional injection molding. Thereafter, the samples obtained via traditional injection molding are abbreviated as "static samples".

2.3. 2D wide-angel X-ray scattering

The 2D wide-angle X-ray scattering (2D WAXS) experiments were conducted on a SEIFERT (DX-Mo8*0.4s) diffractometer equipped with a 2D Mar345 CCD X-ray detector. The wavelength of the monochromatic X-ray from Mo radiation was 0.071 nm and the sample-to-detector distance was 324 mm. The samples were placed with the orientation (flow direction) perpendicular to the projection beams. The backgrounds of all the 2D WAXS patterns had been extracted thus allowed a qualitative comparison between various samples. Azimuthal scans (0–360°) of 2D WAXS were made for the corresponding lattice planes of HDPE and POM at a step of 1°. The orientation level of various planes could be calculated by the order parameter f,

$$f = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \tag{1}$$

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\phi) \sin\phi \cos^2 \phi d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin\phi d\phi} \tag{2}$$