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Large scale formation of various highly oriented structures in polyethylene/polycarbonate microfibril blends subjected to secondary melt flow

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ABSTRACT

A strong shear flow was imposed on the melt of polycarbonate (PC) microfibril reinforced high density Polyethylene (HDPE) during a secondary melt flow process, i.e. gas assisted injection molding (GAIM). Classic shish-kebabs and typical transcrystallinity were simultaneously observed in the entire thickness of the GAIM HDPE/PC microfibril composites, which were closely related to the strong shear flow that was further amplified and distributed by incorporated PC microfibrils. Interestingly, some nano-sized ultrafine PC microfibril inclined to absorb extended chain bundles to form shish nuclei on its surface first, which subsequently evolved into hybrid shish-kebab superstructures. It was deemed that the induced formation of hybrid shish-kebab superstructures on nano-sized ultrafine PC microfibril was due to the absorbing of extended chain bundles for hybrid shish nuclei with the strong shear flow serving as the driving force. Importantly, large scale formation of these highly oriented crystalline superstructures can bring significant mechanical reinforcement in GAIM HDPE/PC microfibril composite. For GAIM HDPE/PC microfibril composites, its yield strength is increased by 68% and 66%, compared to the GAIM HDPE parts and the common injection molded (CIM) HDPE/PC composites, respectively; meanwhile, the Young's modulus is enhanced by 253% and 17%, compared to the GAIM HDPE parts and the CIM HDPE/PC composites, respectively.

1. Introduction

Flow-induced orientation and subsequent crystallization of semi-crystalline polymer melt are of great importance in the industrial processing (e.g., extrusion, injection molding) of polymers, and has attracted much attention [1,2]. From an industrial viewpoint, shish-kebab structure is very attractive because it can obviously improve the mechanical properties and decrease the permeability of polymer products. Since its first discovery in 1960s, Pennings et al. and Keller et al. had devoted great efforts to elucidate the structure of shish-kebab from stirred solution [3–5] and deformed bulk polymer melt [6,7]. Keller adopted the coil-stretch transition (CST) concept for polymer melt and proposed the existence of a critical orientation molecular weight (M^*) under a particular flow field (shear flow and extensional flow) [8,9]. That is, linear polymer chains having a molecular weight above M^* can remain in the stretched state after flow due to its long relaxation time, while shorter chains relax back to the coiled state due to the corresponding short relaxation time. On the basis of this argument, high molecular weight species, which can remain in the stretched state upon deformation, are mainly responsible for the shish-kebab formation. However, recently, in situ synchrotron radiation small-angle X-ray scattering (SR-SAXS) measurements on extensional flow induced crystallization revealed that the necessary condition for shish formation in PE is the network stretching rather than CST [10]. Even more interestingly, a nanohybrid shish-kebab (NHSK) structure, where inorganic nanofiller, such as carbon nanotube (CNT) and whisker, formed the “shish” while polymer single crystal formed “kebab”, has been reported firstly by Li et al. [11–14], and later by Fu et al. [15,16]. The formation mechanism was ascribed to “size-dependent soft epitaxy”, in which strict lattice matching was not required due to the geometric confinement. Under intense shear condition, the growth of soft-epitaxy can happen on whiskers with a large diameter. Thus, these works open a new way for preparation of high-performance polymer composites in industrial processing.

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For in-situ microfibril reinforcing semicrystalline polymer composites, a lot of researches have found that the mechanical properties such as strength, stiffness, etc., depend on the aspect ration and its distribution as well as microfibril orientation distribution [17–19]. However, little attention is focus on the formation of oriented crystalline superstructures in polymer/in-situ microfibril composites, and the effect the combination of shear flow and the in-situ microfibril with various aspect ratios on the formation of oriented crystalline superstructures has hardly been studied. If oriented crystalline superstructures, such as shish-kebabs, transcrystallinity, a hybrid shish-kebab structure can be formed in polymer/in-situ microfibril composites, in which microfibril can act as shish and induce polymer crystalline lamellas (kebab) to epitaxially grow on the surface of the microfibril, one expects a dramatic enhancement of interfacial interaction and resulting mechanical performance in the microfibril polymer composites.

In current work, polycarbonate (PC) in-situ microfibrils are introduced into high density polyethylene (HDPE) matrix, and PC microfibrils with various diameters (200–700 nm) can be prepared through in situ hot-stretch. On the one hand, PC microfibrils act as nucleating agents for HDPE. On the other hand, a gas-assisted injection molding (GAIM), which imposes large shear stress on polymer melt subjected to the secondary flow, has been particularly played attention [20,21]. Thus, it is expected that introduction of PC microfibrils lead to homogenized and magnified shear field during melt secondary flow stage [22,23], which result in that polymer chains across thickness direction are stretched. In this case most of stretched HDPE chains are probable to retain the highly deformed state due to combined effect of heterogeneous nucleation of PC microfibrils and fast cooling rate of GAIM process. Finally, highly oriented crystalline structures, such as shish-kebab, transcrystallinity or hybrid shish-kebab superstructures, can form across the thickness direction of the HDPE/PC microfibril composites.

To examine the distribution of oriented crystalline superstructures across the thickness direction of the HDPE/PC microfibril composites molded by GAIM, the composites were characterized by scanning electron microscope (SEM) and two-dimensional small-angle X-ray scattering (2D-SAXS). The results indicate that transcrystallinity, hybrid shish-kebab and typical shish-kebab superstructures distribute in the entire thickness direction of GAIM HDPE/PC microfibril composites. In this way, not only skin-core structure is successfully suppressed in the composites, but also highly oriented superstructures are obtained across the thickness of the composites, which remarkably contribute to material performances.

2. Experiment

2.1. Materials

The materials used were PC and HDPE. PC (Mold K1300) with a number-average molecular weight of 2.8–3.2 $\times$ 10^4 g mol^{-1} and a molecular weight distribution index of 2.1, derived from bisphenol A, was from Teijin Chemical Co., Ltd., Japan. HDPE (TR480) was a commercially available resin from Sinopec JinFei petrochemical Co., Ltd. (Shanghai, China). It has a weight-average molecular weight of 1.7 $\times$ 10^5 g/mol and a melt flow rate of 0.14 g/10 min, measured at 190 °C under 2.16 kg. To avoid hydrolysis, PC was dried in a vacuum oven at 100 °C for at least 12 h prior to processing.

2.2. Preparation of PC microfibrills and samples

PC pellets after drying were dry-mixed with HDPE in a fixed weight ratio of 20/80, and then the mixture was blended in an SHJ-20 twin-screw extruder with a temperature profile of 190, 250, 265, and 260 °C from hopper to die. Preparation of PC microfibrills was performed on a single-screw extruder with a slit die with 98 mm width and 1.2 mm thickness. The temperature profile from hopper to die was 180, 240, 255, 260, and 260 °C, respectively. The extrudate was hot-stretched by a take-up device with two pinching rolls to form the PC microfibril. Air knife was used to cool the microfibril blend. Different hot stretched rates (HSR, the ratio of the area of the transverse section of the die to the area of the transverse section of the extrudate) were achieved by altering the speed of the take-up device. In this study, HSR was set as 1.0 and 20.0. After being pelletized, the pellets were molded by both a gas-assisted injection molding (GIAM) and common injection molding (CIM) processing. For GAIM processing, its main feature is to impose to a strong shear field on the polymer melt, and provide a fast cooling rate of polymer, which immensely increase the relaxation time of polymer chains [24]. The temperature profiles of the injection molding machine were 170, 190, 190, and 190 °C from hopper to nozzle. Other processing parameters for GAIM included gas pressure (10.4 MPa), gas delay time (1s) and mold temperature (30 °C). For the sake of briefness, GAIM microfibril blend and GAIM HDPE stand for the samples of HDPE/PC microfibril composite and pure HDPE part prepared by GAIM, while CIM microfibril blend represents the sample of HDPE/PC microfibril molded by CIM.

2.3. SEM observations

To get a clear observation of the crystalline morphology in the injection-molded samples, a small block was cut from the injection-molded samples, and then the block was cryogenically fractured along the flow direction after immersion in liquid nitrogen for 50 min. The smooth fracture surface was etched in a mixed acid solution containing 49.7 wt.% concentrated sulfuric acid (H_2SO_4), 49.7 wt.% concentrated nitric acid (HNO_3) and 0.6 wt.% potassium permanganate ($KMnO_4$) for 6 h to remove the amorphous region of HDPE on the fracture surface under ambient temperature (20 °C). After careful cleaning and drying, the surface was covered with a thin layer of gold and the crystalline morphologies in different zones of the parts were observed by a SEM instrument, JSM-5900LV (JEOL, Japan), operating at 20 kV.

2.4. Differential scanning calorimetry

A different scanning calorimeter (model Q-20, TA Instrumental, USA) was used to investigate crystallization behavior of the materials. Samples of 5.0–7.0 mg were melted at 170 °C for 5 min to eliminate the thermal history and then cooled to 40 °C at a constant rate of 10 °C/min under a nitrogen atmosphere.

2.5. Rheology tests

The viscoelastic properties of neat HDPE, common blend and microfibril blend were examined by a stress-controlled dynamic rheometer AR2000-EX (TA, USA) in a parallel-plate geometry. All samples were compressed into disks with a diameter of 25 mm and a thickness of 1 mm at 190 °C and 10 MPa. The strain and oscillation frequency range were 1.0% and 0.01–100 Hz, respectively.

2.6. 2D SAXS characterization

To characterize the crystalline structure and the orientation in the GAIM samples, 2d-SAXS measurements were performed at room temperature on a Rigaku Denki RAD-B diffraction meter at the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). Wavelength of the monochromatic X-ray from Cu Ka radiation is 0.154 nm. For 2d-SAXS measurements, the sample-to-