Observation of Shear-Induced Hybrid Shish Kebab in the Injection Molded Bars of Linear Polyethylene Containing Inorganic Whiskers

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1. Introduction. Shear-induced orientation and crystallization in polymer melt are extremely important in the industrial processing (e.g., extrusion, injection molding), and has attracted more and more attention.[1−5] The well-documented shish kebab structure is usually a predominant feature of their morphology, when polymers are crystallized from an oriented or strained melt.[6,7] The shish kebab structure in PE has been intensively studied, since it was first reported by Pennings in 1965.[8] Keller and co-workers[9−11] has proposed the coil−stretch theory: the threadlike shish forms when some of the chains undergo a transition from a coiled conformation to a highly elongated state during flow. According to this theory, the longest chains play the key role for shish kebab formation, considering that only chains longer than a threshold chain length M^* undergo the coil−stretch transition under specified flow conditions. As reported by Hsiao and co-workers,[12] the stretched polymer chains longer than M^* could aggregate to form extended chain fibrillar crystals and the remaining coil polymer chains could then crystallize upon the fibrillar crystals in a folded periodic fashion, forming the shish kebab morphology. The extended chain fibrillar crystals are the shishs and the folded lamellae are the kebabs. However, recent work by Kornfield et al.[13] indicated that long chains were not the dominant species in shish although they were important for shish formation. Even more interestingly, a nanohybrid shish kebab (NHSK), where inorganic nanofiller, such as carbon nanotube (CNT), formed the "shish" while polymer single crystal formed the "kebab", has been reported by Li et al., on the studies of PE or nylon-6,6 solution crystallization from a mixture with CNTs.[14−17] The formation mechanism was attributed to "size-dependent soft epitaxy", in which strict lattice matching was not required due to the geometric confinement. However, for larger diameters of the carbon fibers, the geometric confinement was weak, and lattice matching would play a major role and dictate the orientation of the polymer chain.[15]

Whiskers, with large length/diameter ratio, are fiber-shaped single crystals. Owing to their small diameters, whiskers are nearly free of internal defects and yield a strength close to the maximum theoretical value. A lot of works have been done on the preparation of various polymer/inorganic whiskers (such as aluminum borate whisker and potassium titanate whisker) composites.[18−21] And it was found that whiskers could have a much higher specific strength than short glass or carbon fibers and reinforce thermoplastics more effectively.[22−24] Therefore, whiskers are considered to be an attractive alternative to short glass or carbon fibers for reinforcing thermoplastics and have attracted considerable interests of scientists and engineers.[18−24]

In this work, a new type of SiO_2−MgO−CaO whisker (SMCW) and linear polyethylene were melt blended and then subjected to dynamic packing injection molding (DPIM), in which the melt is first injected into the mold and then forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the mold wall to the molding core part. Our interest is to explore the feasibility of the formation of hybrid shish kebab, with whisker serving as the shish and PE crystal forming the kebab, in the injection-molded bars. Since the diameter of whisker is much larger than that of CNT, if successful, our work could provide a new understanding of the formation of shish kebab under effect of shear. More importantly, since the sample was prepared via injection molding instead of solution crystallization, this work could also open a new way for preparation of high-performance polymer composites in industrial processing.

2. Experimental Section. 2.1. Materials. High-density polyethylene (PE) ($M_w = 2.2 \times 10^5$ g/mol), supplied by Yansan Petrochemical Corp., had a MFI of 5 g/10 min and a density of 0.968 g/cm^3. The whisker (SMCW), as shown in Figure 1(parts a and b), was produced in Mianyang Guangda Company (Sichuan, China). It is a kind of light yellow crystal material with a density of 3.0 g/cm^3. Its diameter ranges from 0.2 to 2 μm (mainly from 0.2 to 0.5 μm), and its length is in the range 5−50 μm. Silicohydride KH-500, used as the coupling agent for SMCW treatment, was supplied by Chenguang Research Institute of Chemical Industry (Chengdu, China).

2.2. Modification of SMCW and Preparation of the Sample. SMCW was first treated for 8 min with 10 wt % KH-550 solution in a high-speed mixer (the rotation speed was 800−1000 rpm). After that the mixture was exposed in air for 3−4 h and then was dried at 90 °C for 4 h. The ultimate powder was used as inorganic filler for PE.

PE and the modified SMCW with content of 10 wt % were melt-mixed using a twin screw extruder. The temperature of the extruder was maintained at 150, 190, 190, 200, 200, and 190 °C from hopper to die, and the screw speed was 110 rpm. After pelletization and drying, the PE/SMCW composite was molded through DPIM. Its main feature is to introduce shear to the cooling melt during the packing stage by two pistons that moved reversibly with the same frequency. Shear rate was about 10s^{-1} calculated from the geometry of the mold. The width and thickness of the test samples were about 6.0 and 3.5 mm. The schematic representation of the equipment and the processing parameters have been described.[25] We also carried out injection molding under static packing by using the same processing parameters but without shear for comparison purpose. The sample obtained by DPIM is called dynamic sample, while the sample obtained by static packing injection molding is called static sample. Macroscopically, the main feature of dynamic sample is the shear-induced morphologies with core in the center, oriented zone surrounding the core and the skin layer in the cross-section area of the sample. Static sample usually shows skin-core structure, as viewed in the cross-section area.

2.3. Scanning Electron Microscope (SEM). The specimens were mainly characterized via SEM. They first cryogenically fractured in the direction parallel to flow direction in liquid nitrogen (−170 °C). After the surface was coated with a thin layer of gold, the dispersion of SMCW in PE matrix and its interfacial interaction with PE were examined by an X-650 Hitachi scanning electron-microscope at 20 kV. For the observation of crystal morphology, the specimens were also

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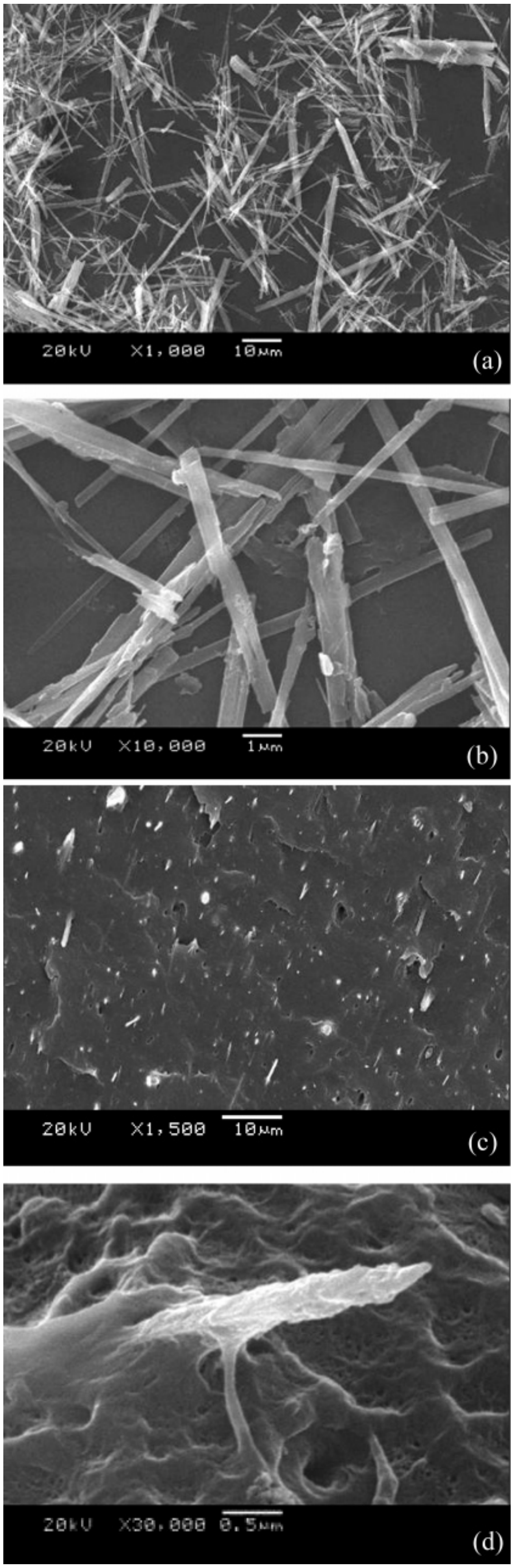

Figure 1. SEM images of SMC whiskers at (a) ×1000 and (b) ×10000 and SEM images to represent the dispersion morphologies of SMC whiskers in as-prepared composites at (c) ×1500 and (d) ×30000.

etched by 1% solution of potassium permanganate in a mixture of sulfuric acid, 85% orthophosphoric acid.[26]

3. Results and Discussion. 3.1. The Dispersion of Whiskers and Interfacial Adhesion in PE/SMCW Composites. It is well-known that the dispersion of a kind of filler in polymer matrix is a key for the enhancement of mechanical properties of polymer composites. A good dispersion can be achieved by surface modification of the filler and appropriate processing conditions. In our work, SEM is employed as an easy and simple method to assess the dispersion of SMCW in PE matrix and its interfacial interaction with PE. To obtain an overall review of the whiskers dispersion, the SEM fractured surfaces (in the direction parallel to flow direction) of PE/SMCW composites are investigated with low magnification, as shown in Figure 1c. From this figure, one observes a good dispersion of SMCW in PE matrix even its content is high as 10 wt %. This can be ascribed to the good interfacial adhesion of SMCW with PE matrix. As is shown in the figure that the interface between PE and whiskers is blurrier and no obvious cavities can be seen. To see clearly the interfacial adhesion between whiskers and the PE matrix, the SEM photograph with high magnification is shown in Figure 1d. One can observe clearly that the SMC whisker is embedded in the matrix and the exposed part of the whisker is attached with a layer of PE matrix, suggesting a really good interfacial interaction between the modified whiskers and PE matrix. In a word, the modified SMCW can be well dispersed in PE matrix and the interfacial adhesion between is strong.

3.2. Hybrid Shish Kebab Structure in PE/SMCW Composites. The detailed crystalline morphology at the interface between the whisker and PE matrix is obtained via etching out the amorphous part of PE. The main feature of our dynamic packing injection-molded PE samples is shish kebab morphology, particularly, in the shear layer.[27] Figure 2 shows the typical crystalline morphology of the injection-molded bar of PE/SMCW composites after being etched. A peculiar transcrystalline-like structure has been observed in the skin layer of the injection-molded bar of PE/SMCW composites. As shown in Figure 2a, one observes that the PE crystal lamellae are arranged perpendicular to the whisker axis periodically only on the up and down two surfaces of the whisker, but no PE crystal lamellae can be found on the viewed surface. The formation of transcrystalline structure in polymer/filler composites has been well documented,[28−33] particularly under the effect of shear.[30,31] This phenomenon can be explained as due to the preferential heterogeneous nucleation at the interface between different components. The prerequisite for transcrystallization is the presence of a high density of active nuclei on the substrate/fiber surface. The closely packed nuclei hinder the full extension of spherulites which are then forced to grow in one direction, namely perpendicular to the substrate/fiber surface.[32,33]

Very interestingly, for the shear layer, as shown in Figure 2b, one observes that the whisker is decorated with disk-shaped objects that are periodically located along the whisker axis. The periodicity of the polymer lamellae varies from 50 to 150 nm. The kebabs are approximately 20−25 nm thick (along whisker direction) with a lateral size of 50 nm to micrometers. These disk-shaped objects are edge-on views of the PE crystal lamellae. This result is in good agreement with Figure 1d, which shows that a layer of PE matrix is decorated on the surface of the whisker. This indicates that the good interfacial adhesion between PE matrix and SMCW can be ascribed to, at least in part, the epitaxy growth of PE crystal lamellae on SMCW. It can be clearly seen that this kind of crystalline morphology is similar to the NHSK structure observed in the PE/CNT and PE/CNF system, as reported by Li et al.[14,15] Here one observes for the first time that in an injection-molded bar of PE/whisker composites, the whisker forms the central fibril (shish) and the PE crystal lamella (kebab) orients perpendicularly to the whisker axis, thus forming the hybrid shish kebab (HSK) structure.

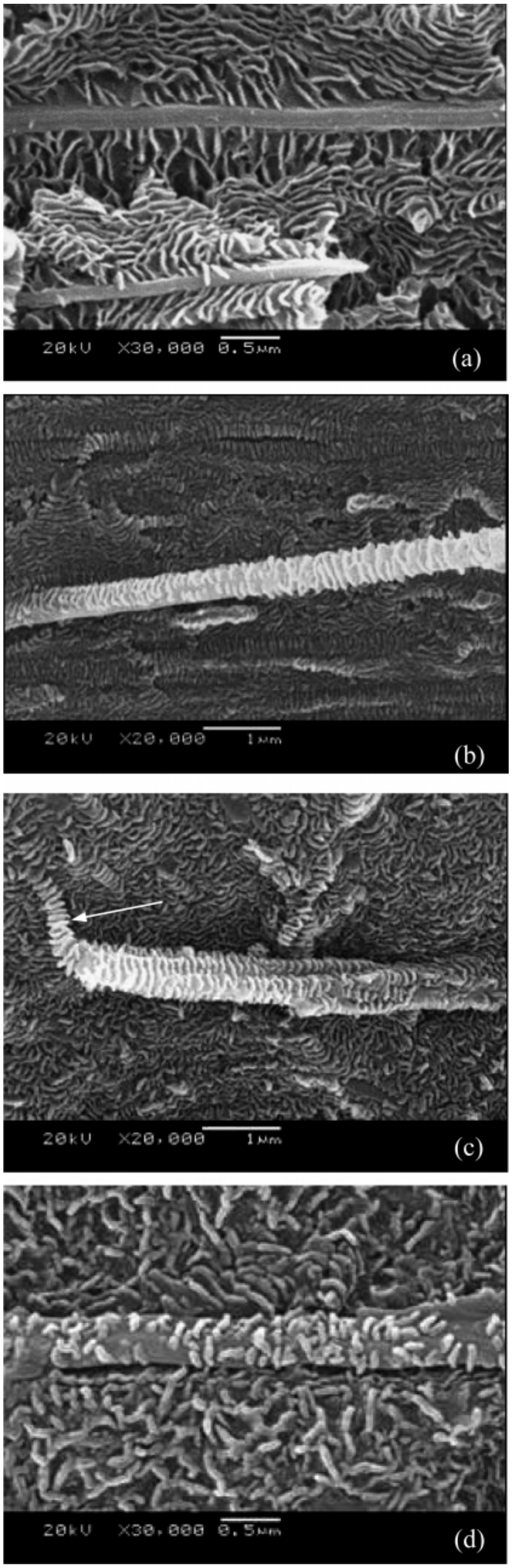

Figure 2. SEM micrographs to represent the crystallization morphology of the PE/SMCW composites along the flow direction. Key: (a) dynamic sample, skin layer; (b) dynamic sample, shear layer; (c) dynamic sample, core layer; (c) static sample, core layer.

Furthermore, it can be observed that the "disk" is composed of several PE crystal lamellar columns instead of one whole circular PE crystal lamellar column, which is different from the case in the PE/CNT system. This may be ascribed to the much larger diameter of SMCW (200−500 nm) than that of CNT (10-25 nm). More evidence of the HSK structure can be also found in the core layer of the dynamic sample, as shown in Figure 2c. The multidisk columns of PE lamellae are seen to be located on the whisker surface and oriented (kebab) perpendicularly to the whisker axis. Here one also observes a bending of the shish kebab at the end of the whisker, similar to that reported by Petermann[34] in a study of shish kebab growth in an oriented thin film of iPS, and can be called as self-supported growth process. In the case of oriented thin film of iPS, iPS forms the shish, and its molecular chains are flexible and thus can be bended. In our case, SMCW forms the shish, and it is rigid and thus cannot be bended. One observes that at the end of SMCW, the kebab of PE continues to grow without SMCW serving as a shish. If it is the case, this could be the first evidence that kebab grows without shish. This observation might be due to the resolution of the instrument or due to the coverage of a layer of polymers on the shish etc., and a detailed characterization is ongoing in our group.

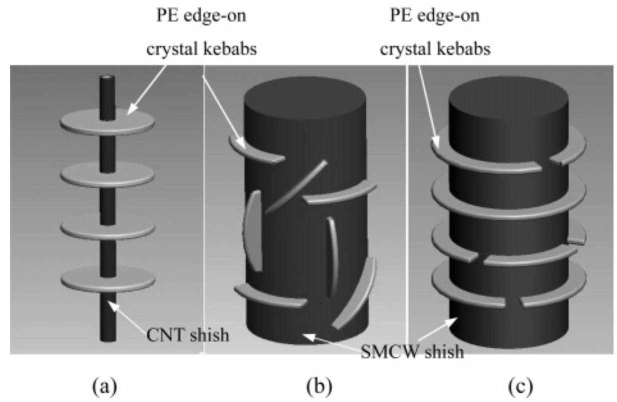

Figure 3. Schematic representation: (a) NHSK structure observed in PE/CNT solution; (b) and (c) HSK structure observed in our static sample and dynamic sample of PE/SMCW composites.

The change of crystal morphology from transcrystallization at the skin to the hybrid shish kebab up to the center of the injection-molded bar may be related to the temperature and shear stress gradient along the sample thickness, and worth to be further investigated. To see the importance of oscillatory shear function on the formation of HSK structure, the crystal morphology of the static sample (without shear) is examined, and this is shown in Figure 2d. Although in this case the surface of the whisker is also decorated with a great deal of PE crystal lamellae, the PE crystal lamellae are not oriented perpendicular to the whisker axis, but randomly distributed on the surface of the whisker. This result suggests the importance of shear on the formation of hybrid shish kebab structure, particularly for the filler with a large diameter.

3.3. The Mechanism of Shear-Induced HSK Structure. The schematic representation of the NHSK structure observed in PE/CNT solution reported by Li et al.[14,15] and HSK structure observed in our dynamic sample of PE/SMCW composites is shown in Figure 3. For the NHSK structure, as shown in Figure 3a, the CNT formed the "shish" and the single "disk-shaped" PE crystal lamellar (kebab) periodically grew on the CNT. In the formation of this NHSK structure, shear was not introduced, because the CNT provided a 1D nucleation surface. The formation mechanism of NHSK structure was considered as the "soft epitaxy". Because of the small diameters, CNTs themselves can be considered as rigid macromolecules and PE chains might prefer to align along the tube axis regardless of the lattice matching. In our case, the HSK morphology is rather different and the size of the “shish” (SMCW) is much larger, as shown in Figure 2b and Figure 2c. For dynamic sample, the kebabs are formed by several PE crystal lamellae that are decorated on the surface of SMCW and are aligned perpendicular to the whisker axis, as can be seen in Figure 2b. However, one can only observe SMCW with randomly decorated PE crystal lamellae in static sample: the lamellar normal is parallel, perpendicular, or oblique to the SMCW axis, as shown in Figure 2d. As for the formation mechanism of HSK structure, we presume that strict lattice matching and epitaxy should be the main growth mechanism due to the much larger size of the whiskers. After treated by silicon coupling agent(KH-550), SMCW could have a strong interfacial interaction with PE, as indicated by SEM(Figure 1d). With a diameter of 200-500 nm, SMCW can provide 3D nucleation surface. The epitaxial growth of PE crystals on such surface of SMCW could lead to different orientations of the PE lamellar normal, as observed in the core layer of the static sample, as shown in Figure 3b. Nevertheless, this situation changes with the presence of shear stress, because the PE molecular chains can be oriented in the direction parallel to the shear flow direction under the prolonged shear stress. This leads to the formation of HSK structure with PE crystal lamella (kebab) perpendicular to the whisker (shish), as shown in Figure 3c. The effect of shear could be considered as to adding more active nucleation sites on whisker surface thus weakening the requirement of lattice matching, resulting in the growth of so-called soft-epitaxy on much larger diameter of whisker.

4. Conclusion. In this work, a new type of whisker and a linear PE were melt blended and then subjected to dynamic packing injection molding. A hybrid shish kebab structure, with PE crystal lamellae periodically decorated on the surface of SMCW and aligned approximately perpendicular to the long axis of the whiskers, has been observed for the first time in the injection-molded bar of PE/SMCW composites. The effect of shear could be considered as to adding more active nucleation sites on whisker surface thus weakening the requirement of lattice matching, resulting in a growth of so-called soft-epitaxy on much larger diameter of whisker. Our work provides a new understanding of the formation of shish kebab under effect of shear. More importantly, since the sample was prepared via injection molding, this work could also open a new way for preparation of high-performance polymer composites with hybrid shish kebab structure in industrial processing.

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