Influence of Diameter on the Templated Crystallization of Polyethylene/Carbon Material Fiber Composites under Intense Shear Flow

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ABSTRACT: In this study, carbon fibers (CFs) and carbon nanofibers (CNFs) were introduced into polyethylene (PE) and intensive shear flow was imposed on the melt during the melt second flow caused by gas penetrating the melt during the gas-assisted injection molding (GAIM). The effect of fiber diameter on crystalline morphologies of obtained composites was deeply studied. The results revealed the fact that no matter whether CFs or CNFs were introduced into the PE matrix or not, the orientation degree of PE lamellae would increase during the melt second flow. Hybrid shish-kebab structures were difficult to be formed in GAIM CF/PE composites and only a few oriented PE lamellae overgrew on the local surface of CFs. However for GAIM CNF/PE composites, the formation of hybrid shish-kebab structures was clearly observed in the entire thickness. The structural diversity was mainly ascribed to the difference of CF diameter, showing obvious size-dependent effect.

1. INTRODUCTION

In all the polymer composite material systems, the interfacial adhesion between the polymer matrix and the embedded fibers is the key to building high-performance polymer-based composites.1−7 A common method to enhance the interfacial bonding is the surface functionalization of inorganic fibers. Current strategies to decorate the surface of inorganic fibers mainly include oxidation treatment,3 grafting-to,4 grafting-from,5 and so on. However, to a certain extent, these methods would destroy the surface structure of inorganic fibers and be adverse to the entire properties of composites.

It is well known that interfacial crystalline morphology has a significant influence on the interfacial adhesion between the polymer matrix and fibers.6 Inorganic fibers are apt to attract molecular chains and template the growth of polymer crystals. By using different crystalline ways, a connection between the polymer lamellae and fiber surface can be established, leading to the development of new crystalline morphology. A fascinating morphology is the “hybrid shish-kebab” (NHSK) structure reported by Li et al.,7 in which certain semicrystalline polymers such as polyethylene (PE), polyvinylidene fluoride, and nylon-6,6 (PA66) formed periodic, dis-shaped crystal on the surface of carbon nanotubes (CNTs).8,9 Therewith, the structure was constructed with the aid of supercritical CO2 instead of solution crystallization.10−12 Fu et al. found that a rough surface of NHSK could greatly promote the interfacial interaction between CNTs and polymer matrix.13 On the basis of this, the control of interfacial crystalline morphology is regarded as a noncovalent method to improve the interfacial adhesion between the polymer matrix and fibers.

The formation mechanism of hybrid shish-kebab structure was studied by Li et al.,14 and they proposed a “size-dependent soft epitaxy” theory. As described by this theory, CNTs could be considered as rigid macromolecules because of the small diameter, thereby, geometric confinement was the major factor when polymer chains started to crystallize on the surface and these polymer chains preferred to align along the long axis of CNTs regardless of the lattice matching. However, the diameter of carbon nanofibers (CNFs) was much larger than Rg of a typical polymer chain, as a result, polymer behaved as though it was on a flat surface. Because a variety of graphic sheet orientations exist for CNFs, epitaxial growth of the
polymer crystals would lead to different orientations of the polymer chains/lamellar normal, which abided by the strict lattice matching. Based on the study of Li et al., we are inspired to explore whether larger diameter fibers can also induce the hybrid shish-kebab structure following the “size-dependent soft epitaxy” mechanism under an intense shear field and if there exists a critical diameter to form the hybrid shish-kebab structure.

In our previous studies, the hybrid shish-kebab structure was formed massively in the entire thickness by the incorporation of CNFs, where CNFs acted as the stable “shish” and PE lamellae periodically decorated on its surface. In the melt second flow process, an intense shear caused by gas penetration was imposed on the melt and drove PE chains to stretch or orient along the CNF axis, which largely reduced the configurational and/or conformational entropy of the polymer before the extended chains deposited on the fiber surface. In this case, the entropy penalty of extended PE chains adsorbed on the CNF surface was much less than the random chains deposited on the surface because of the effect of shear flow. Even though the van der Waals interaction between the polymer and CNF surface was weak, the extended PE chains could successfully be adsorbed on the CNF surface because of the vast decrease of the entropy penalty to form a polymer underlayer crystal. Subsequently, a subglobule was formed and it acted as the crystal nucleus. Finally, other oriented PE chains began to epitaxially grow from the subglobules in the form of folded chains to reduce the polymer surface energy and form kebabs perpendicular to the CNF axis, complying with the “soft epitaxy” crystallization mechanism regardless of the strict lattice match. This study encourages us to further study whether the fiber with larger diameter, such as carbon fibers (CFs), can also induce the hybrid shish-kebab structure.

In this paper, two kinds of CFs with quite different diameters were introduced into the PE matrix to further explore the effect of fiber diameter on the formation of hybrid structures under the intense shear. To clearly observe the crystalline morphologies and distribution of oriented crystalline structures across the thickness direction of gas-assisted injection molding (GAIM) CFs/PE composites, the composites were characterized by a scanning electron microscope and two-dimensional small-angle X-ray scattering (2D-SAXS).

2. RESULTS AND DISCUSSION

2.1. Phase Morphologies of CF/PE and CNF/PE Composites. For fiber-reinforced polymer composites, the dispersion of fibers in the polymer matrix has a great importance for the properties and the uniform dispersion of fibers is the prerequisite to further study the relationship between the structure and performance of composites. In general, fibers possess large aspect ratio and strong van der Waals forces, as a result, they are easily to agglomerate and the uniform dispersion is difficult to be achieved. However, it can be clearly observed in our study (Figure 1) that both CFs and CNFs were uniformly dispersed in the PE matrix and no agglomerates presented in the whole observing area. This result indicated that solution premixing was conducive to the good dispersion of CNFs and CFs in the PE matrix.

2.2. Nonisothermal Crystallization of Neat PE, CF/PE, and CNF/PE Composites. As shown in Figure 2, the onset crystallization temperature \( (T_c) \) of neat PE was about 116.4 °C, whereas it increased to 117.3 and 122.7 °C for CF/PE and CNF/PE composites, respectively, which indicated that the crystallization ability of PE was improved after adding CFs and CNFs. The improvement of crystallization ability was resulted from the heterogeneous nucleating effect of CFs and CNFs. However, it should be noticed that the heterogeneous nucleating ability of CNFs was more remarkable for PE crystallization compared with CFs. This was mainly ascribed to the fact that CNFs possessed a larger specific surface area and it resulted in high-density active sites of heterogeneous
nucleation. Besides, CNFs with higher surface energy contributed to stronger interfacial interaction between the fiber and surrounding polymer matrix than CFs with a low surface energy. In addition, the nucleating effect could be further enhanced under the shear field because of the shear-induced crystallization.

2.3. Relaxation Behavior of Neat PE, CF/PE, and CNF/PE Composites. The relaxation behavior of PE and composites is characterized by the continuous relaxation spectrum which is obtained by ARES software. The nonlinear regularization program developed by Weese and Honerkamp is used.\textsuperscript{16,17} Figure 3 exhibits the continuous relaxation spectra of the PE and composites. The value of corresponding maximum peak reflects the approximating relaxation behavior of the system. By comparison with neat PE, there was an obvious increase of the relaxation time after the addition of CFs and CNFs and the relaxation time of CNF/PE composites presented the highest value. The existence of fibers could hinder the relaxation of stretched polymer chains, leading to the increase of relaxation time. Compared with CFs, the interaction between CNFs and polymer was stronger because of its much smaller diameter, which could provide more effective inhibiting effect on the relaxation of stretched polymer chains. As a consequence, it was difficult for the stretched PE chains, caused by the intense shear during the melt second flow, to relax into the random coil in the CNF/PE composite, and then more stretched PE chains would be preserved in the cooling stage to form a large number of oriented crystalline structures.

2.4. Crystalline Morphologies of GAIM CF/PE and CNF/PE Composites. To better exhibit the crystalline morphologies of GAIM composites subjected to the melt second flow, the amorphous phase of PE was selectively extracted and the crystalline morphologies along the thickness of GAIM samples were studied by scanning electron microscopy (SEM). It can be seen in Figure 4 that CFs were parallel to the flow direction, whereas the PE crystal lamellae were orientated in the direction perpendicular to the flow direction. These morphologies were ascribed to the effect of intense shear field caused by the melt second flow. In previous studies,\textsuperscript{16,19} highly oriented crystal morphologies could be observed only at a depth of about 500 μm to the outmost surface of the GAIM samples. However, the scale of the highly oriented crystal morphologies was greatly broadened in this study by the introduction of fibers, and these morphologies were even formed in the gas channel layer (Figure 4c). It can be also observed that the degree of orientation and regularity of PE lamellae was the highest in the subskin layer (Figure 4b) and it decreased in areas close to the gas channel layer (Figure 4c), through careful observation, a distinct interspace between CFs and PE lamellae could be found (shown as the insets in Figure 4) and only a small amount of PE lamellae overgrew on the local surface of CFs.

For GAIM CNF/PE composites, as shown in Figure 5, hybrid shish-kebab structures can be clearly observed in the entire thickness direction. Significantly, the long axis of CNFs was parallel to the melt flow direction, and the PE crystal lamellae was decorated on the surface of CNFs and perpendicular to the axis of CNFs, indicating a strong epitaxial growth of PE chains on the surface of CNFs under intense shear effect. Combined with aforementioned results, it was reasonable to conclude the formation process of hybrid shish-kebab structure as the following steps. First, the stretched PE chain bundles around CNFs were adsorbed on the surface to form a polymer underlayer and this layer could subsequently induce the folded PE chains to overgrow on the surface and finally evolve into the hybrid shish-kebab structure.

From the discussion above, it can be known that the complete hybrid shish-kebab structure could be formed only when small-diameter fillers (CNFs) were introduced. In the case of CF with much bigger diameter, only some local hybrid crystal structures were induced. In addition, the oriented PE lamellae in GAIM CNF/PE composites were closely stacked in the entire cross-section and they were more compact and regular than GAIM CF/PE composites. These visible distinctions resulted from the difference in the diameter of incorporated CFs. Under this consideration, we proposed that the formation of hybrid shish-kebab structure abide by size-dependent effect.

2.5. Orientation and Distribution of the Crystalline Structures for GAIM CF/PE and CNF/PE Composites. 2D-SAXS measurement was employed to study the oriented crystalline structures and their distribution along the thickness direction of injection molding parts. As shown in Figure 6, for GAIM CF/PE composites, two sharp triangular streaks in the equatorial direction were observed from the skin layer to the

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**Figure 3.** $H(\tau)$ vs $\tau$ for the characterization time of PE, CF/PE, and CNF/PE composites.

**Figure 4.** Crystalline morphologies of GAIM CF/PE composites in different parts: (a) skin layer; (b) subskin layer; (c) gas channel layer. The flow direction is vertical.
gas channel layer, indicating the fiber aligned along the melt flow direction. Besides, two-spot pattern in the meridional direction appeared in all the different zones of CF/PE composites and this demonstrated that the oriented PE lamellae was perpendicular to the shear flow direction. For GAIM CNF/PE composites, two sharp triangular streaks in the equatorial direction and the two-spot pattern in the meridional direction can be simultaneously observed in all the zones, which can further confirm that the extended PE chains were adsorbed on the CNF surface and then these folded PE chains crystallized to kebabs perpendicular to the fiber axis. In other words, the highly oriented crystalline structures distributed across the entire thickness of GAIM CNF/PE composites. It can be also clearly seen in Figure 6 that the scattering signals of 2D-SAXS patterns of GAIM CNF/PE composites were more intense than that of GAIM CF/PE composites in all the different zones. This result is well in accordance with the above SEM results.

To further quantitatively study the highly oriented crystalline structures of GAIM samples, the azimuthal scans of 2D-SAXS patterns and the orientation parameter were investigated. As presented in Figure 7a,b, the intensity peaks integrated from the equatorial scattering signal were very high in all the zones from the skin layer to gas channel layer for both GAIM CF/PE and CNF/PE composites, indicating the highly oriented crystalline structures were distributed in the entire thickness direction. Additionally, the subskin layers exhibited relatively stronger scattering peak compared to other zones in both GAIM CF/PE and CNF/PE composites. This was because the largest shear and fast melt cooling rate were generated in the subskin layer. To determine the distribution of oriented crystal lamellae, the degree of crystal orientation in different layers of GAIM CF/PE and CNF/PE composites was calculated by Herman’s orientation function quantitatively, and the results are displayed in Figure 8. It was found that all the layers in these two composites showed high oriented degree, indicating that highly oriented structures were formed in the whole layers. Furthermore, in comparison with GAIM CF/PE composites, the value of orientation degree at each layer of GAIM CNF/PE composites was higher. Apparently, these results demonstrate that the introduction of CNFs was more efficient than CFs for the formation of highly oriented
crystalline structures. The distribution angle of both CFs and CNFs was further calculated by the butterfly pattern of 2D-SAXS. The distribution angle of both CFs and CNFs is ranged from $-40^\circ$ to $40^\circ$, and the most of fibers are within range from $-20^\circ$ to $20^\circ$, in which the angle of shear flow direction is set as $0^\circ$.

Figure 9a presents the one-dimensional scattering intensity distribution profiles of GAIM CF/PE and CNF/PE composites. The scattering peaks shifted to smaller $q$ from the skin layer to gas channel layer for both composites, indicating the increase of long spacing. The resultant correlation functions were presented as a function of the different layers and the inset expressed how the average thickness of the amorphous layers $d_a$ and long spacing $d_{ff}$ were derived by the correlation function. The value of long spacing ($d_{ff}$), the thickness of lamellae ($d_c$), and the thickness of amorphous layer ($d_a$) are listed in Figure 10. Apparently, all fibers (CNFs) induced the polymer chains to overgrow on the surface to form the hybrid shish-kebab structure in solution crystallization under the static state, where epitaxial nuclei were formed directly on the substrate. This process follow the principle of strict lattice match and epitaxy. However, it has been reported in our previous study that the CNFs would be coated by a homogeneous polymer underlayer prior to the periodical PE lamellae overgrowth on the surface of CNFs. The homogenous polymer underlayer acted as a key role in the formation of hybrid shish-kebab structures and nucleation in epitaxial growth abides by the two-dimensional mode.

In this study, it can be confirmed that the introduction of CNFs inducing PE crystallization to form the complete hybrid shish-kebab structure in the entire thickness direction of GAIM CNF/PE composites. Although for GAIM CF/PE composites, only a few local hybrid structures were formed on the surface of CFs. Through careful analysis, it can be speculated that the main reason for the difference in crystalline morphologies was originated from diameter diversity of the CFs, in other words, the formation of hybrid shish-kebab depended on fiber size, showing significant size-dependence. To better understand the formation of the hybrid structures, a schematic representation was presented in Figure 11. During the melt second flow, an intense shear acting as assistant driving force was imposed on the melt to make random coil PE chains stretch or orient along the fiber axis, which was equivalent to improve the ordered degree and meanwhile reduced the entropy of PE chains. As a result, the entropy penalty of subsequent oriented PE chains deposited on the fiber surface decreased drastically and could be overcome even by the weak van der Waals interaction to achieve the adsorption. Additionally, because of the effective improvement of relaxation time by incorporation of fibers, it was difficult for many oriented PE chains to relax at the following cooling and crystallization stage. Subsequently, the neighboring oriented PE chains were adsorbed on the fiber surface to form a polymer underlayer. For the CNFs, it possessed high-density active sites of heterogeneous nucleation and high surface energy because of their small diameter. Therefore, CNFs had a stronger van der Waals interaction with the PE matrix and could adsorb the surrounding oriented chains on the surface to form a homogeneous polymer underlayer. Subsequently, a subglobule appeared and acted as the crystal nucleus. Finally, other oriented PE chains began to epitaxially grow from the subglobules in the form of folded chains to decrease the total interfacial energy and grew perpendicular to the CNF axis, complying with the "soft epitaxy" mechanism regardless of the lattice match. Resultantly, a hybrid shish-kebab structure was formed, where the fiber aligned along the flow direction and the periodical PE kebabs
were perpendicular to the CNF axis. Although for CFs, because of its large diameter, the van der Waals interaction between the CF surface and polymer chains was too weak to make the oriented chains adsorbed on the surface even if the entropy penalty was dramatically reduced. Nevertheless, because of the energetically heterogeneous of CFs, there was a high surface energy of local surface enough to achieve the adsorption to form a local polymer underlayer and then the folded PE chains overgrew on the surface to form the local hybrid structure.

In summary, CNFs and CFs induced the PE chains epitaxial crystallization to form different hybrid structures in the entire thickness direction of GAIM composites and the crystalline structure formation has a size-dependence. Besides, we believed that there was a critical diameter of CF for the formation of the hybrid shish-kebab structure and this specific diameter will be deeply explored in the subsequent research.

3. CONCLUSIONS
In this study, it was found that the introduction of either CFs or CNFs could significantly increase the orientation degree of crystal structures subjected to the melt second flow. However, the oriented crystal structures presented an obvious difference in composites with various diameters of CFs. CNFs can efficiently induce PE epitaxial crystallization on its surface to form a hybrid shish-kebab structure; nevertheless, only some local hybrid structures could be formed in the presence of CFs. Based upon serious analysis, we suggested that the structural diversity resulted from the difference of CF diameter, namely, the formation of crystalline structure has a size-dependent characteristic. During the melt second flow, the intense shear drove PE chains to stretch or orient along the fiber axis, which drastically reduced the entropy of the polymer. Then, a low entropy penalty of oriented PE chains deposited on the fiber surface and it acted as a main role in determining the polymer–surface interaction. Meanwhile, the van der Waals interaction between the polymer and the fibers also played a crucial function to adsorb the polymer chains on the fiber surface. Therefore, CNFs could adsorb the neighboring oriented PE chains on its surface to form a homogeneous polymer underlayer because of the synergistic effect of the entropy penalty decrease and the van der Waals interaction. Subsequently, the folded PE chains epitaxially grew to form the subglobules on the surface and finally formed the hybrid shish-kebab structure. While, because of the large diameter of CFs, the van der Waals interaction between the CF surface and polymer chains was too weak to adsorb the oriented chains on its surface even with a low entropy penalty. However, because of the energetically heterogeneous of CFs, there was a local surface with a high surface energy to adsorb the oriented chains and then the folded PE chains overgrew on the local surface to form the local hybrid crystal structure. Furthermore, we propose that there was a critical size of fiber diameter for the formation of the hybrid shish-kebab structure.

Through this study, massive highly oriented crystal structures were obtained in all regions of CFs reinforced PE composites subjected to the melt second flow. More importantly, the effect of different diameters of CFs on the formation of the hybrid crystal structures was deeply explored, which can provide some guidance for the preparation of high-performance polymer composites in industrial processing.

4. EXPERIMENT SECTION
4.1. Materials. A commercial HDPE (6098) was produced by Qilu Petrochemical Co., China. It has a weight-average molecular weight of 5.09 × 10^5 g/mol and a melt flow rate of 0.1 g/10 min (190 °C/2.16 kg, ASTM D1238), and the value of molecular weight distribution is 8.2. CNF, Pyrograf-III, was obtained from Applied Sciences, Inc. (Cedarville, OH). CF (T300) was purchased from Toray, Japan. Figure 12 shows the
morphologies of CFs and CNFs, it can be clearly observed that the surface of CFs exists apparent longitudinal streaks and the surface of CNF is fairly smooth. Additionally, the diameter, surface roughness, and surface energy of the fibers are listed in Table 1.

| materials | diameter (nm) | length (μm) | surface roughness (nm) | surface energy (mJ/m²) |
|-----------|--------------|-------------|------------------------|------------------------|
| CNF       | 100          | 200         | 10                     | 94.7                   |
| CF        | 7000         | 1000        | 98.8                   | 48.8                   |

4.2. Sample Preparation. In order to uniformly disperse CFs in the PE matrix, solution mixing method was employed. First, a certain amount of CNFs and CFs was, respectively, dissolved in n-butanol, and then treated for 30 min by ultrasonication. At the same time, a given mass of PE was dissolved in xylene (145 °C). Subsequently, the dispersed CNF and CF solutions were mixed adequately with PE solution, and then removed the solvent via vacuum suction filtration. After drying, the obtained blends were further mixed with PE (the content of CFs is 5 wt %) in a torque rheometer (XSS-300, Shanghai, China) at 200 °C. After being pelletized, the pellets were molded by GAIM. During the processing of GAIM, short shot melt (vol. 70%) was pushed and penetrated by high pressure gas (nitrogen). During the processing, a strong shear field was imposed on the polymer melt, and flow of the high pressure gas could increase a cooling rate of polymer, which were in favor of the orientation of polymer molecular chains and could hinder the relaxation of oriented molecular chains. The temperature profiles of the injection molding machine were 170, 190, 200, and 200 °C from the hopper to nozzle, and other processing parameters for GAIM included gas delay time (1 s), gas pressure (10 MPa), and mold temperature (30 °C).

4.3. Measurements. 4.3.1. Scanning Electron Microscopy Observations. Selective etching was employed as an appropriate technique to get a clear observation of the crystalline morphology in GAIM samples. Before etching, a small block was cut from the middle part of the sample and then cryo-fractured along the flow direction after immersion in liquid nitrogen for 1 h. The smooth fracture surface was etched in a mixed acid solution containing 49.7 wt % concentrated sulfuric acid (H₂SO₄), 49.7 wt % concentrated nitric acid (HNO₃), and 0.6 wt % potassium permanganate (KMnO₄) for 3–4 h to remove the amorphous region of PE. After careful cleaning and drying, the surface was covered with a thin layer of gold and the crystalline morphologies in different scanning calorimeter measurements. A different scanning calorimeter (model Q-20, TA Instruments, USA) was used to investigate the crystallization behavior of the materials. Samples of 5.0–7.0 mg were heated from 40 to 190 °C at 40 °C/min, maintained the temperature 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 to prevent thermal degradation.

4.3.3. Rheological Instrument Measurements. The viscoelastic properties of neat PE, CF/PE, and CNF/PE composites were examined by a stress-controlled dynamic rheometer AR2000-EX (TA, USA) in a parallel-plate geometry. All the samples for rheological measurements were compression molded to disks with a diameter of 25 mm and a thickness of 1 mm at 190 °C and 10 MPa. Then, frequency sweep was conducted in an oscillation frequency range from 0.01 to 100 Hz at 200 °C and the applied strain was 1% (in the linear viscoelastic region of the composite melts). Creep testing was performed under the shear stress of 10 Pa at 200 °C. The measurement would stop when the strain is greater than 40% for ensuring the test was in the LVE zone. To minimize the thermal degradation of the matrix, all the rheological experiments were conducted in a nitrogen atmosphere and a new sample was used for each run.

4.3.4. 2D-SAXS Measurements. To characterize the crystalline structures and the orientation in GAIM composites, 2D-SAXS measurements were implemented at room temperature on a Rigaku Denki RAD-B diffraction meter at the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The sample-to-detector distance was held at 1960 mm, and wavelength of the monochromatic X-ray from Cu Kα radiation is 0.124 nm. Samples were placed with the orientation (flow direction) perpendicular to the projection beams. 2D-SAXS images were recorded through MAR165 CCD, and the data were processed by FIT2D software. The orientation parameter of PE crystals was calculated by the Herman’s orientation, which is defined as.

\[ f = (3 \cos^2 \phi - 1)/2 \tag{1} \]

where \( \cos^2 \phi \) is the orientation factor defined as

\[ \cos^2 \phi = \int_{0}^{\pi/2} I(\phi) \cos \phi \sin \phi \, d\phi / \int_{0}^{\pi/2} I(\phi) \sin \phi \, d\phi \tag{2} \]

where \( I(\phi) \) is the scattering intensity at \( \phi \) which is the angle between the normal of a given (hk0) crystal plane and the shear flow direction. For our samples, the orientation parameter was calculated mathematically using Picken’s method.²⁴

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Notes
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