Role of Melt Plasticizing Temperature in Morphology and Properties of PE100 Pipes Prepared by a Rotational Shear System

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ABSTRACT: To increase the maximum internal pressure that a polyethylene (PE) pipe can withstand, a novel rotational shear system (RSS) was constructed in this study to fabricate PE pipes with enhanced hoop strength by applying hoop shear on the pipes using a rotational mandrel. The microstructure and morphology with the influences of melt plasticizing temperature on PE pipes processing under rotational shear were investigated indirectly using small-angle X-ray scattering and wide-angle X-ray diffraction (SAXS/WAXD) measurements. In the SAXS patterns, equatorial streaks and meridional scattering peaks were clearly observed in all three samples prepared at different melt plasticizing temperatures, 215, 235, and 255 °C. Their presence indicated that shish−kebab crystals form in rotational shear. Compared to those at the low melt temperature, the increase in the melt temperature enhanced the amount and the dimensions of shish formed. However, the shish also relaxed faster at the high melt temperature. This behavior was attributed to the enhancement of the molecular chain’s athletic ability. The hoop tensile strength and the heat resistance of the pipes peaked at the melt plasticizing temperature of 235 °C, 75.2 MPa, 102.4 °C, up 1 MPa, 0.2 °C (compared to the 215 °C) and 7.8 MPa, 3.2 °C (compared to the 255 °C). The axial strength increased with an increase of melt plasticizing temperature. However, the increase of melt plasticizing temperature worsens the inherent good tensile toughness of PE100 pipes as the axial elongation at break decreases.

1. INTRODUCTION
Polyethylene (PE) pipes have been successfully used as gas or water transport pipes because of their comprehensive advantages, such as lightweight, low cost, corrosion resistance, and easy processing. However, with the widespread use of PE pipes, their performances, especially the hoop strength, still need to be optimized. Therefore, many efforts have been devoted to achieving the reinforcement of PE pipes. The methods that allow PE pipes to self-reinforce during processing have received much attention for their outstanding stability and ease of operation.

Until now, many self-reinforcement approaches are available to change the molecular orientation in the plastic pipe to prepare the high-performance PE pipes, such as the solid deformation processing, die-drawing, vibration extrusion, and rotation extrusion, among which rotation extrusion has attracted much attention. Compared with other self-strengthening methods, during the PE pipes’ rotation extrusion, the molecular chains are largely aligned in the hoop direction via applying the hoop shear field to improve the pipe’s properties in the hoop directions. At the same time, a transportation pipe under internal pressure withstands hoop stress twice as much as the axial stress. Shen et al. focused on the mechanical and thermal properties of the PE pipes with a sleeve-rotating die. In addition, they observed a double peak on the differential scanning calorimetry (DSC) curve and inferred the existence of the shish−kebab structure. Wang et al.
al.\textsuperscript{20–27,30} designed a rotation extrusion system that could achieve the independent or integrated rotation of both the mandrel and die, improving both short-term and long-term mechanical properties of the pipe. Also, the result showed a highly oriented lamellar structure that was clearly visible by scanning electron microscopy (SEM). They concluded that the oriented lamella is a kebab structure in the shish–kebab structure and the shish structure is too small to be distinguished.

These studies show that the performances of plastic products are related to their microstructure and morphology. Changes in the processing parameters, applied shear and temperature in particular, have a great influence on the final orientation and crystal structure, both of which are decisive for performance.\textsuperscript{31,32} Therefore, a detailed study of the formation of the flow-induced structure and the influences of the processing conditions can help to understand the possible mechanisms of the crystallization process, thus providing an effective way for the improvement of material properties.

It has been identified that a critical flow intensity is necessary to form the shish.\textsuperscript{33,34} The shear rate needs to be larger than the reciprocal of the Rouse relaxation time for the molecular chains (i.e., $\dot{\gamma} > 1/\tau$) so that the chains can be oriented along the direction of flow.\textsuperscript{35} Additionally, a critical amount of mechanical work is required to bring the oriented chains together and form a stable shish. Although the specific flow conditions of shish formation have been identified, the mechanism responsible for the initial shish–kebab formation and the effects of processing conditions are still under discussion.\textsuperscript{29,36–46} The first theory that made a breakthrough was the coil-stretch transition proposed by de Gennes,\textsuperscript{36} which was based on molecular dynamics studies for different shear modes in dilute solutions. Moreover, Keller\textsuperscript{37} concluded the relationship between the critical strain rate ($\dot{\varepsilon}_c$) and molecular weight ($M$) during the coil-stretch transition: $\dot{\varepsilon}_c = M^{-1.5}$. However, Han et al.\textsuperscript{40,41} observed shish–kebab structures at a shear rate below 1 s\textsuperscript{-1}. They argued that the shish originated from the topographically deformed entangled network bundles instead of a stretched single-molecule chain. Balzano et al.\textsuperscript{47} found that shish was even able to form at the temperature that was slightly above the equilibrium melting temperature of the polymer crystal. Also, Keum et al.\textsuperscript{42} showed that shish could grow by an autocatalytic process after the shear flow had stopped. These theories above partly explained the ability to form shish–kebab crystals in products after shear.

It should be pointed out that the formation of shish–kebab depends on the competition between the shear-induced orientation and the molecular relaxation after shear.\textsuperscript{38} As an important processing parameter, temperature plays a key role in both orientation and relaxation. The high temperature provides enough kinetic energy for the polymer molecular chains to orient in the shear flow direction. Meanwhile, high temperatures also make them relax easily after shear.\textsuperscript{49} Li et al.\textsuperscript{50} defined four temperature intervals based on different structures formed at a certain temperature. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measured the effect of temperature on the structure through the slow stretch of a cross-linked PE network. The formation of shish crystals was clearly observed in two intervals of moderate temperatures. Many scholars proposed that kebabs were probably grown under diffusion-controlled conditions and originated from coiled chains. Also, experimental analysis\textsuperscript{51} and simulation results\textsuperscript{52} showed that kebab crystals could be produced massively without the help of stretching flow. Alfonso et al.\textsuperscript{53} investigated the dissolution of flow-induced shish precursors in isotactic polypropylene and offered an Arrhenius-type equation ($\tau(T) = \tau(0)e^{U/RT}$), which described the temperature dependence of precursors’ lifetime. Hsiao et al.\textsuperscript{59} examined the thermal stability of the shear-induced shish–kebab structure by gradually heating. They suggested that the melting of shish started at a higher temperature and its speed was lower than that of kebab crystals. Further research was drawn by Phillips et al.\textsuperscript{59} who investigated that the average length of shish decreased quickly to half of the peak value and then decreased more slowly. However, the average diameter of shish first kept increasing after shear and then began to decline slowly until the end of the isothermal process.

These shish–kebab-related mechanism studies were mainly conducted through a simple shear flow or stretch flow, but such flows were different from what was used in many actual polymer processing methods. Besides, there is almost no research focusing on the shear-induced crystallization of the different initial temperature melts, which were extruded into the mold of the same temperature, even though such a process is very common in the actual production of PE pipes. Until now, studies on the influences of the temperature variation in pipe extrusion are still rare. Especially, related report on melt plasticizing temperature has not been found. Besides, there is no direct research on the structural parameters of shish–kebab in the prepared pipes under rotational shear. On the other hand, compared with the improvements of the axial strength achieved in the die-drawing samples, the improvements obtained in the rotational extruded pipes so far have been unsatisfactory. Unfortunately, although the hoop strength was improved, the axial strength was slightly reduced under some experimental conditions.

To explore the confusion found in the systematic processing–morphology–property study of rotational pipe extrusion, we have designed and constructed a novel rotational shear system (RSS) that can impose hoop shear on polymer melt using a rotating mandrel under a precisely controlled speed, melt plasticizing temperature, and shear time. In this study, a PE with bimodal molecular weight distribution was used as a material for the prepared pipes under rotational shear due to the key role of long-chain segments of a polymer in initiating and rapidly propagating the shish. Using the RSS, for the first time, we clarified the relationship between the morphology (especially its gradient in the wall thickness direction) of the pipe and the melt plasticizing temperature. The pipes prepared at suitable melt plasticizing temperatures showed performances that were significantly higher than those of the conventional extruded pipes. The results indicated the formation of the possible shish–kebab interlocking structure, which improved both the hoop strength and axial strength. The purpose of this research is to investigate the influence of the melt plasticizing temperature on the formation of the shish–kebab crystals under rotational shear and to lay a solid foundation for the widespread application of the high-performance PE pipe.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

A commercially available HDPE pipe resin (JHMGC100S) was purchased from Jilin Chemical Industry Co., Ltd., with a melt flow index rate of 6.4 g/10 min, measured at 190 °C under 21.6 kg.
2.2. Sample Preparation. In this study, a self-designed rotational shear system was adopted to prepare PE100 pipes, as shown in Figure 1. This system has the following features: first, the rotational velocity and cooling process could be easily controlled by the independent die system and thus hoop shear imposed on the melt could be controlled. Second, the system had a hollow mandrel, through which cooling oil could be transmitted to cool the interior surface of the pipe. As a result, its inner and outer walls could be cooled at a similar speed. See the previous papers for more information on this equipment.55,56 In this work, the mandrel rotated for 100 s during the cooling process at a speed of 7 rpm, the mold temperature was 150 °C, and the PE pipes were extruded at various melt plasticizing temperatures set at 215, 235, and 255 °C.
comparision, the conventional pipe was also carried out under the same processing conditions (the melt plasticizing temperature was 235 °C) but without mandrel rotation and the pipe was named as C-235 °C. The outer diameter and the wall thickness of the final PE100 pipes obtained in this experiment were 63 and 5 mm, respectively.

As shown in Figure 2, the prepared PE100 pipe was made into various standard samples to characterize its properties and microstructure and divided into three layers along the thickness direction, that is, an inner layer, a middle (core) layer, and an outer layer. The thicknesses of the layers were ~1, ~3, and ~1 mm.

2.3. DSC Analysis. The thermal analysis of the samples was performed by a Q200 modulated differential scanning calorimeter (TA Instruments). The samples (3–5 mg) from each layer of the PE pipe were heated in a nitrogen atmosphere from 40 to 160 °C at a heating rate at 10 °C/min. The melting point, \( T_m \), denotes the minimum value of the thermograms during heating. The crystallinity is derived from integrating the DSC traces with respect to a baseline drawn as a tangent to the trace at 50 and 140 °C and relating the derived heat to the melting enthalpy of hypothetical 100% crystalline polyethylene of 293 J/g.

2.4. Measurements of SAXS and WAXD. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements were performed at the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelengths of X-ray radiation were 0.124 nm (SAXS) and 0.154 nm (WAXD). Two-dimensional (2D) SAXS and WAXD patterns were collected via an X-ray detector of Pilatus 2M. The Mar CDD X-ray detector of Pilatus 2M had a resolution of 1475 × 1679 pixels. The sample was mounted on a three-dimensional elevator platform with its thickness direction parallel to the Y-axis. The distance between the sample and detector was 1900 mm for SAXS and 184 mm for WAXD. The SAXS and WAXD image acquisition time of each data frame was 5 s. From the inner layer to the outer layer, three different layers, 450 (inner layer), 250 (core layer), and 50 μm (outer layer) down from the outer surface, were scanned, respectively. Finally, Fit-2D and origin software were used to analyze the data. The background for all samples was subtracted before calculation.

2.5. SEM Observation. To get a clear observation of the crystalline morphology in the samples, the SEM experiments were performed using a field-emission SEM (Apreo SHVoc, FEI) instrument (with an accelerating voltage of 20 kV). A small block was cut along the hoop direction of the prepared pipe, which was etched by a mixed acid solution after polishing. Finally, the treated surface was carefully washed with the aid of an ultrasonic cleaning machine. All of the samples were sputter-coated with gold before observation.

2.6. Vicat Softening Temperature (VST) Tests. Vicat softening temperatures were measured at 120 °C/h using a Davenport-type HDT/V-3116 apparatus according to GB/T 1633-2000. The average value of the five samples was reported.

2.7. Mechanical Property Measurement. For testing the axial strength of the PE100 pipes, dumbbell-shaped samples were cut from the molded pipe in the axial direction according to GB/T 8804-2003 and then tested up to the point of fracture at 10 mm/min constant crosshead movement in a universal testing machine (Instron Instrument Model 5576, Instron/ America). The samples of the hoop strength tests were cut from the extruded pipe in the hoop direction into 8 mm wide rings and then tested under the same testing conditions as those used for the axial samples. Five samples were measured for each process condition.

3. RESULT AND DISCUSSION

3.1. Orientation Results. WAXD experiments were performed to explore the changes of orientation during prepared pipes under rotational shear at different melt plasticizing temperatures. 2D WAXD patterns for various layers of samples prepared at selected temperatures are shown in Figure 3. Obviously, one can observe two Debye rings in the isotropic WAXD pattern, which are assigned to the 110 (inner circle) and 200 (outer circle) lattice planes of the orthorhombic form of PE100, respectively. When the melt plasticizing temperature of the experiment is increased, both the 110 reflection and the 200 reflection are gradually concentrated on the equator. As the melt plasticizing temperature is further increased, the concentration decreases, and the concentration of the core layer is higher than that of the inner and outer layers. It could be predicted that the core layer of the 235 °C sample has the highest orientation. In addition, the shish–kebab structure can be speculated as indicated by the green arrow in Figure 3. The description of shish–kebab will be mentioned in subsequent sections.

Figure 4 depicts, as a typical result, the azimuthal scans of the intensity distribution of the 110 reflections. To quantitatively evaluate the orientation level, the orientation parameter \( f_H \) was calculated using Herman’s orientation parameter, which was defined as follows

\[
f_H = \frac{3 \cos^2 \varphi - 1}{2}
\]

where \( \cos^2 \varphi \) is an orientation factor defined as follows

\[
\cos^2 \varphi = \frac{\int_0^{\pi/2} I(\varphi) \cos^2 \varphi \sin \varphi \, d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi \, d\varphi}
\]

where \( \varphi \) is the azimuthal angle and \( I(\varphi) \) represents the diffraction intensity. The values of the orientation parameter \( f_H \)
of 1 and $-0.5$ mean that the crystals are oriented perpendicularly or parallel to the flow direction, respectively. The calculated orientation parameters based on Herman’s method for all layers are shown in Figure 4d.

As shown in Figure 4d, the orientation parameters of all layers have the same tendency along with the increase of melt plasticizing temperature, which increase first and then decrease. It is well known that the higher the temperature of the polymer melt, the higher the activity of the polymer segment. The high melt temperature provides enough kinetic energy for the movement of the polymer molecular chains, making them easier to stretch and orient in the shear flow direction. As the melt temperature is further increased, the relaxation time of the polymer segment decreases after
rotational shear (100 s); lots of orientation structures have relaxed, although 255 °C had the most orientation molecular chains. Therefore, the orientation parameters of 235 °C are the highest. Moreover, the orientation of the core layer is higher than that of the inner layer and outer layer for all samples, which could be ascribed to the temperature gradient in the polymer melt. That is, the cooling rate in the inner and outer layers is faster than that in the core layer, cannot getting enough time for shear flow. As analyzed above, the orientation parameter 0.965 of the 235 °C core layer is the highest.

3.2. Morphological Structure. The shish–kebab structure for the PE100 pipe prepared under rotational shear could be demonstrated by the DSC experiment. Figure 5 depicts the thermal behavior of the core layer for 235 °C during a heating scan at a rate of 10 °C/min. This DSC melting curve is a typical fingerprint of melt-crystallized PE with the characteristic shish–kebab structure. The integration of the DSC curve yields a crystallinity value of 64.4%. On the other hand, it should be noted that the DSC thermogram exhibits two melting peaks, located at 133.09 and 134.51 °C, respectively. The lower melting peak and the higher one can be tentatively ascribed to the melting of chain-folded kebab lamellae and shishlike formation, respectively. As shown in Table 1, the crystallinity of the core layer is higher than that of the other layers. Counting the crystallinity of all of the layers, 235 °C shows the highest average crystallinity of 62.59%, followed by 215 °C (62.38%), 255 °C (60.54%), and C-235 °C (52.44%). Generally speaking, the shear flow field can induce crystallization.\(^5\) The rotational shear is shown to increase the crystallinity at every melt plasticizing temperature. The slight difference in the crystallinity of the shear samples can be likely ascribed to the number of their orientation structures after rotational shear.

Figure 6 further shows the crystal morphologies at different regions for the prepared PE100 pipes under rotational shear. Clearly, all regions were covered with the shish–kebab crystals that align along the shear flow direction. It shows that the mechanical work in all regions has exceeded the threshold of shish formation. However, there is a slight difference in the number and distribution of the shish–kebab crystals. The number of shish crystals at the core layer is more than that at
the inner layer and outer layer for all samples, and the thickness and length of kebab crystals increase corresponding to the increase of the melt plasticizing temperature.

The differences between the three layers are mainly the result of the cooling rate. The characterization results above show that the core layer has the most representative dense shish−kebab structure and its orientation parameter and crystallinity are also higher than those of the inner layer and outer layer. To elucidate the differences in the structural features affected by the melt plasticizing temperature, we present in Figure 7 the 2D SAXS patterns for core layers. These patterns clearly exhibited the emergence of equatorial streaks and meridional scattering peaks. The feature of equatorial streaks in SAXS can be considered as the sign of shish formation, and the meridional scattering peaks indicate the development of kebabs aligned perpendicularly to the shear flow direction. The apparent discrepancy between the intensities derived from the different SAXS patterns could be attributed to the various shish−kebab structures at different melt plasticizing temperatures.

Some important structural parameters of the kebab formation, like the average thicknesses of the amorphous and crystalline regions as well as the long period, can be evaluated by considering the scattering intensity distribution along the meridional direction. One-dimensional scattering intensity distribution curves taken along the meridional direction are shown in Figure 8a. The peak position of \( I(q) \) is related to the value of the long period (\( L_{\text{shish}} \)) corresponding to the average...
of the smaller value obtained from the correlation function to the average thickness of the amorphous layers ($L_{am}$). The average thickness of the crystalline lamellae ($L_c$) can be obtained by subtracting the average thickness of the amorphous layers from the $L_{shish}$.

For the determination of the average lateral length of the kebab crystals ($L_{kebab}$), rectangle scans across the kebab reflections are included in Figure 8c. The intensity distribution profile was fitted with one Gaussian function, and the width of the resultant Gaussian function ($\Delta q_2$) is directly related to the lateral length of the lamellar crystals using the following equation:

$$L_{kebab} = \frac{2\pi}{\Delta q_2}$$

The values of $L_{ac}$, $L_{am}$, $L_{c}$ and $L_{kebab}$ for the samples are given in Figure 8d. With an increase of melt plasticizing temperature, the long period increases slightly (around 2.48 nm, 255 °C), which is accompanied by a rise in the average thickness of the kebab crystals (around 2.87 nm, 255 °C) and the amorphous layers (around 0.79 nm, 235 °C) and the lateral length of the kebab crystals (around 4.20 nm, 235 °C).

On the other hand, the values of $L_{ac}$, $L_{am}$, $L_{c}$ and $L_{kebab}$ are the lowest at 215 °C. As discussed previously, the relaxation time of the polymer segment at high melt temperatures is shorter after rotational shear (100 s); some of the kebab lamellae that have not been fully stacked are relaxed, which give rise to an increase of long period. However, the high melt temperature provides enough kinetic energy for the movement of the oriented molecular chains, making them easier to be folded into kebab lamellae. Above all, the average thicknesses of both the crystalline lamellae and the long period increase at high melt plasticizing temperatures.

The diameter of the shish was estimated by applying the Guinier approximation61 by analyzing the intensity distribution along the equatorial scattering streak that started from the maximum intensity. As shown in Figure 9a, the radius of gyration ($R_g$) of the shishlike formation can be approximated from the slope of the linear region at low $q_2$ of a plot of ln($I(q_2)/q_2^2$) versus $q_2$ according to the equation

$$I_{shish} = \int_{0}^{0.3} \int_{-30^\circ}^{30^\circ} I(q_2, \phi) dq_2 d\phi \propto \frac{1}{q_2} e^{-q_2^2 R_g^2/2}$$

The diameter of the shish is

$$D_{shish} = 8^{1/2} R_g$$

Strictly speaking, the Guinier approximation is only applicable for monodisperse systems in the small-angle limit, where the criterion $R_g q_2 < 1$ is maintained.54

The average length of the shish ($L_{shish}$) can be determined using the Ruland streak method63 to analyze the equatorial streak feature in SAXS. If all azimuthal curves can be fitted by Lorentz functions, the observed azimuthal width, $B_{obs}$, can be related to $L_{shish}$ by the following equation

$$B_{obs} = \frac{1}{L_{shish}} \frac{\pi}{\pi} \int_{-\pi/2}^{\pi/2} I(q_2, \phi) d\phi = B_{obs} + \frac{2\pi}{L_{shish} q_2}$$

$B_{obs}$ is the misorientation of shish. As indicated in Figure 9b, $L_{shish}$ can be obtained from the slope of $B_{obs}$ versus $1/q_2$.
The shish structure parameters $D_{\text{shish}}$ and $L_{\text{shish}}$ are presented in Figure 9b,d, respectively. On the whole, $D_{\text{shish}}$ increases with an increase of melt plasticizing temperature, but $L_{\text{shish}}$ decreases at further high melt plasticizing temperatures. Therefore, it could be assumed that the relaxation of shish is more reflected in the length.

The corresponding mechanism of shish–kebab formation of PE100 pipes prepared at different melt plasticizing temperatures was proposed, as illuminated in Figure 10. The shish precursor, a long-range ordered structure, also known as amorphous shish structure, is formed under rotational shear flow. In addition, the number of shish is more at high temperatures because the PE chains are easier to orient. However, the shish precursors are consumed continuously at high temperatures and the consumption of precursors is mainly reflected in the reduction of their number and length. Furthermore, the diameter of shish is larger at high temperatures because of the aggregation of more molecular chains. Higher temperatures lead to a more perfect kebab and result in an increase of kebab crystals’ overall size. Moreover, the sparse shish provides more space for the kebab to grow at higher temperatures, resulting in a longer and slightly distorted kebab. However, less shish gives rise to a decrease of kebab number, which eventually leads to a decrease of crystallinity at 255 °C.

3.3. Heat Resistance and Mechanical Properties. The VST of the PE100 pipes prepared at different melt plasticizing temperature is shown in Figure 11. As seen in Figure 11, the
VST of PE100 pipe prepared via a mandrel rotation at 7 rpm increases significantly compared with that of C-235 °C. The VST of the 235 °C is the maximum value, 102.4, higher by 25.7 °C (compared to the VST value of the C-235 °C) and 3.2 °C (compared to that of the 255 °C), and remained at 102.2 for 215 °C.

In general, there are three options to increase the heat resistance of a polymer: increasing the $T_g$, increasing the crystallinity, and reinforcing.63 The dense shish—kebab crystals play the role of self-reinforced. On the other hand, VST is largely related to the crystallinity of the inner layer because it is defined as the temperature that needle penetrates into the inner layer of sample by 1 mm according to GB/T 1633-2000. The crystallinity of PE100 pipes for the inner layer calculated by DSC is shown in Table 1. As one can see, the result of VST is highly consistent with crystallinity.

Figure 12 illustrates the effect of melt plasticizing temperature on the round strength of the PE100 pipe prepared via a mandrel rotation at 7 rpm. At a high mandrel rotation speed, the hoop strength increased with an increase of melt plasticizing temperature; a further increase led to a decrease in the hoop strength. When the melt plasticizing temperature is 235 °C, the hoop strength reached the maximum value, 75.2 MPa, higher by 237% compared to the value of the C-235 °C. Clearly, there is an optimum temperature range for the enhancement of the hoop strength that appears between 215 and 235 °C. Similar to the change in VST, the hoop strengths varied due to the various orientation parameters, crystallinities, and $L_{\text{kebab}}$ induced by the melt plasticizing temperature during the mandrel rotational shear.

In most cases, the increase in the hoop strength occurs along with a decrease in the axial strength due to the hoop orientation of molecular chains.64 However, it is gratifying that the axial strength is also improved with the application of rotational shear as detailed in Figure 13a; the stress–strain curves and the photographs of the samples are shown in Figure 13b. To represent the destruction of the pipe during the actual use process, the tensile strength is defined as the maximum stress the samples can withstand before yielding. Moreover, the results clearly confirm that the axial strength increased with an increase of melt plasticizing temperature. However, the increase of melt plasticizing temperature worsens the inherent good tensile toughness of PE100 pipes as the elongation at break decreases. This unsatisfactory phenomenon probably arises from an increase in the thickness and length of the kebab. The molecular chain undergoes disorder to partly order and then folds into the lattice during nucleation and growth of kebab from the shish scaffold. The axial strength is mainly a result of the enhancement of the shish–kebab interlocking structure,65 and the toughness mainly comes from the partly ordered molecular chains between the shish–kebabs that are discharged into the crystal lattice. Increased molecular chain folding and premature cessation of shear at high melt temperatures lead to a decrease in partly ordered molecular chains. The schematic illustration of the microstructure evolution under axial stretching is shown in Figure 13c.

To better describe the relationship between the morphology and properties of PE100 pipes prepared at different melt plasticizing temperatures, the radar map shown in Figure 14 is given. The VST and hoop strength peaked at 235 °C are the result of the highest orientation parameter, crystallinity, and $L_{\text{kebab}}$. The axial strength is increased corresponding to the increase of melt plasticizing temperature, which could be related to the increase of $L_c$ and $L_{\text{kebab}}$. In addition, the increase of kebab crystals’ overall size also results in a decrease of axial elongation at break.

4. CONCLUSIONS

In the present work, the influences of melt plasticizing temperature on the morphology and performance of PE100 pipes prepared under rotational shear have been thoroughly researched. Detailed SEM and SAXS/WAXD studies indicated that the content and dimensions of the shish–kebab structure through the layers varied with the melt plasticizing temperature. It was found that when the melt plasticizing temperature was 235 °C, the highest overall orientation parameter and the largest overall $L_{\text{kebab}}$, $L_{\text{shish}}$ and crystallinity were produced under rotational shear. However, the result showed that $L_c$ and $L_c$ increased monotonously with an increase of melt plasticizing temperature, which could be attributed to the fact that the shear flow has a lower influence on the growth of kebab crystals. Due to the improvements in the shish–kebab structure, chain orientation, and crystallinity, the heat resistance and mechanical properties (hoop strength) of the pipes prepared at 235 °C were significantly increased. Moreover, the axial strength of the pipes was also improved and reached the peak value at 255 °C because of the probably interlocking structure of the shish–kebabs. Combined with the above results, the optimum plasticizing temperature is around 235 °C.

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**Notes**

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Effect of melt vibration on structure and mechanical properties of HDPE tube by self-reinforcement and the study of the structure and properties of high-density polyethylene pipes after up to 30 years in use. Polym. Test. 2009, 28, 737−745.

(6) An, F. Z.; Wang, Z. W.; Hu, J.; Gao, X. Q.; Shen, K. Z.; Deng, C. Morphology Control Technologies of Polymeric Materials During Processing. Macromol. Mater. Eng. 2014, 299, 400−423.

(7) Tang, H. I.; Hiltner, A.; Baer. Biaxial orientation of polypropylene by hydrostatic solid state extrusion. Part III: Mechanical properties and deformation mechanisms. Polym. Eng. Sci. 1987, 27, 876−886.

(8) Taraia, A. K.; Ward, I. M. Production and properties of biaxially oriented polyethylene tubes. J. Appl. Polym. Sci. 1996, 59, 627−638.

(9) Chen, K.; Zhou, N.; Liu, B.; Wen, S. Effect of vibration extrusion on the structure and properties of high-density polyethylene pipes. Polym. Int. 2010, 59, 117−123.

(10) Yan, S. M.; Gao, X. Q.; Deng, C.; Yu, Q.; Wang, L.; Zhang, J.; Shen, K. Z. Effect of Vibration Extrusion on Mechanical Properties and Structure of HDPE/OMMT Nanocomposites. Polym.-Plast. Technol. Eng. 2011, 50, 1091−1095.

(11) Gao, X.; Zhang, J.; Chen, C.; Shen, K. Z. Effect of vibration extrusion on high-density polyethylene. J. Appl. Polym. Sci. 2007, 106, 552−557.

(12) Gao, X. Q.; Deng, C.; Xu, J.; Li, Z. M.; Zhang, J.; Shen, K. Z. Effect of melt vibration on structure and mechanical properties of HDPE/nano-CaCO3 blends. Polym. Bull. 2010, 65, 59−68.

(13) Gao, X. Q.; Deng, C.; Lei, J.; Ao, H.; Zhang, J.; Shen, K. Z. Study on Rheology of LLDPE under Compound Stress Field of Vibration and Shear in Extrusion Molding. Polym.-Plast. Technol. Eng. 2009, 48, 1180−1184.

(14) Groos, B. U.K. Patent UK0463711964.

(15) Shepherd, G. W.; Clark, H. G.; Pearsall, G. W. Extrusion of polymer tubing using a rotating mandrel. Polym. Eng. Sci. 1976, 16, 827−830.

(16) Jiang, L.; Shen, K. Z.; Ji, J. L. Extrusion of high hoop strength HDPE tube by self-reinforcement and the study of the structure and properties of the sample. Chem. J. Chin. Univ. 1998, 19, 638−641.

(17) Jiang, L.; Shen, K. Z.; Ji, J. L.; Guan, Q. A mandrel-rotating die to produce high hoop strength HDPE pipe by self-reinforcement. J. Appl. Polym. Sci. 2015, 69, 323−328.

(18) Intawong, N.; T.; Wongchaleo, C.; Sombatsompop, N. Rheological properties, flow visualization and extrude swell of NR compound by rotating-die rheometer. Polym. Eng. Sci. 2008, 48, 1191−1198.

(19) Intawong, N.; Kantala, C.; Lotaisong, W.; Sombatsompop, N. A Die Rotating System for Moderations of Extrusion Load and Pressure Drop Profiles of Molten PP and Wood/Polypropylene Composites in Extrusion Processes. J. Appl. Polym. Sci. 2011, 120, 1006−1016.

(20) Nie, M.; Bai, S. B.; Wang, Q. High-density polyethylene pipe with high resistance to slow crack growth prepared via rotation extrusion. Polym. Bull. 2010, 65, 609−621.

(21) Nie, M.; Wang, Q.; Bai, S. B. Morphology and Property of Polyethylene Pipe Extruded at the Low Mandrel Rotation. Polym. Eng. Sci. 2010, 50, 1743−1750.

(22) Nie, M.; Bai, S. B.; Wang, Q. Effect of the Inner Wall Cooling Rate on the Structure and Properties of a Polyethylene Pipe Extruded at a High Rotation Speed. J. Appl. Polym. Sci. 2011, 119, 1659−1666.

(23) Nie, M.; Bai, S. B.; Wang, Q. Structure and Performance of Polyethylene Pipe Prepared by Mandrel and Die Opposite Rotation Extrusion. Acta Polym. Sin. 2011, 11, 1291−1297.

(24) Nie, M.; Wang, Q. Control of rotation extrusion over shish-kebab crystal alignment in polyethylene pipe and its effect on the pipe’s crack resistance. J. Appl. Polym. Sci. 2013, 128, 3149−3155.

(25) Nie, M.; Li, X.; Hu, X. Y.; Wang, Q. Effect of Die Temperature on Morphology and Performance of Polyethylene Pipe Prepared via Mandrel Rotation Extrusion. J. Macromol. Sci., Part B: Phys. 2014, 53, 1442−1452.

(26) Lin, P.; Min, N.; Qi, W. Geometric Structure Effects of Mandrel on Structure and Performance of Polyethylene Pipes Prepared via Rotation Extrusion. Chin. Plast. Ind. 2016, 5, 84−87.

(27) Pi, L.; Dan, G.; Min, N.; Qi, W. Highly endurable hydrostatic pressure polyethylene pipe prepared by the combination of rotation extrusion and lightly cross-linked polyethylene. J. Polym. Res. 2018, 25, 177.

(28) Kmetty, A.; Barany, T.; Karger-Kocis, J. Self-reinforced polymeric materials: A review. Prog. Polym. Sci. 2010, 35, 1288−1310.

(29) Kimata, S.; Sakurai, T.; Nozue, Y.; Kasahara, T.; Yamaguchi, N.; Karino, T.; Shibayama, M.; Kornfield, J. A. Molecular Basis of the Shish-Kebab Morphology in Polymer Crystallization. Science 2007, 316, 1014−1017.

(30) Pi, L.; Hu, X. Y.; Nie, M.; Wang, Q. Role of Ultrahigh Molecular Weight Polyethylene during Rotation Extrusion of Polyethylene Pipe. Ind. Eng. Chem. Res. 2014, 53, 13828−13832.

(31) Wang, K.; Chen, F.; Zhang, Q.; Fu, Q. Shish−kebab of polylefin by “melt manipulation” strategy in injection-molding: A convenience pathway from fundament to application. Polym. 2008, 49, 4745−4755.

(32) Krishnaswamy, R. K.; Lamborn, M. J. The influence of process history on the ductile failure of polyethylene pipes subject to continuous hydrostatic pressure. Adv. Polym. Technol. 2010, 24, 226−232.

(33) Mykhaylyk, O. O.; Champon, P.; Graham, R. S.; Fairclough, J. P. A.; Olmsted, P. D.; Ryan, A. J. The Specific Work of Flow as a Criterion for Orientation in Polymer Crystallization. Macromolecules 2008, 41, 217−221.

(34) Mykhaylyk, O. O.; Champon, P.; Impradice, C.; Fairclough, J. P. A.; Terrill, N. J.; Ryan, A. J. Control of Structural Morphology in Shear-Induced Crystallization of Polymers. Macromolecules 2010, 43, 2389−2405.

(35) Ahmad, M.; Bailly, C.; Keunings, R.; Nekoomanesh, M.; Arabi, H.; van Ruymbeke, E. Time Marching Algorithm for Predicting the Linear Rheology of Monodisperse Comb Polymer Melts. Macromolecules 2012, 44, 647−659.

(36) De Gennes, P. G. Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients. J. Chem. Phys. 1974, 60, 5030−5042.

(37) Keller, A.; Kolnara, J. Chain Extension and Orientation: Fundamentals and Relevance to Processing and Products. Colloid. Polym. Sci. 1993, 92, 81−102.

(38) Li, L. B.; de Jeu, W. H. Shear-Induced Smectic Ordering as a Precursor of Crystallization in Isotactic Polypolypropylene. Macromolecules 2003, 36, 4862−4867.

(39) Avila-Orta, C. A.; Burger, C.; Somani, R.; Yang, L.; Marom, G.; Medellin-Rodriguez, F. J.; Hsiao, B. S. Shear-induced crystallization of isotactic polypropylene within the oriented scaffold of noncrystalline ultrahigh molecular weight polyethylene. Polymer 2005, 46, 8859−8871.

(40) Zhang, C. G.; Hu, H. Q.; Wang, D. J.; Yan, S.; Han, C. C. In situ optical microscope study of the shear-induced crystallization of isotactic polypropylene. Polymer 2005, 46, 8157−8161.

(41) Zhang, C. G.; Hu, H. Q.; Wang, X. H.; Yao, Y. H.; Dong, X.; Wang, D. J.; Wang, Z. G.; Han, C. C. Formation of cylinder...
structures in shear-induced crystallization of isotactic polypropylene at low shear rate. *Polymer* 2007, 48, 1105–1115.

(42) Keum, J. K.; Zuo, F.; Hsiao, B. S. Formation and stability of shear-induced shish-kebab structure in highly entangled melts of UHMWPE/HDPE blends. *Macromolecules* 2008, 41, 4766–4776.

(43) Roozemond, P. C.; Ma, Z.; Cui, K.; Li, L.; Peters, G. W. M. Multimorphological Crystallization of Shish-Kebab Structures in Isotactic Polypropylene: Quantitative Modeling of Parent–Daughter Crystallization Kinetics. *Macromolecules* 2014, 47, 5152–5162.

(44) Liu, D.; Tian, N.; Huang, N.; Cui, K.; Wang, Z.; Hu, T.; Yang, H.; Li, X.; Li, L. Extension-Induced Nucleation under Near-Equilibrium Conditions: The Mechanism on the Transition from Point Nucleus to Shish. *Macromolecules* 2014, 47, 6813–6823.

(45) Cui, K.; Ma, Z.; Tian, N.; Su, F.; Liu, D.; Li, L. Multiscale and Multistep Ordering of Flow-Induced Nucleation of Polymers. *Chem. Rev.* 2018, 118, 1840–1886.

(46) Wang, Z. B.; Mao, Y.; Jarumaneeroj, C.; Thitsak, B.; Tiyapiboonchaiya, P.; Rungswang, W.; Hsiao, B. S. The influence of short chain branch on formation of shish-kebab crystals in bimodal polyethylene under shear at high temperatures. *J. Polym. Sci., Part B: Polym. Phys.* 2018, 105, 359–369.

(47) Balzano, L.; Kukalyekar, N.; Rastogi, S.; Peters, G. W. M.; Chadwick, J. C. Crystallization and dissolution of flow-induced precursors. *Phys. Rev. Lett.* 2008, 100, No. 048302.

(48) Li, K.; Matsuba, G. Effects of relaxation time and zero shear viscosity on structural evolution of linear low-density polyethylene in shear flow. *J. Appl. Polym. Sci.* 2018, 135, 46053.

(49) Kanaya, T.; Polec, I. A.; Fujiwara, T.; Inoue, R.; Nishida, K.; Matsuura, T.; Ogawa, H.; Ohta, N. Precursor of Shish-Kebab above the Melting Temperature by Microbeam X-ray Scattering. *Macromolecules* 2013, 46, 3031–3036.

(50) Liu, D.; Tian, N.; Huang, N. D.; Cui, K. P.; Wang, Z.; Hu, T. T.; Yang, H. R.; Li, X. Y.; Li, L. B. Extension-Induced Nucleation under Near-Equilibrium Conditions: The Mechanism on the Transition from Point Nucleus to Shish. *Macromolecules* 2014, 47, 6813–6823.

(51) Gu, F.; Bu, H.; Zhang, Z. New Observations on the Formation of “Row-Nucleated” Structures of Isotactic Polystyrene. *Macromolecules* 2000, 33, 5490–5494.

(52) Hu, W. B.; Daan, F.; Mathot, V. B. F. Intramolecular Nucleation Model for Polymer Crystallization. *Macromolecules* 2003, 36, 8178–8183.

(53) Cavallo, D.; Azzurri, F.; Balzano, L.; Funari, S. S.; Alfonso, G. C. Flow Memory and Stability of Shear-Induced Nucleation Precursors in Isotactic Polypropylene. *Macromolecules* 2010, 43, 9394–9400.

(54) Phillips, A. W.; Bhatia, A.; Zhu, P. W.; Edward, G. Shish Formation and Relaxation in Sheared Isotactic Polypropylene Containing Nucleating Particles. *Macromolecules* 2011, 44, 3517–3528.

(55) Yang, H.; Luo, X. H.; Shen, K. Z.; Yuan, Y.; Fu, Q.; Gao, X. Q.; Jiang, L. The role of mandrel rotation speed on morphology and mechanical properties of polyethylene pipes produced by rotational shear. *Polymer* 2019, 184, No. 121915.

(56) Du, Z. C.; Yang, H.; Luo, X. H.; Xie, Z. X.; Fu, Q.; Gao, X. Q. The Role of Mold temperature on Morphology and Mechanical Properties of PE pipe Produced by Rotational Shear. *Chin. J. Polym. Sci.* DOI: 10.1016/j.polymer.2019.121915.

(57) Luo, X. H.; Pan, Y. X.; Li, Y. C.; Gao, X. Q.; Lei, J.; An, F. Z.; Li, Z. M.; Shen, K. Z. Effect of oscillatory shear field on the morphology and mechanical properties of β-nucleated isotactic polypropylene. *Polymer Eng. Sci.* 2017, 57, 838–845.

(58) Somani, R. H.; Yang, L.; Zhu, L.; B. S. H. J. Flow-induced shish-kebab precursor structures in entangled polymer melts. *Polymer* 2005, 46, 8587–8623.

(59) Patil, N.; Balzano, L.; Portale, G.; Rastogi, S. Influence of shear in the crystallization of polyethylene in the presence of SWCNTs. *Carbon* 2010, 48, 4116–4128.