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Cite this article as:

Du Zu-Chen, Yang Hao, Luo Xie-Huai, Xie Ze-Xiang, Fu Qiang, Gao Xue-Qin. The Role of Mold Temperature on Morphology and Mechanical Properties of PE Pipe Produced by Rotational Shear[J]. *Chinese J. Polym. Sci.*, 2020, 38(6): 653-664. doi: 10.1007/s10118-020-2363-4

View online: <https://doi.org/10.1007/s10118-020-2363-4>

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The Role of Mold Temperature on Morphology and Mechanical Properties of PE Pipe Produced by Rotational Shear

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Abstract The role of mold temperature on the morphology and properties of rotational shearing polyethylene (PE) pipes was studied via a self-developed rotational shear system (RSS). The result indicated that when the mold temperature was 150 °C, the hoop tensile strength and Vicat softening temperature were enhanced rapidly, which were 383.6% and 137.9% higher than those of the conventional PE pipes, respectively. Morphology and crystal structure studies by SEM and DSC revealed that once the rotational shear was applied, the shish-kebab structure began to appear. With the increase of the mold temperature, due to the relaxation of most of the oriented molecular chains, the preservation of shish-kebab structure became difficult. When the mold temperature was 190 °C, only the inner layer of the pipes, where the cooling rate was the largest, could preserve the shish-kebab structure. According to WAXD, there was less shish structure, and the growth of kebab was distorted in the inner layer of the pipes at 210 °C. The result of SAXS suggested that the length of shish changed most within the temperature range from 170 °C to 190 °C. The results of DSC and WAXD showed less change in crystallinity and degree of orientation between the two temperatures. It can be concluded that the reduction of shish length leads to a decrease in mechanical properties and heat-resistance.

Keywords Shish-kebab; Rotational shear; Mold temperature; PE pipe

Citation: 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. *Chinese J. Polym. Sci.* 2020, 38, 653–664.

INTRODUCTION

As substitutes for traditional metal pipes, plastic pipes have been widely used in transportation and distribution of natural gas and water due to their good corrosion resistance, durability, and cost-effectiveness.^[1–3] Nevertheless, poor mechanical strength and heat-resistance of polymer hinder polymer pipes from completely replacing metal pipes in some aspects. Therefore, many efforts have been devoted to achieving the reinforcement of polymer materials. The methods that allow polymer materials to self-reinforce during processing have received much attention for their outstanding stability and ease of operation.^[4,5] Technology for self-reinforcing polymer materials is usually achieved by applying force field in the melting process of polymer.^[6] Guo *et al.* modified the polymer by ultrasonic extrusion and found that ultrasonic oscillations could improve the surface appearance of the HDPE extrudates.^[7] Gao *et al.* developed a vibration extrusion apparatus to extrude HDPE sheets.^[8] The results showed an apparent improvement in the yield strength of vibration-extruded specimens. Shen found that dynamic packing injection molding (DPIM) technology could remarkably enhance the tensile strength of HDPE in both flow direction and transverse direction.^[9]

With regards to polymer pipes, due to the orientation of molecular chains along the flow direction during extrusion, the hoop strength is inferior to the axial one.^[4,10,11] However, performance testing demonstrated that transportation pipes experience at least twice as much the hoop stress as the axial stress under inner pressure.^[12] Therefore, it is crucial for plastic pipes to enhance their hoop strength. Rotational extrusion, an outstanding self-reinforcing method in which the molecular chains are largely aligned in the axial direction via applying hoop shear force field in the extrusion process, is regarded as an effective way to improve the hoop mechanical properties.^[13–17] As the original conceiver of this innovative apparatus, Groos achieved the enhancement of HDPE pipes' hoop strength.^[13] Based on this, Shen *et al.* developed a mandrel-rotating apparatus and found that the excellent strength enhancement was due to a high degree of macromolecular orientation.^[16] Subsequently, Wang *et al.* did a great amount of systematic research on the pipes prepared via mandrel rotation extrusion, and the result showed a highly oriented lamellar structure that was clearly visible by SEM.^[17–20] They concluded that the oriented lamella shows a kebab structure in the shish-kebab structure, and shish structure is too small to be distinguished.^[18]

These studies show that the enhancement of hoop strength of rotational pipes is related to the microstructure of the polymer, such as the orientation of molecular chains and the crystalline morphology. Compared with the isotropic spherulites, the shish-kebab structure formed in the shear flow-

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Received September 7, 2019; Accepted October 13, 2019; Published online December 4, 2019

field can give the material considerable enhancement in the orientation direction.^[4] Doufas *et al.*^[21] and Coppola *et al.*^[22] proposed a micro-rheological theory for describing flow-field induced crystallization. It is known that the formation of shish-kebab is the result of competition between molecular chain stretching and relaxation, which can be quantitatively described by De value.^[21]

$$De = \gamma \times \lambda$$

In the formula, γ is the strain rate and λ is the terminal relaxation time of the molecular chain. A large number of experiments have proved that the larger the De value, the easier the formation of shish-kebab.^[23,24] Therefore, it is necessary to restrain the relaxation of molecular chains in order to make shish-kebab finally configure in PE pipes.^[25] The kinematic ability of molecular chains is closely related to the processing temperature: the molecular chains are highly mobile at high temperatures, contributing to the decrease of relaxation time and the difficult maintenance of shish-kebab structure.^[26–28] However, because of the high viscosity of polymer melt at low temperature, the flow field is unstable during rotational shearing, leading to uncontrollable performance of the rotational pipes.^[29] Consequently, it is crucial to study the influence of processing temperature, especially mold temperature, of the rotational pipes.^[24,30,31]

The effect of temperature field on the shish-kebab structure is mostly studied on a parallel plate shearing device called Linkam,^[25,32,33] and it is difficult to obtain an abundant and clear shish-kebab structure in the process of pipe extrusion.^[18] Simultaneously, the improvement of hoop mechanical strength of pipes by rotational extrusion is far from the theoretical expectation. Due to the different cooling rates in the thickness direction of rotational shear pipes, further study on the morphology and distribution of crystals still needs to be made as well. Moreover, the relationship between mechanical properties of polymer rotational pipes and the size of shish-kebab, such as the diameter and length of shish and the thickness and lateral length of kebab, has not been studied. In order to solve these problems, our group has developed an elaborate rotational shear system, which can realize the preservation of much shish-kebab structure along the hoop direction in each layer of pipes. Using the rotational shear system by adjusting the mold temperature, we firstly studied the changes of crystalline morphology and macroscopic properties in a specific temperature range in order to obtain the relationship between them. Besides, due to the different cooling rates in thickness direction, we studied the change of inner, core, and outer layers. At last, with the cooling rate kept unchanged, we focused on the inner layer of the rotational pipes to study the structural dimensions of shish-kebab at different temperatures, including kebab thickness, kebab lateral length, shish diameter, and shish length and clarified the relationship between the size of shish-kebab crystal and the mechanical properties. All in all, at different temperatures, not only the existence of shish-kebab structure leads to the enhancement of circumferential mechanical properties of rotational pipes, but also the size of shish-kebab can significantly affect the mechanical properties of rotational pipes. This provides a solid theoretical foundation for rotational pipe extrusion.

EXPERIMENTAL

Material

The polymer used in this work is a kind of commercial HDPE. The material, labeled JHMG100S, was purchased from Jilin Petro-Chemical Co., Ltd., China. Its melt flow rate was 6.4 g/10min, measured at 190 °C under 2.16 kg. It is a kind of typical pipe material (PE100) with bimodal molecular weight distribution. It contains both the low-molecular-weight component and the high-molecular-weight component. The polymer pipe material can not only increase the minimum necessary strength (MRS), but also inhibit slow fracture growth (SCG) and rapid fracture growth (RCP), and have excellent environmental stress cracking (ESCR) resistance.^[34]

Apparatus and Sample Preparation

A home-made pipe RSS was adopted to fabricate the PE pipes with a diameter of 64 mm and the thickness of 5 mm, as shown in Fig. 1. The apparatus provided single rotational shearing field for PE pipes. In this study, the process started with PE100 being plasticized and extruded into the mold by the extruder. At this time, three stages of the extruder were at 160, 195, and 235 °C, respectively. When the mold was filled, the mandrel began to rotate at 7.5 r/min, and the mandrel rotation lasted for 2.5 min. At the same time, the cooling system was turned on. Mold temperature was set as 150, 170, 190, or 210 °C. The pipe was taken out after being cooled to room temperature. For the conventional sample, PE100 was plasticized and extruded into the mold by the extruder and extruder parameters were set the same as those of the rotational sample. The mandrel did not rotate when the mold was filled and the mold temperature was set as 170 °C. The pipe was demolded when it was cooled to room temperature. Rotational pipe preparation is shown in Fig. 2.

Characterizations

Hoop tensile property

A universal tensile testing machine (Instron Instrument Model 5576, Instron, America) was used to test the hoop tensile strength of rotational shear pipes at room temperature with a crosshead speed of 10 mm/min.

Vicat softening point (VST)

According to ISO 2507:1995, VST test was operated at 120 °C/h using a Davenport type HDT/V-3116 apparatus. Sampling method is shown in Fig. 3.

DSC analysis

Thermal analyses of the sample were conducted using a Q200 modulated differential scanning calorimeter (TA instrument, USA). Samples (3–5 mg) from the inner, core, and outer layer of the PE pipes were heated from 40 °C to 160 °C in a nitrogen flow with a heating rate of 10 °C/min.

SEM observation

Scanning electronic microscopy (SEM) was applied to study the morphology of the pipe throughout the wall thickness. The samples were cut from the pipes along the axial direction, chemically etched with a mixed acid solution after polished, and then sputter-coated with gold. The SEM images were obtained using a field-emission SEM (Apreo S HiVac, FEI, USA) instrument (with an accelerating voltage of 20 kV).

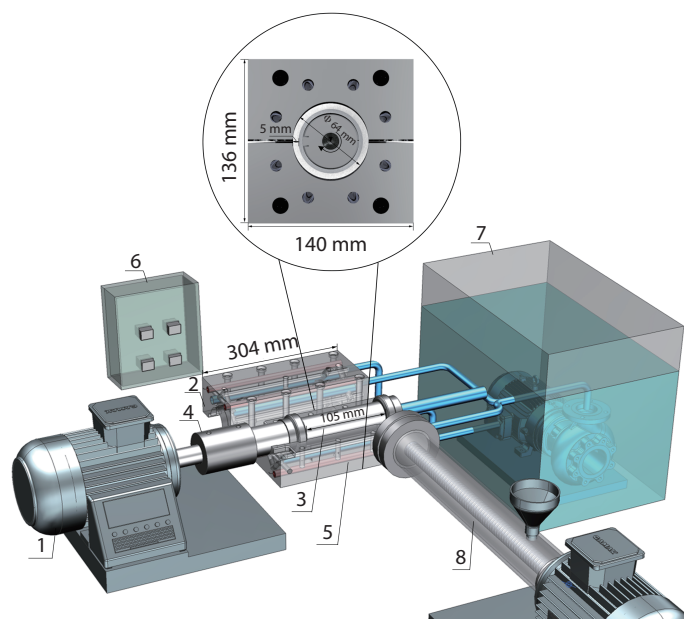


Fig. 1 Schematic diagram of the rotational shear system (RSS) consisting of a rotational shear unit, a temperature control and pressure monitoring unit, and a plasticization unit. 1-Motor, 2-mold, 3-mandrel, 4-coupling, 5-heater, 6-electric box, 7-cooling control, and 8-extruder. The inset shows the cross-section view of the rotational shear unit.

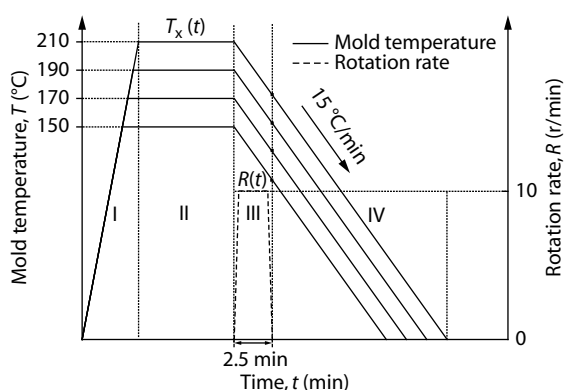


Fig. 2 Mold temperature and rotation speed during rotational pipe preparation. I-Plasticization stage, II-filling stage, III-shear stage, and IV-solidification stage.

WAXD analysis

Two-dimensional wide-angle X-ray diffraction experiments were performed using a Bruker D8 X-ray diffractometer (Germany) with Cu K α radiation ($\lambda = 0.154056$ nm) operating at 40 kV and 40 mA. Five points were selected equidistantly along the axial direction of the pipes. The orientation parameter of crystals was evaluated using Herman's method, which is defined as follow:

$$f_H = \frac{3(\cos^2\varnothing) - 1}{2}$$

where $\cos^2\varnothing$ is an orientation factor defined as follow:

$$\cos^2\varnothing = \frac{\int_0^{\pi/2} I(\varnothing) \cos^2\varnothing (\sin\varnothing) d\varnothing}{\int_0^{\pi/2} I(\varnothing) \sin\varnothing d\varnothing}$$

where $\varnothing$ is the angle between the normal of a given (hkl) crystal plane and the shear flow direction, and $I(\varnothing)$ represents the

diffraction intensity. Orientation parameter $f_H = 1$ means that polymer chains orient along the hoop direction completely; $f_H = -0.5$ means that polymer chains orient vertically to the hoop direction completely. For an unoriented sample, f_H equals 0. The location of the 5 spots is shown in Fig. 3.

SAXS analysis

Small-angle X-ray scattering (SAXS) measurements were performed on BL16B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray radiation is 0.124 nm (SAXS). Two-dimensional (2D) SAXS patterns were collected via X-ray detector of Pilatus 2M. The Mar CDD X-ray detector of Pilatus 2M has 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 sample-to-detector distance was 1900 mm for SAXS. The patterns were acquired at 3 spots across the thickness of the pipe wall at 0.5, 2.5, and 4.5 mm away from the inner wall surface (see Fig. 3). The SAXS image acquisition time of each data frame was 5 s. Finally, software Origin and Fit-2D were utilized to process the data. Background for all samples was subtracted before calculation.

High pressure capillary rheometry

A high pressure capillary rheometer (RG120) was used to measure the viscosity of polymers at different shear rates. Preheating time was set as 300 s.

RESULTS AND DISCUSSION

Properties of Rotational Shearing Pipe at Different Mold Temperatures

Obviously, what matters to evaluate the quality of pipes is its mechanical properties. As shown in Fig. 4, once the hoop shear was applied, the hoop tensile strength and modulus of PE pipes were significantly enhanced. Simultaneously, the tensile strength

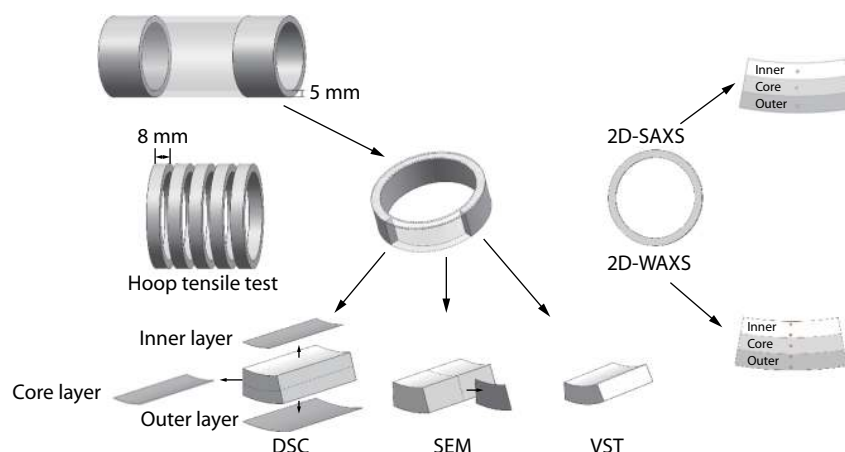


Fig. 3 Schematic diagram of specimen sampling from the pipe for various tests.

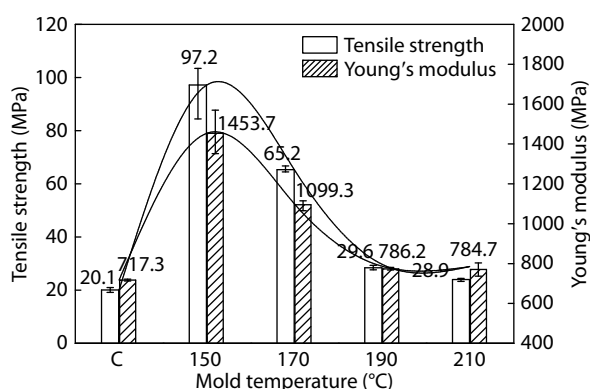


Fig. 4 Hoop tensile strength and tensile modulus of rotational PE Pipes fabricated at different mold temperatures.

th and modulus decreased with the increase of mold temperature. The tensile strength and modulus of rotational pipes at 150 °C were 97.2 and 1453.7 MPa, respectively, which are 383.6% and 102.7% higher than those of the conventional pipes (20.1 and 717.3 MPa). Apparently, mechanical properties of the pipes have been greatly strengthened. Nevertheless, when the mold temperature rose to 210 °C, the mechanical properties of rotational pipes decreased sharply, with tensile strength and modulus (23.9 and 784.7 MPa) only increased by 19% and 9.4%, respectively, compared with those of conventional pipes. Furthermore, as can be seen from the error bars, the experimental data of the 150 °C samples is highly volatile and unstable, while the results of other data are relatively stable. Fig. 5 shows the tensile fracture specimens of conventional pipes and rotational pipes at two different mold temperatures. It can be observed that fractures in another region also appear in the rotational pipes at 150 °C. After fracture, the specimens were divided into two layers, which signifies that the delamination cracking has occurred in the rotational sheared pipe.

There is no doubt that heat-resistance is also significant for the properties of a pipe. Fig. 6 shows Vicat softening temperature of rotational pipes at different mold temperatures. On the whole, the Vicat softening point of rotating shear pipes was higher than that of conventional pipes. When the mold temperature was 150 °C, the maximum value was raised from 76.7 °C to 105.8 °C, increasing by 37.9%, which greatly im-



Fig. 5 Fracture specimens of the rotational PE pipes after tension. From left to right are the conventional pipe, the rotational PE pipe at 150 °C, and the rotational PE pipe at 170 °C.

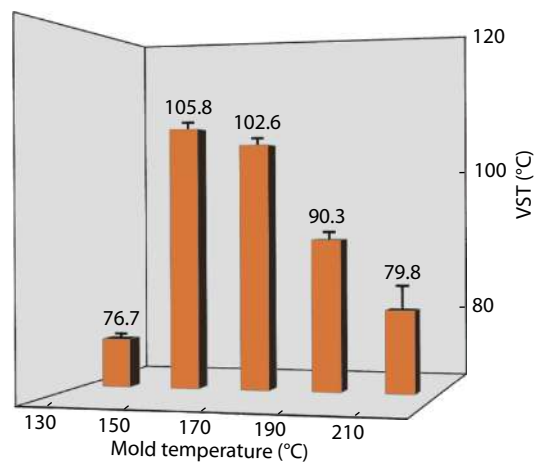


Fig. 6 Vicat softening temperature of rotational PE pipes fabricated at different mold temperatures.

proves the using temperature of the pipes. However, the Vicat softening temperature decreased continuously with the further increase of mold temperature. When the mold temperature was 210 °C, the Vicat softening point was only 3.1 °C higher than that of the conventional pipe.

The data of mechanical properties and heat-resistance of rotational pipes show that huge promotion of properties and heat-resistance can be realized when the mold temperature

was set at 150 and 170 °C. More pervasively, although the rotational pipes at 150 °C revealed better properties compared with those at 170 °C, fracture sample diagram shows that two fractures appeared in rotational specimens at 150 °C, and the specimens were obviously divided into two layers. At lower temperatures, the viscosity of polymer melt under rotational shear was higher, so the flow of the polymer melt was swinging, leading to property instability of its products. In evaluating the performance of products, besides assessing the mechanical properties of pipes, the stability of pipe should be taken into consideration too. Therefore, in the experiment, the pipes made at 170 °C possessed the best comprehensive performance.

Crystal Content Measured by DSC

It is well known that the mechanical properties of semi-crystalline materials are related to their crystal content and morphology. Fig. 7(a) shows DSC curves of the inner layer of the pipes at different temperatures, which illustrates that at 150, 170, and 190 °C, an evident bulge (acromion) appears on the curve at a higher melting peak temperature (about 132 °C). In the meanwhile, compared with the conventional pipe, the crystallinity of the rotational pipes was slightly improved (from 52.7% to 55.8%, Fig. 7b). Generally, a shear flow field can induce crystallization.^[28] Nevertheless, Table 1 indicates that the small increase in crystallinity alone cannot explain the huge increase

in mechanical strength and heat-resistance. As a result, it can be concluded that crystal morphology might have changed.

Morphology of Rotational PE Pipe from SEM

From SEM images shown in Fig. 8, distinctions can be easily pointed out. The results of the inner, core, and outer layers of the conventional pipes show no difference, and the lamellae are scattered and randomly stacked together, conforming to the morphological structure of spherulites. Once the rotational shear was applied to the pipe at the mold temperature of 150 °C, a highly oriented lamellar structure can be observed clearly in inner, core, and outer layers, which is in accordance with “shish-kebab” morphology mentioned in literature.^[35] For the pipes processed via rotational shearing at 170 °C, similarly, there are a large number of “shish-kebab” structures in these three layers, but slightly differently, the spread of shish-kebab is more well-distributed and compact in the rotational pipe at 170 °C than those at 150 °C. This microphenomenon well explains the fracture delamination of rotational pipes at 150 °C. Furthermore, with the mold temperature increasing to 190 °C, even though shish-kebab structure is found in the inner layer, no clear shish-kebab structure can be observed in the core and outer layers. For the mold temperature of 210 °C, only some oriented lamellae exist in the inner layer, and the crystal types of the middle and outer layers are restored to random orientation spherulites.

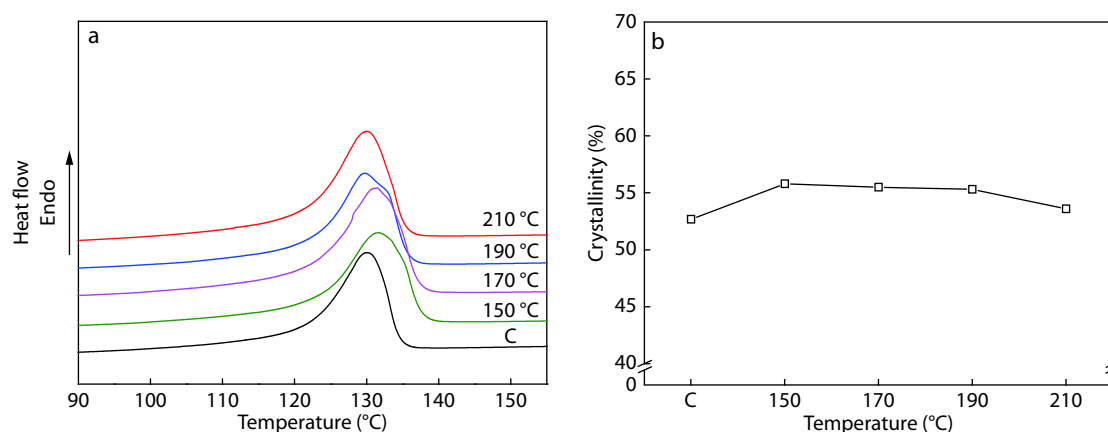


Fig. 7 (a) DSC heating curves of the inner layer of rotational PE pipes at different mold temperatures; (b) Average crystallinity of three layers of rotational PE pipes prepared at a different mold temperatures.

Table 1 DSC test results of rotational pipes prepared at different mold temperatures.

Mold temperature (°C)	Location	Melt temperature (°C)	Melt enthalpy (J/g)	Crystallinity (%)
C	Inner	130.1	150.1	51.2
	Core	130.3	154.4	52.7
	Outer	129.7	158.6	54.1
150	Inner	132.7	158.6	54.1
	Core	131.8	170.2	57.3
	Outer	131.4	164.3	53.7
170	Inner	132.0	165.5	56.3
	Core	131.5	165.6	56.5
	Outer	131.6	165.1	56.3
190	Inner	130.2	168.1	57.4
	Core	130.8	155.0	52.2
	Outer	129.7	164.9	56.3
210	Inner	130.0	162.0	55.3
	Core	130.8	152.7	51.4
	Outer	129.5	158.4	54.1

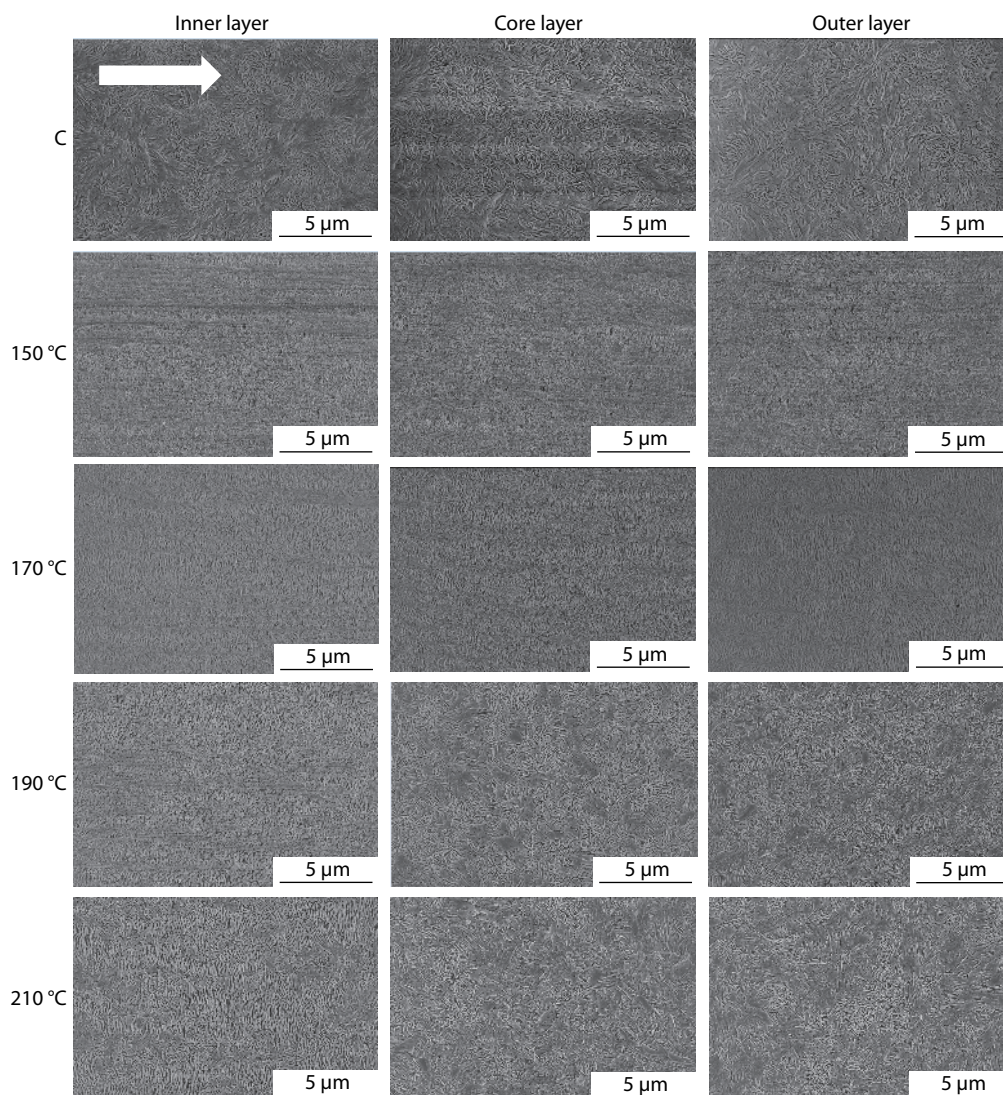


Fig. 8 SEM images of etched inner, core, and outer layers of the PE pipes prepared at different mold temperatures. The arrowhead represents shear direction.

The existence of shish-kebab can notably improve the mechanical strength and heat resistance of polymers,^[36–38] which is consistent with the results of excellent mechanical properties and heat resistance of rotational pipes prepared at the mold temperature of 150 and 170 °C. The formation and recovery of shish-kebab are influenced by three factors: mold temperature, shear rate, and cooling rates. Higher mold temperature undoubtedly speeds up the relaxation process, thus shortening the relaxation time. As a result, there was no shish-kebab in the three layers at 210 °C. Meanwhile, the cooling rate of the mandrel is higher than that of the mold, meaning that the inner layer has a shorter relaxation time. In addition, the special molecular structure of PE100 possesses a typical bimodal molecular weight distribution.^[34] Therefore, at 190 °C, there were only shish-kebab in the inner layer, and some oriented lamellae were even retained at 210 °C. What is more, the shear rate varies in the thickness direction, so further analysis should be carried out. In the meanwhile, only SEM analyses were used to characterize the existence of shi-

sh-kebab and other types of crystals. To characterize the size of crystals, subsequent characterization methods are needed.

Flow Simulation by Polyflow

In order to quantitatively analyze the shear of melt along the thickness direction, Polyflow simulation was used to calculate the shear rate. A high pressure capillary rheometer was used to measure the viscosity of polymer samples at different shear rates. Power law equation was used to fit the viscosity of PE100 at different shear rates. Physical properties of PE100 are listed in Table 2. Based on the way of melt flow, drag equation was adopted to calculate the actual melt flow. Fig. 9 displays the shear rate distribution along the thickness of the pipe at

Table 2 Physical properties of PE100.

Temperature (°C)	K	n	λ
150	1314	0.2401	0.022
170	319	0.2469	0.035
190	315	0.2541	0.044
210	965	0.2764	0.016

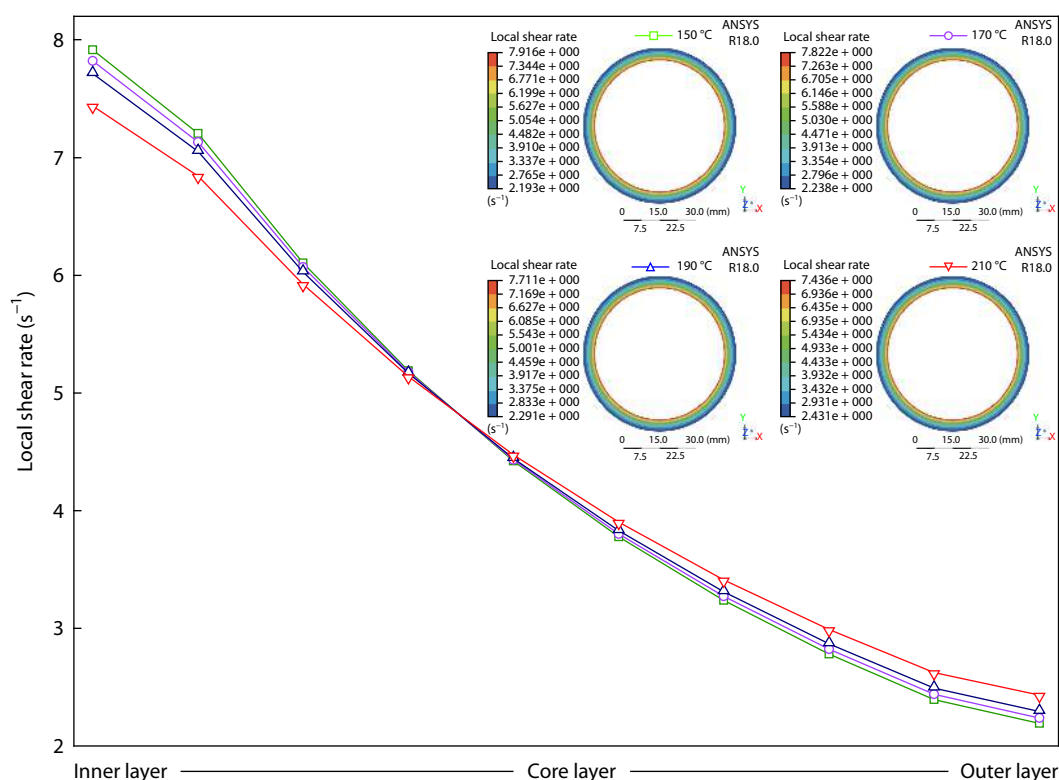


Fig. 9 Shear rate distribution along the thickness of the pipe at different mold temperatures.

different mold temperatures. Along the thickness direction, the shear rate decreased from the inner layer to the outer layer. The higher the shear rate, the more stable the shish-kebab structure.^[39] The difference of shear rate distribution along the thickness led to the difference of morphology along the thickness. As can be seen, with the increase of temperature, there was little change in the shear rate of the core layer, while the shear rate of the inner layer decreased slightly and the shear rate of the outer layer increased slightly. This is attributed to the different physical properties of HDPE at different temperatures and the selection of flow models.

$$\dot{\gamma}(r) = -r \frac{d}{dr} \left(\frac{v_{\theta}}{r} \right) = \frac{2}{n} \omega \frac{r^{-\frac{2}{n}}}{R_1^{-\frac{2}{n}} - R_2^{-\frac{2}{n}}}$$

Orientation Analysis of Rotational PE Pipes (WAXD)

To further verify the orientation structure changes observed in SEM, the orientation of molecular chains in rotational PE100 pipes prepared at different mold temperatures was analyzed by two-dimensional wide-angle X-ray diffraction (2D-WAXD). The diffraction intensity distribution of conventional and rotational samples consists of two basic diffraction rings, including (110) and (200), from inner to outer layers, respectively. For conventional samples, the intensity distribution of diffraction patterns of (110) and (200) crystal planes is uniform, which indicates that the structures of these locations were randomly distributed. For the rotational samples, diffraction arc concentrated in the meridional direction can be observed clearly, which indicates that the polymer molecular chain is strongly oriented along the shear direction. Furthermore, the lower the mold temperature, the sharper the diffraction arc. When the temperature was 150

and 170 °C, diffraction focused arcs are found in the inner, core, and outer layers, while isotropic circles are observed in the core layer with the temperature rising to 190 °C and diffraction focused arcs merely exist in the inner layer. This is because the orientation of molecular chains due to the competition between stress-induced orientation and subsequent relaxation.

In order to reflect 2D-WAXD image in Fig. 10 more scientifically, Fig. 11 collects the azimuth scanning and orientation factor of each layer of the rotational sample prepared at different mold temperatures. Fig. 11(d) corroborates the results observed in SEM images well. It can be seen that when the mold temperature was 150 °C, the average orientation degree was the highest, where the effect of de-orientation was the weakest and the cooling rate was the highest.

It is shown that when the mold temperature is 210 °C, double peaks appear at 180° from the two-dimensional wide-angle image in Fig. 10 and the crystal plane azimuth scanning image of Fig. 11(a), which is different from the peak shape of other samples, indicating that the orientation degree has changed at this time. Combining with the results of electron microscopy of 210 °C samples in Fig. 8, the inclination of free growth of epigenetic lamellae will lead to the distortion of lamellae when the number of shish structures is small,^[40] thus reducing the orientation of lamellae and molecular chains.

Structure of Shish-kebab (SAXS)

Fig. 12 shows the selected *in situ* SAXS patterns of three layers at different temperatures. The meridional maxima in the SAXS pattern indicate the existence of kebab-like lamellar structures; in the meantime, some well-oriented lamellae were perpen-

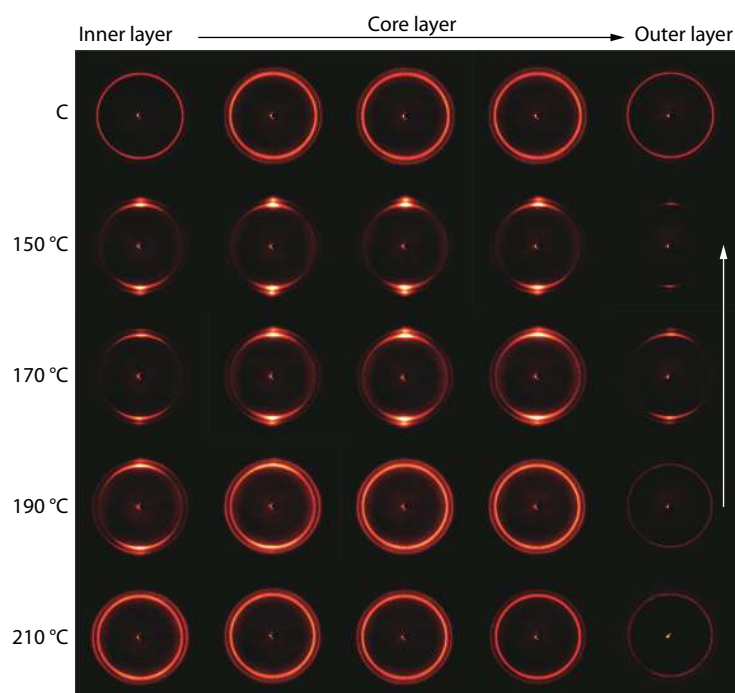


Fig. 10 2D-WAXD patterns of conventional and rotational PE100 pipes prepared at different mold temperatures. Five spots from the inner surface to the outer surface were investigated (The white arrow indicates the melt flow direction).

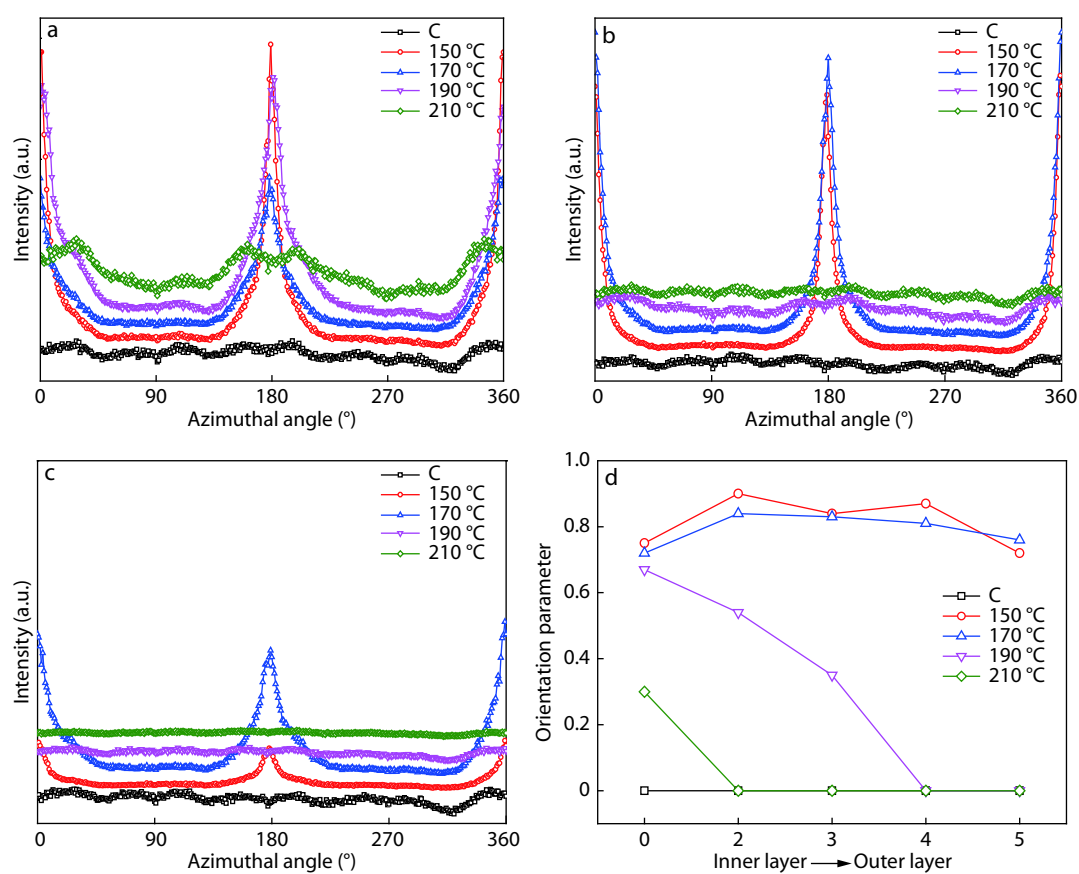


Fig. 11 Azimuth scanning map and orientation factor of crystal plane of PE pipes layers at different mold temperatures: (a) Inner layer; (b) Core layer; (c) Outer layer; (d) Orientation factor.

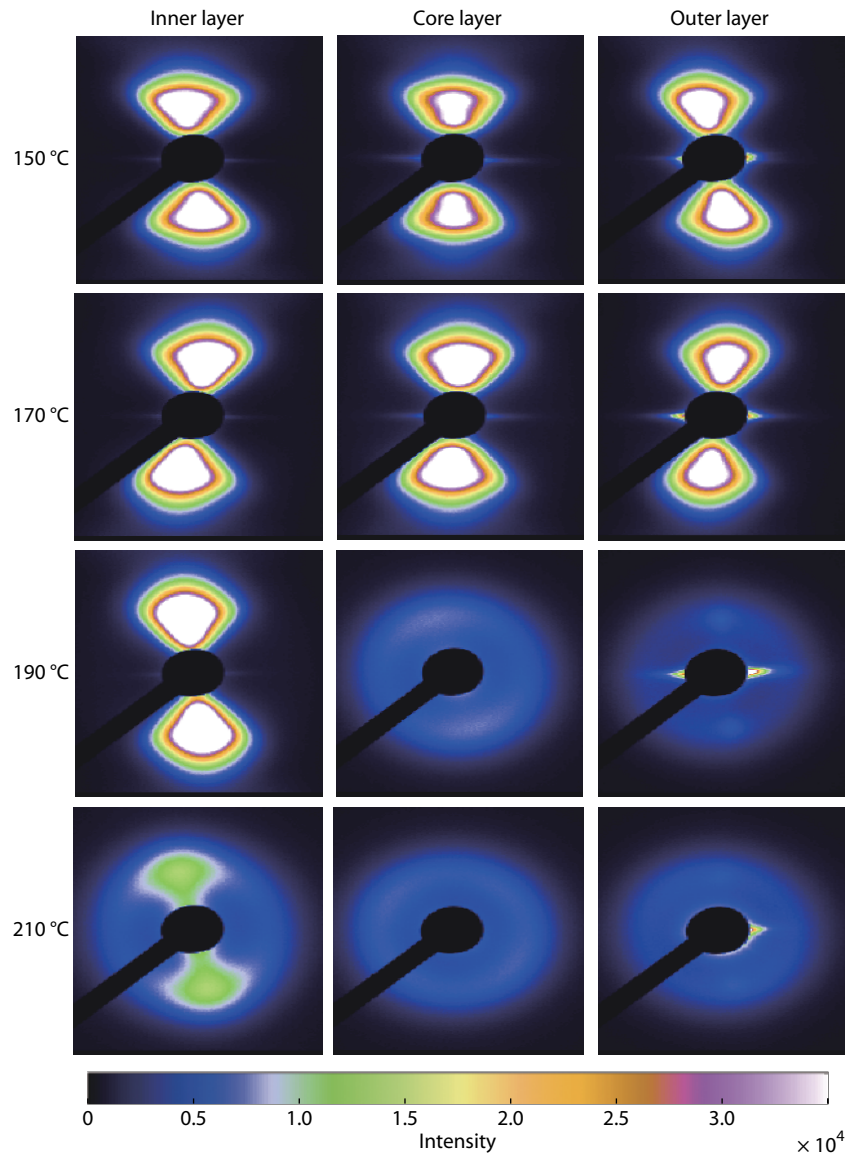


Fig. 12 SAXS patterns for rotational PE pipes prepared at different temperatures.

dicular to the flow direction, and the equatorial streak indicates the existence of shish.^[41] It can be seen that from the inner to outer layers, the PE pipe shows the scattering patterns of shish-kebab at 170 and 190 °C, while shish-kebab scattering patterns only appear in the inner layer at 190 °C; when the mold temperature continues to rise to 210 °C, shish-kebab scattering patterns could no longer be observed, and only oriented lamellar patterns appear in the inner layer. So, the results of SAXS are in good agreement with those observed by SEM. The present analysis results well explain the high mechanical strength of pipes at 150 and 170 °C, but whether the size of shish-kebab contributes to the mechanical strength of rotational shearing pipes at 150 °C higher than that of pipes at 170 °C remains a question. As a result, the analytical calculation of SAXS for the rotational shearing PE pipes has been handled. In order to avoid data duplication and redundancy, the inner layer of pipe was taken for data analysis.

Kebab structure parameters

Structural parameters, such as the average thicknesses of the amorphous and crystalline regions as well as the long spacing, of the kebab formation were first taken into calculation. Fig. 13 (top) shows the one-dimensional correlation function $K(Z)$ derived from one-dimensional scattering intensity distributions at different temperatures. The average thickness of crystalline lamellae (L_c) can be obtained by subtracting the average thickness of amorphous layers (L_a) from the long spacing (L). The values of L_a , L_c , and L for the sample are given in Table 3. I - q curve is obtained by rectangular integration in the kebab direction, as shown in Fig. 13 (bottom). The half width (Δq) satisfies the following formula and the values of L_{SAXS} (lateral length) for the sample at different temperatures are collected in Table 3.

$$L_{\text{shish}} = \frac{2\pi}{\Delta q}$$

According to the kebab data, the lateral length of kebab

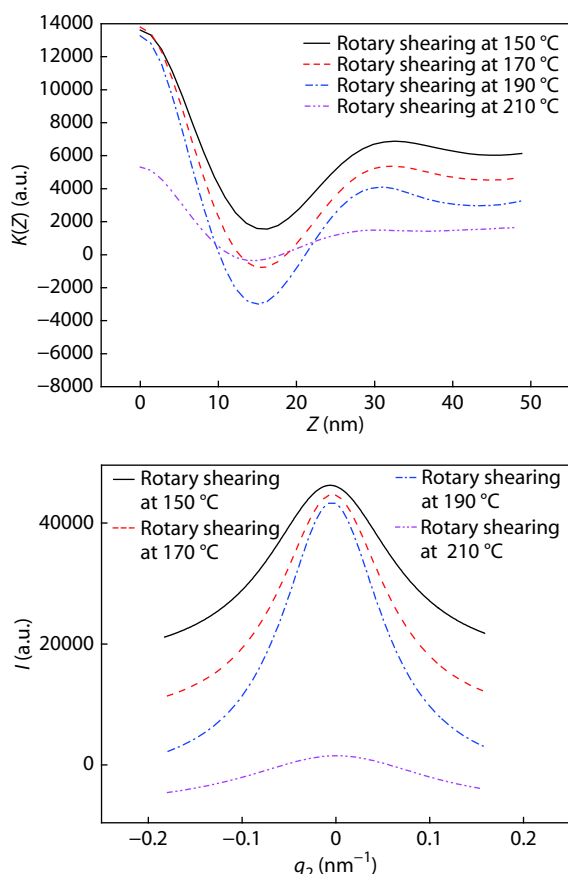


Fig. 13 One-dimensional SAXS intensity profiles along inner layer of rotational pipes at different temperatures.

Table 3 Kebab structure parameters at different temperatures.

Temperature (°C)	L_a (nm)	L_c (nm)	L (nm)	L_{SAXS} (nm)
150	11.92	20.84	32.77	38.35
170	11.67	20.88	32.55	45.70
190	11.60	19.59	31.19	48.06
210	11.01	18.83	29.84	25.34

changed obviously with the increase of temperature. The lateral length increased first and then decreased sharply. Kebab thickness decreased slightly with the increase of temperature.

Shish structure parameters

Then, the direction of shish was integrated to get the shish parameters, including the average diameter and the average length of shish. $I(q)$ curve was obtained by sector integration of small angle scattering pattern along the shish direction; $\ln(I(q))q$ - q^2 curve was then made, leaving only the maximum to the minimum, and the point set shown in Fig. 14 (top) was obtained. The diameter of shish can be evaluated by "Guinier approximation". Shish diameters calculated using the following formula are shown in Table 4.

$$\text{Slope} = \frac{-R_g^2}{2}$$

$$D_{\text{shish}} = 8^{0.5} R_g$$

The average length of shish unit along the long axis direction (L_{shish}) and the orientation difference of shish (b_ϕ) can be

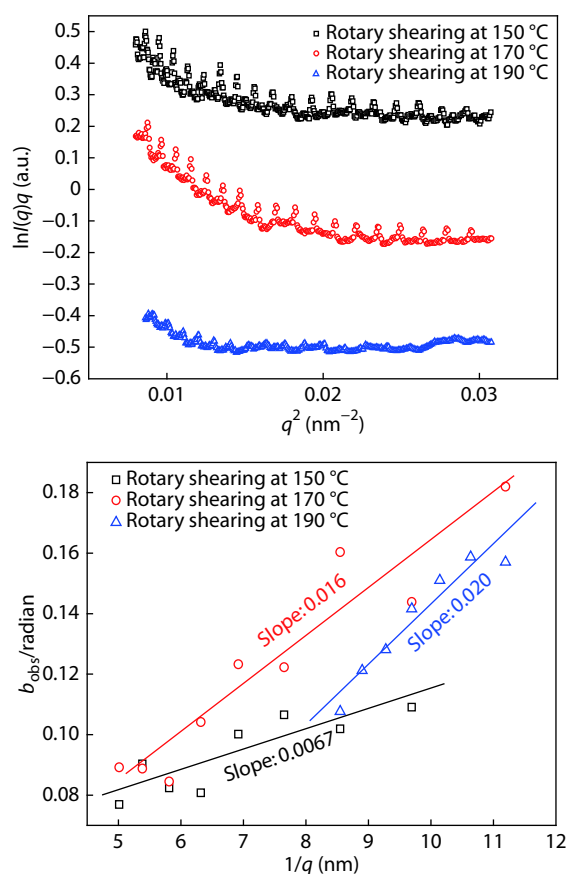


Fig. 14 Guinier plot of $\ln(I(q)q)$ versus q^2 showing selected lines during rotary shearing at different temperatures (top) and plot of azimuthal integral width (b_{obs}) versus the value of $1/q$ (bottom).

Table 4 Shish structure parameters at different temperatures.

Temperature (°C)	D_{slope}	L_{slope}	D_{shish} (nm)	L_{shish} (nm)
150	-23.99	0.0067	19.59	943.42
170	-34.04	0.016	23.34	399.95
190	-23.10	0.020	19.22	319.92

calculated using model from Perret and Ruland. As shown in Fig. 14 (bottom), this point set consists of the integral width of the azimuthal curve (b_{obs}) at a series of different q values along the equator (shish). The integral width (b_{obs}) satisfies the following formula. By plotting b_{obs} versus $1/q$, the reciprocal of the slope is $2\pi/L_{\text{shish}}$. The value of L_{shish} is shown in Table 4.

$$b_{\text{obs}}(q) = \frac{1}{I(q, \frac{\pi}{2})} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} I(q, \varphi) d\varphi$$

$$b_{\text{obs}} = b_\phi + \frac{2\pi}{L_{\text{shish}} \times q}$$

The data suggests that when the mold temperature rose from 150 °C to 170 °C, the diameter of shish (D_{shish}) increased to a certain extent, while the length of shish (L_{shish}) fell off a cliff, from 943.42 to 399.95. The diameter and length of shish decreased when the die temperature reached 190 °C.

Changes of shish-kebab at different mold temperatures

The formation of shish-kebab conforms to coil-stretch transition

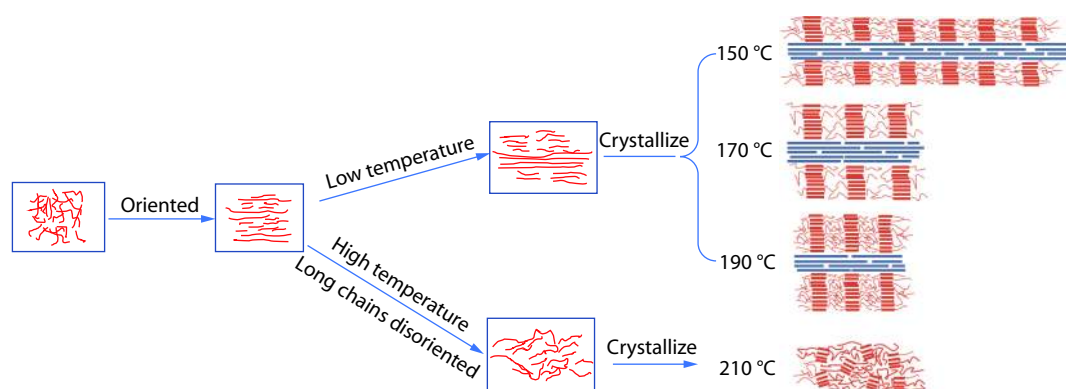


Fig. 15 Schematic diagram of shish-kebab structure obtained at different mold temperatures.

mechanism under high temperature shear,^[42] which tallies with the cross-linked network mechanism under low-temperature shear.^[43] Under this experimental condition, the set temperatures belong to the category of high-temperature shearing temperature, which is suitable for coil-stretch transition. In order to better describe the different structures of shish-kebab at different temperatures, the schematic diagram shown in Fig. 15 is given. Because of the long length of shish, the fragments are intercepted proportionally for drawing.

It is not difficult to find out that the changes of shish structure, especially the length of shish, are most extreme in the temperature field. In the early stage of shearing, there is no crystal formation in the polymer melt, while a flow-induced precursor, a long-range ordered structure which is also called amorphous shish structure, is formed.^[44] The precursor is constantly being consumed at higher temperatures and the depletion of the precursor is mainly reflected in the decrease of its length. Furthermore, the difference in shish length well explains that the mechanical properties and heat-resistance of the rotary shear pipe at 150 °C are higher than those at 170 °C. Compared with the shish diameter at 150 °C, the diameter of shish at 170 °C increases, and the diameter of shish at 190 °C decreases. Combined with the variation of shish length, the following conjecture can be drawn: the diameter of shish is compensated by a small proportion of the disoriented shish.

For kebab structure, the thickness decreases slightly with the increase of temperature field. The lateral length of kebab increases with the increase of temperature but decreases sharply when the temperature is 210 °C. With the increase of temperature, the activity of molecular chains is stronger, and the growth of kebab is more perfect, so the overall size of kebab increases. Once the shish support is lost, the growth of oriented lamellae (kebab) will be largely influenced. Without the support of shish, the distortion of lamellae (kebab) occurs. As a result, the effect of shish on kebab growth depends on whether it exists or not, rather than its size.

CONCLUSIONS

The structure and properties of PE pipes prepared at different mold temperatures have been studied by self-made rotational shear system (RSS). Results of mechanical properties and heat-resistance indicated that mechanical strength and heat-resistance of the rotational shear pipes at 150 and 170 °C were

remarkably improved compared with those of traditional pipes. Detailed DSC studies showed that the crystallinity increased during rotational shearing. Microstructure measured by WXR and SEM revealed that shish-kebab structure was distributed in three layers of the rotational pipes prepared at the mold temperature of 150 and 170 °C, contributing to the improvement of mechanical strength and heat resistance at these two mold temperatures. Additionally, the optimum performance of rotational shearing pipes at 150 °C was due to its long shish length. With the increase of temperature, shish structure was hard to keep because of the intensification of its de-orientation, making shish structure only exist in the inner layer at 190 °C. When the temperature was 210 °C, without the support of shish, the distortion of lamellae occurred in the inner layer, and therefore, there were random spherulites in the core layer and outer layer.

ACKNOWLEDGMENTS

The work was financially supported by the Science and Technology Program of Sichuan Province, China (No. 2018G20332) and the National Natural Science Foundation of China (No. 21627804).

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