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Effect of Different Shear Modes on Morphology and Mechanical Properties of Polypropylene Pipes Produced by Rotational Shear

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Abstract Oriented “shish-kebab” structures could be obtained by shearing to enhance the mechanical properties of polymer samples markedly. However, the effect of shear mode on mechanical properties is still uncertain. The study of stepped hoop shear field on the isotactic polypropylene (iPP) pipe was developed through applying a self-designed rotational shear system (RSS). The effect of stepped shear field on the microstructure and comprehensive properties of iPP pipe was investigated by the comparison with continuous shear. It could be found that the loosely-assembled shish-kebabs with the larger size were formed in the continuous shear pipes, but the smaller and tightly-stacked ones existed in the pipes with stepped shear. Surprisingly, due to differential morphologies under different shear modes, better comprehensive mechanical properties were obtained in the pipes with stepped shear.

Keywords iPP pipe; Shish-kebab; Rotational Shear; Shear mode

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INTRODUCTION

Isotactic polypropylene (iPP) pipes have been widely used in indoor cold and hot water supply and heating systems because of its excellent characteristics, such as corrosion resistance, lightweight, non-toxic and environmental protection.^[1–3] However, in practical use, the hoop stress of iPP pipes is twice as much as its axial stress, and the main failure form in iPP pipes for fluid transportation is hoop fracture.^[4–6] This phenomenon can be explained by the thermodynamically stable α -spherulite and the molecular chains oriented along the direction of melt flowing in iPP pipes produced by the conventional extrusion.^[7–9] The morphology results in excellent axial strength but poor hoop strength of iPP pipes. How to improve the hoop strength of iPP pipes by polymer processing has been paid considerable attention.

To enhance the performance of iPP pipes, blending,^[10,11] adding fillers^[12,13] and fiber winding reinforcement^[1,14] have been carried out in the past period. However, high processing costs and difficulty in recycling waste are regarded as the most common problems in processing methods mentioned previously. Obviously, it is feasible to enhance mechanical properties via varying morphologies of polymer. A massive number of researches have shown that the specific structure of crystals (e.g. shish-kebab) in polymer can be ob-

tained by adding an external force field, and then the properties of the polymer products can be improved.^[15–19] Researches conducted by Kawaguchi *et al.* have shown that the anisotropic shish-kebabs have higher strength in the orientation compared to isotropic spherulites, which leads to the improvement in strength and stiffness of the material.^[20] In a follow-up study, Shen *et al.* found that a large number of oriented shish-kebabs can be formed by dynamic packing injection molding (DPIM), thus improving the mechanical properties of the polymer samples remarkably.^[21,22] Additionally, Li *et al.* obtained iPP containing a lot of shish-kebabs by controlling processing conditions, and the reinforced and toughened iPP were obtained.^[23] Based on these researches, it is obvious that the hoop stress field can be established by rotational shear during processing pipes, and shish-kebabs along the hoop direction of pipes are formed. As a result of that, the hoop properties of pipes could be improved significantly.

During recent decades, researchers have found that it will have a greater impact on the crystallization behavior of polymer when the rotational shear is applied to plastic pipe extrusion.^[24–29] In the past few years, several attempts have been made to study the effect of rotational shear on the mechanical properties of plastic pipes. Wang *et al.* investigated the effect of continuous shear field on the mechanical properties of iPP, and found that the formation of shish-kebabs and β -crystals had been promoted under continuous shear field.^[27] In addition, Gao *et al.* studied the effects of mold temperature and mandrel rotation speed on the microstructure of shish-kebabs and concluded that under the pro-

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cessing condition based on continuous shear field, the mechanical properties and heat resistance of polyethylene (PE) pipes can be further improved by changing these processing parameters.^[5,6] The processing of rational shear pipes based on continuous shear field provides an effective method for industrial production to a certain extent. However, in some areas of application, the hoop strength of these plastic pipes with continuous shear field is still not satisfactory. To further increase the hoop strength of plastic pipes, a few scholars have turned their attention to the stepped shear field which consumed less energy than continuous shear. Kitade *et al.* studied that long-branched chain polypropylene (LCB-PP) not only formed highly oriented shish-kebabs, but also formed sub-lamellar crystals attached to kebabs under stepped shear field.^[30] Additionally, Venerus *et al.* found that the diffusion coefficient of heat in the flow and neutral direction of polyisobutylene melt had increased and decreased immediately after stepped shear was applied.^[31] These studies have put forward a new insight into polymer processing, but the analysis of the morphology and properties of polymer materials have not yet been fully investigated.

Aim to further study the effect of continuous shear field and stepped shear field on the comprehensive properties and crystallization behavior of *i*PP, a novel rotational shear system (RSS) as shown in Fig. 1 was developed to provide different rotational shear modes for *i*PP pipes. Supported by this

device, the crystallization behavior of *i*PP pipe under different shear modes, the effect of shear field on morphology in *i*PP and the relation between condensed structure and mechanical properties of pipes was thoroughly investigated. Besides, 0.1 wt% TMB-5 (β -nucleating agents) were added to improve the toughness of *i*PP pipes.^[32,33] Finally, under the synergistic action of β -nucleating agents and shish-kebabs, the *i*PP pipes with excellent comprehensive properties were manufactured.

Through the in-depth study on the crystallization behavior of polymers under different shear modes, the effect of shear stress on morphology in *i*PP can be deeply understood. Besides, compared with continuous shear, stepped shear does less shear work to polymer melt in the processing of pipes, and the load requirements of the equipment are reduced. Consequently, a theoretical basis for the industrial production of plastic pipes is put forward. It is believed that this study can provide a theoretical and practical basis for the industrialization of continuous extrusion of plastic pipes.

EXPERIMENTAL

Material

Isotactic polypropylene (*i*PP): grade T30S, density 0.897 g/cm³, melt index 3.0 g/10min (2.16 kg, 230 °C), produced by Petro-China Lanzhou Petrochemical Company.

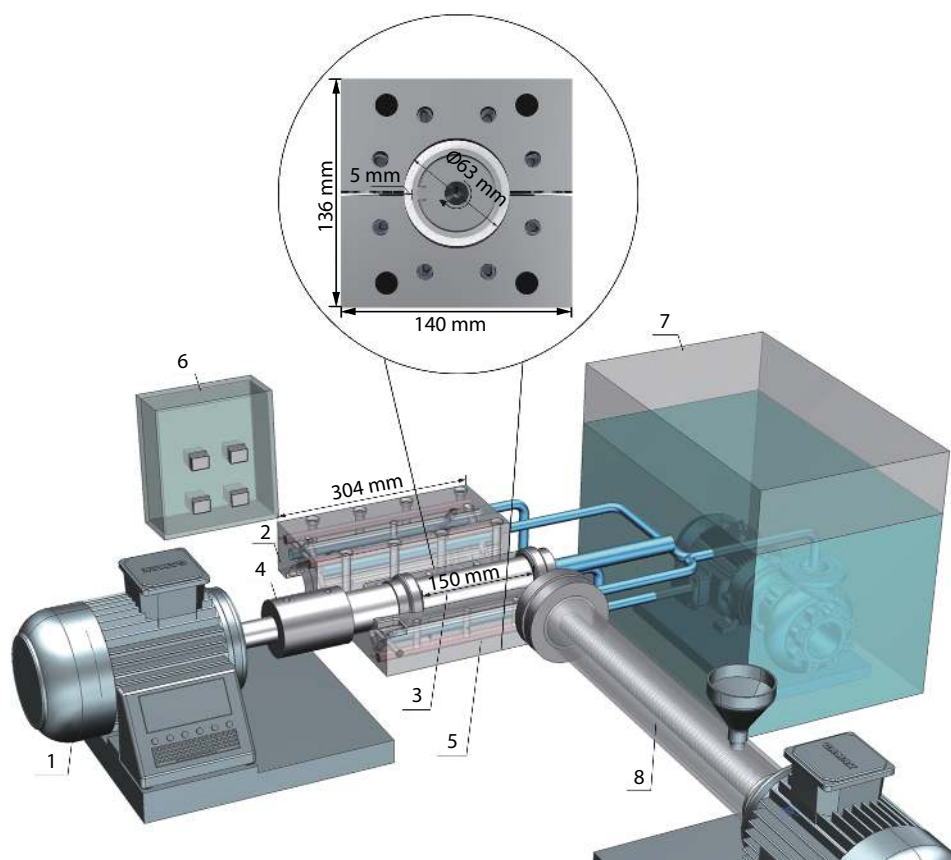


Fig. 1 Schematic diagram of RSS^[6]: 1-motor, 2-mold, 3-mandrel, 4-coupling, 5-heater, 6-electric box, 7-cooling control, and 8-extruder.

β -Nucleating agent: amide β -nucleating agent TMB-5, produced by China Shanxi Fine Chemical Research Institute.

Apparatus and Sample Preparation

The RSS was adopted to fabricate the *i*PP pipes with the external diameter of 63 mm and the thickness of 5 mm under different shear modes. In this experiment, no shear, continuous and stepped shear modes were used for research. In continuous shear mode, the *i*PP was continuously rotationally sheared at a constant shear rate of 6 r/min for 90 s. In the stepped shear mode, the mandrel increased from 0 r/min to 6 r/min at a constant rate of change over 1 s, and then immediately decreased to 0 r/min at a constant rate of change over 1 s, repeating the cycle for 90 s. A schematic diagram of the specific continuous and stepped shear mode is shown in Fig. 2. In the course of the experiment, the particles were prepared with blending, extruding and granulation of *i*PP and 0.1 wt% TMB-5 through a twin-screw extruder, and then were dried for 12 h. In the preparation of the rotational pipes, the process started with the particles being plasticized and extruded into the

mold by the extruder. Simultaneously, every part between the hopper of the extruder and the head reached 140, 210, 210 and 210 °C. In addition, the temperatures of the mandrel and the mold were fixed at 150 °C in this study. As soon as the mold was filled, the mandrel began to rotate according to the set shear mode and the cooling oil circulated to cool down the mold at the speed of 0.22 °C/s. The pipe was demolded when it was cooled to room temperature.

The mandrel and the mold were controlled independently, and the shearing action of the melt in the hoop direction was given by the rotation of the mandrel. With the system, β -crystals and shish-kebabs in the hoop direction can be obtained. Based on this, the strengthening mechanism of pipes under different shear modes can be fully understood.

Characterizations

Scanning electron microscopy (SEM) observation

In order to observe the various crystalline forms of *i*PP sample and the fiber bonds between adjacent shish-kebabs, the experiments using a field-emission SEM (ApreoSHVoc, FEI, USA) instrument (with an accelerating voltage of 20 kV) were performed. A sample was taken along the hoop direction of the pipe after shear (as shown in Fig. 3) for low-temperature polishing. After that, the amorphous portion of the sample was removed by etching with a mixed acid and potassium permanganate. Finally, the samples were washed by ultrasonic cleaning machine and sprayed with gold after drying.

Differential scanning calorimetry (DSC) analysis

The thermal analysis of the sample was carried out by Q2000 differential scanning calorimeter for the melting and crystallization properties of the sample (as shown in Fig. 3). Considering the uneven melt flow rate and cooling rate, the inner, core and outer layers of the sample were scraped to have 3–5 mg of samples for analysis. In the experiment, the temperature of *i*PP sample increased from 40 °C to 160 °C at the rate of 10 °C/min. The melting enthalpy of the sample can be obtained by the DSC curve, and the crystallinity of the sample

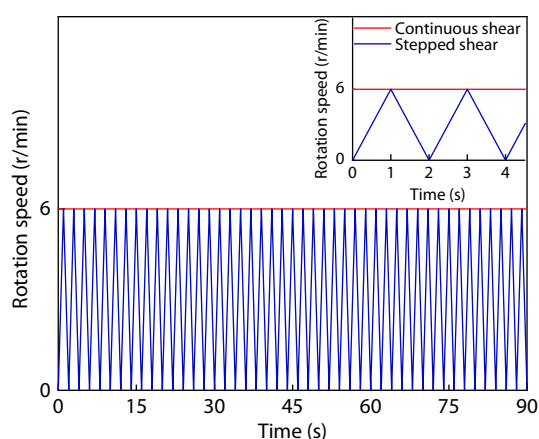


Fig. 2 Schematic diagram of continuous and stepped shear modes.

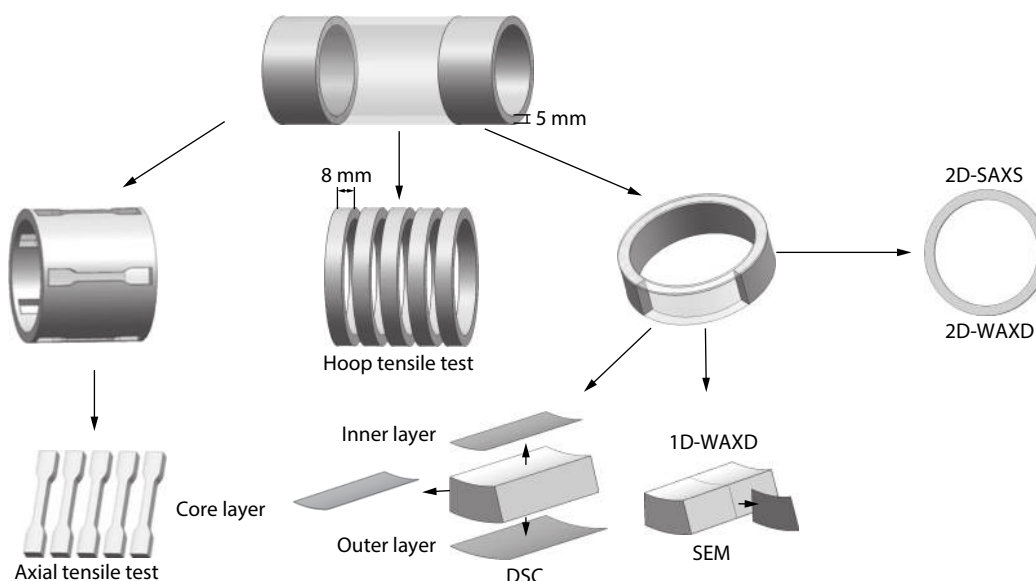


Fig. 3 Diagram of *i*PP pipe with rotational shear test sampling.

can be calculated by Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

in which ΔH_m is the melting enthalpy measured by the sample, and ΔH_m^0 is the standard melting enthalpy of completely crystallized *i*PP. For *i*PP samples in which α -crystal and β -crystal exist at the same time, the standard melting enthalpy of α -crystals in *i*PP is 177 J/g and the standard melting enthalpy of β -crystals in *i*PP is 168.5 J/g.

Wide-angle X-ray diffraction (WAXD) analysis

During the experiment, Bruker D8 DISCOVER (Germany) with CuK α radiation ($\lambda = 0.154$ nm) operating at 40 kV and 40 mA was used to analyze the samples (as shown in Fig. 3) by wide angle X-ray diffraction, and the orientation and crystallization of the samples were obtained. The relationship between the diffractive intensity and azimuth angle of each crystal plane on one dimension was obtained by one-dimensional wide-angle X-ray diffraction, and the diffractive intensity of each crystal plane index was calculated. Combined with Turner-Jones formula,^[34] the relative amount of the β -crystals K_β was calculated:

$$K_\beta = \frac{I_{\beta(300)}}{I_{\beta(300)} + I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)}} \quad (2)$$

in which $I_{\beta(300)}$, $I_{\alpha(110)}$, $I_{\alpha(040)}$ and $I_{\alpha(130)}$ are the diffraction peak integral intensity of β -crystal (300), α -crystal (110), (040) and (130) planes, respectively. The 1D-WAXD test was controlled to avoid the phase transition or recrystallization in the heating process of DSC, which makes the measured K_β more reliable.

In the 2D-WAXD test of pipe samples, the orientation of the molecular chains in the inner layer of the samples was usually characterized by the calculation of the peak at half height in the fitting curve, which was calculated as follow:

$$\Pi = \frac{180^\circ - H}{180^\circ} \times 100\% \quad (3)$$

in which H is the width of the peak at half height in the I/A (intensity/azimuth) curve obtained from 2D-WAXD.

Small-angle X-ray scattering (SAXS) analysis

Measurements of small angle X-ray scattering were performed by Xeuss2.0 (France) small angle X-ray scatter with CuK α radiation. The samples were cut to 1 mm and placed at 2500 mm from the fracture. The SAXS image acquisition time of each data frame was 5 min.

Mechanical properties measurement

In this experiment, the hoop and axial mechanical properties of the pipes were tested by using a universal material testing machine (Instron Instrument Model 5967, Instron/America). The hoop and axial tensile properties of the samples were tested at the rate of 10 mm/min at room temperature. The hoop tensile specimen was annular and the axial tensile sample was dumbbell (as shown in Fig. 3).

RESULTS AND DISCUSSION

The Results of Mechanical Properties Testing

As mentioned above, in practical use, the hoop stress of the pipe is about twice as much as the axial stress.^[4] However, the

hoop performance of the pipe is generally worse than that of the axial direction due to extrusion-traction processing. In the experiment, different modes of hoop shear were applied to improve the hoop performance of the pipes, and the results are presented in Fig. 4.

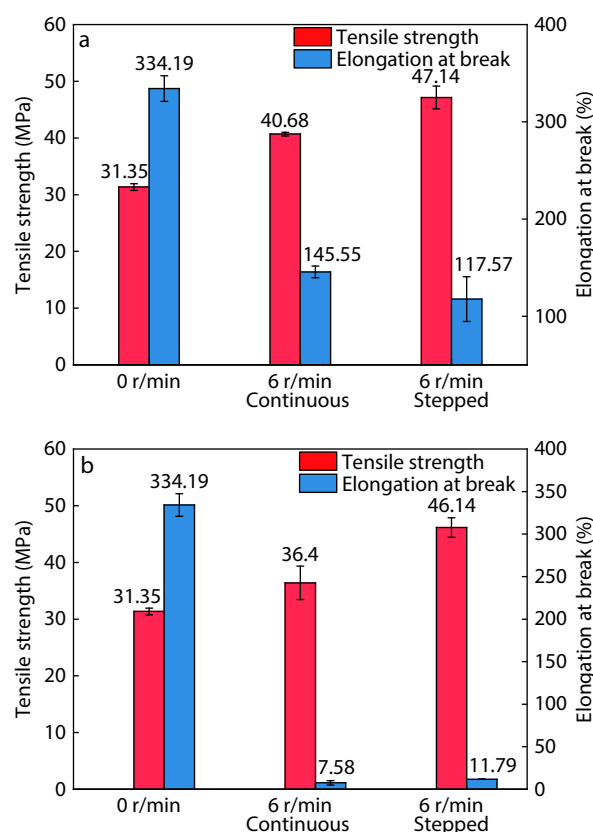


Fig. 4 (a) Hoop mechanical properties and (b) axial mechanical properties of *i*PP pipes.

Fig. 4(a) illustrates that, compared with the sample with non-rotating mandrel, the hoop strength of samples prepared by continuous and stepped shear was improved by 29.8% and 50.4%, respectively. Besides, the hoop elongation at break of samples prepared by continuous and stepped shear decreased in varying degrees, by 56.5% and 64.8%, respectively. Obtained from Fig. 4(b), the axial strength of samples prepared by continuous and stepped shear was improved by 16.1% and 47.18%, respectively. However, the elongation at break of the samples prepared by shear decreased greatly. When the hoop shear fields were applied, the axial and hoop tensile strength of the samples were improved due to the transformation of morphology. And the stepped shear contributed to the improvement of axial and hoop tensile strength more obviously.

Fig. 4 shows that the elongation at break of the samples prepared by rotational shear all decreased. In order to further characterize the toughness of the pipes, the fracture surfaces of the samples were observed by SEM (see Fig. 5).

As can be seen from Fig. 5, most of the fracture zones of the samples prepared by continuous shear were brittle,

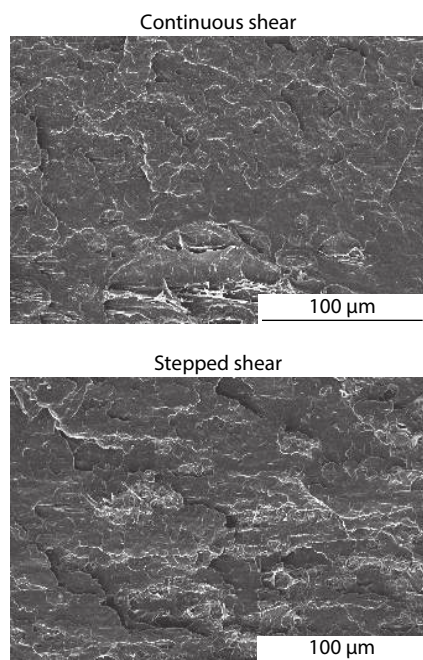


Fig. 5 SEM images of axial tensile section under continuous and stepped shear.

while the fracture zones of the samples prepared by stepped shear were crisscrossed with brittleness and toughness. It is well accepted that β -crystals have a great influence on toughness of materials.^[23,32,35] Consequently, we speculate that the decrease of toughness of the samples with rotational shear is related to the content of β -crystals and further experiments were conducted.

The Results of Crystalline Parameters

Analysis of content of β -crystals (1D-WAXD)

Generally speaking, the toughness of polymer materials will decrease sharply while improving the strength of polymer materials, but for *i*PP, β -crystals will improve the toughness of *i*PP materials.^[33,36,37] β -Crystal has a better absorption effect on impact energy owing to the loose arrangement of molecular chains, and the impact strength of β -PP is 1–2 times higher than that of α -PP.^[36,38] However, β -crystal is thermodynamically unstable. With temperature increasing, β -crystal will transform to thermodynamically stable α -crystal.^[39–41] Naturally, in order to verify the conjecture on the relationship between content of β -crystal and toughness, 1D-WAXD was carried out.

The linear WAXD intensity profiles are shown in Fig. 6. In samples with rotational shear, the diffractive peak of β -crystal plane (*i.e.* (300) β) almost disappeared. This finding is consistent with that of Varga who found the shearing restrained the formation of β -crystal in *i*PP with nucleating agents.^[42] It is obvious that the decrease of toughness of the samples with rotational shear is attributed to the fewer β -crystals owing to the counteraction effect, and the content of β -crystals in the samples obtained by Eq. (2) (see Fig. 6) has also affirmed that. In addition, as Fig. 6 shows, the relative content of β -crystals in sample without shearing ($K_\beta = 17.39\%$) is far more than the others, and that is consistent with the previous analysis. For

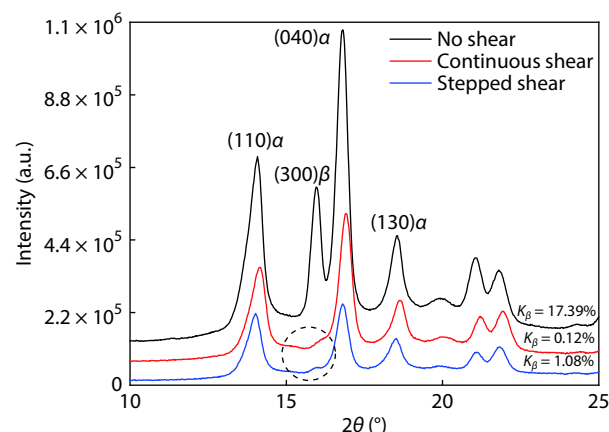


Fig. 6 Linear WAXD intensity profiles.

comparison between samples prepared under different shearing modes, by observing the part of the dotted line, it can be intuitively found that the sample with stepped shear has a more obvious diffractive peak of (300) β . Combined with the content of β -crystals, this result may be explained by the fact that there is a little bit higher content of β -crystals in the sample with stepped shear.

Using De value based on Doi-Edwards theory,^[43] Grizzuti^[44] proposed that the formation of shish-kebab was the result of the counteraction between the stretching of molecular chains and relaxation.

$$De = \gamma \times \tau \quad (4)$$

where γ is the shear rate, and τ is the terminal relaxation time of the molecular chain. Extensive research has shown that shish-kebab with larger De value is easier to form.^[45–47] But for *i*PP with β -nucleating agents, the content of β -crystals decreases sharply as the shear rate increases.^[48–50] In other words, under continuous shearing, the more shish-kebabs and fewer β -crystals will form with shear rate increasing. As a result of that, the increase of tensile strength and the decrease of toughness in *i*PP with β -nucleating agents will occur at the same time. Inspired by Fig. 6, it is possible to produce reinforced and toughened pipes by adjusting the shear mode.

Analysis of crystal morphology (SEM)

Fig. 7 shows the SEM images of the cross-section of *i*PP pipes under different shear modes. The inner layer (close to mandrel), the core layer and the outer layer (close to mold cavity) of pipes were studied to explore the various morphologies in different parts. The arrow indicates the flow direction of the melt.

It is well accepted that spherulite is the main morphology of crystals in *i*PP.^[35,51,52] In the processing engineering, in addition to the formation of the fiber-like crystals, the β -nucleating agent in the melt is self-assembled into the fiber, and the *i*PP is perpendicular to the fiber core through the intermolecular interaction.^[7,12] And the fibrous crystals are formed.

The differences between samples are highlighted in Fig. 7. Under continuous and stepped shear, the samples produced regular oriented crystals (*i.e.* shish-kebab) but different in size. The sample with stepped shear produced small and dense shish-kebabs, but the other produced large and loose ones.

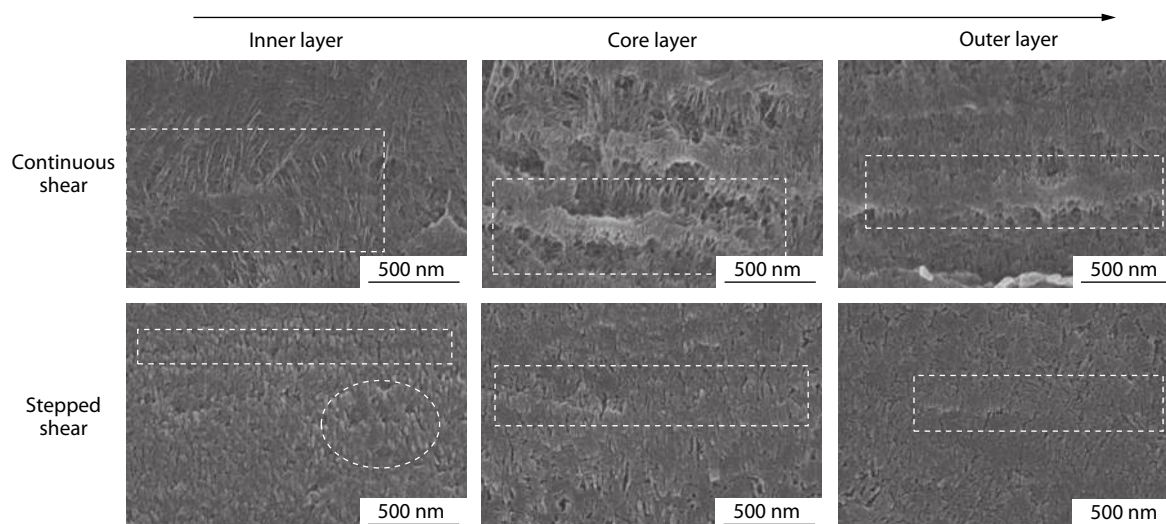


Fig. 7 Scanning electron micrographs of three layers of the inner, core and outer layers under continuous and stepwise rotational shear (the arrow is the direction of melt flow and the clear shish-kebabs are marked with the dotted boxes).

With the action of external stress, the longest chains, as shish precursors, recruiting other chains adjacent to them into formation of the shish.^[15,16] And the shish induced lamellar epitaxial growing along the transverse direction, resulting in the formation of shish-kebab.^[15] With the same maximum shear rate and the same cooling method being used, the *i*PP melt prepared by stepped shear produced less shear heat, resulting in the faster cooling rate and the more oriented structures. Finally, the sample prepared by stepped shear produced small tightly stacked shish-kebabs due to the retention of the straightening oriented molecular chains promoting the formation and growth of shish-kebabs.

It is apparent from Fig. 7 that the content of shish-kebabs in the core layer is the highest. Historically with the increase of shear rate, it is easier to form shish-kebab.^[53] In the experiment, the shear rate decreased gradually from the inner layer to the outer layer. However, because of the cooling mode of RSS, the temperature of melt decreased according to the order of the core layer, the outer layer and the inner layer. Due to the low temperature of the inner melt, the molecular chains were frozen firstly during the processing. Under the synergistic effect of temperature and shear rate distribution, the core layer was subjected to the largest shear work, thus forming the most oriented structures.

Through SEM observation, the morphologies of the polymer under different shear modes can be qualitatively understood. However, quantitative data need further experiments.

Analysis of orientation (2D-WAXD)

Through the SEM observation, it is obvious that different morphologies and sizes of shish-kebabs were formed under stepped and continuous shear. Obtained from Fig. 7, it seems that shish-kebabs in samples with rotational shear are arranged regularly in a certain direction. It is well acknowledged that the orientation of molecular chains will have a great influence on the mechanical properties of polymer materials. Consequently, for further studying the relation between morphology and mechanical properties of samples with rotational shear, 2D-

WAXD measurement was performed to verify the orientation structure observed in SEM.

In Fig. 8, from inside to outside, the two diffractive rings of crystal planes (Debye rings) corresponding to the (110) α and (040) α can be clearly observed. Obtained from the 2D-WAXD images, there is no concentrated diffractive arc in the equatorial direction of the diffractive ring on the (040) α of all samples. In contrast, arc-like diffraction in the meridian direction of the (040) α occurred. The appearance of the arc-like diffraction is due to the more concentrated diffraction of the electron cloud in the orientation of the molecular chains.^[54] Qualitatively speaking, the overall orientation in the core layer and the outer layer of samples is higher than that in the inner layer. In addition, except for the inner layer, the degree of orientation in the sample prepared by stepped shear is higher than that in the continuous one. In order to accurately characterize the orientation of crystals, combined with the Eq. (3), the quantitative results of orientation have been shown in Fig. 9, and it is consistent with the previous analysis.

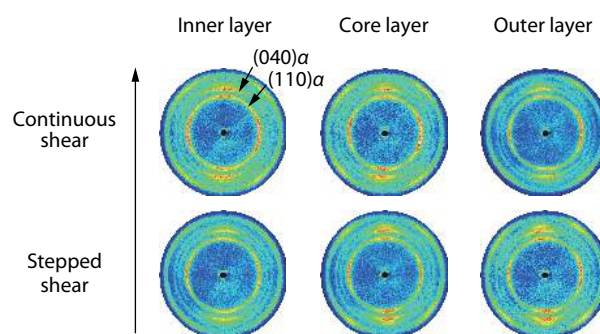


Fig. 8 2D-WAXD patterns of samples with rotational shear (the arrow is the direction of melt flow, and the diffractive rings of (110) α and (040) α are pointed out).

The inner *i*PP melt clings to the mandrel, resulting in lower processing temperature. For the pipes with rotational shear,

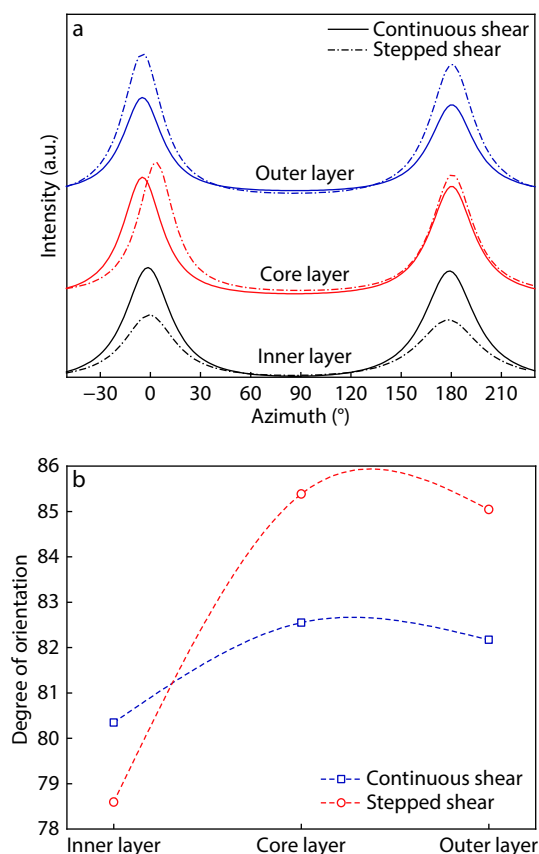


Fig. 9 (a) Azimuth scanning map and orientation factor of samples with rotational shear (the azimuthal profile belongs to (040) a); (b) degree of orientation in each layer.

most of molecular chains in the inner layer cannot fully orient before being frozen, while for the core and outer melt, because of the velocity inertia in the fluid, the shearing force was stronger than that in the inner melt. Due to the synergistic effect of the stronger shearing force and higher temperature, higher oriented crystals were obtained. Moreover, more oriented crystals were retained, and a possible explanation for this might be that the melt under stepped shearing cooled faster due to less shear heat produced by stepped shear.

Analysis of crystal size of crystals (SAXS)

In order to further verify the differences between the size of shish-kebabs observed in SEM images, SAXS measurement was performed, and the SAXS patterns have been shown in Fig. 10.

As can be seen from Fig. 10, in samples with continuous shear and stepped shear, there are acicular diffractive fringes in the equatorial direction, indicating the existence of shish. However, in the meridian direction, there are obvious differences between the fan diffraction images attached to shish. The diffraction image of the sample with stepped shear shows a wide fan diffraction pattern, which qualitatively reflects that there are more kebabs with more compact stacking attaching to shish. For quantitative analysis, one-dimensional electron density correlation function ($K(z)$)^[55,56] of pipes with different shear

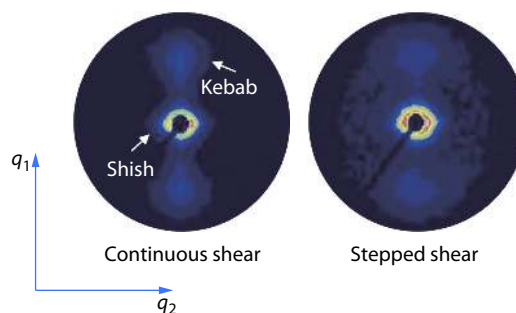


Fig. 10 Small angle X-ray scattering pattern (the scattering vectors along and perpendicular to the fiber axis direction are defined as q_1 and q_2 , respectively).

modes is as follows (see Fig. 11).

$$K(z) = \frac{\int_0^\infty I(q_1) \cos(q_1 z) dq_1}{\int_0^\infty I(q_1) dq_1} \quad (5)$$

in which z is the length along the normal direction of the lamella. Through the analysis of $K(z)$, the long period of the crystal region and amorphous region can be obtained. Fig. 11 shows that $K(z)$ is an autocorrelation one-dimensional function near the origin. The lowest value of the first trough of the curve is along the intersection of the extension line parallel to the Z -axis and the linear part of the first descending interval to fit the extension line of the baseline of the one-dimensional correlation function, and its transverse coordinate value is the average thickness of kebab lamellae in the system (see Fig. 11).^[17] The abscissa corresponding to the maximum of the first wave peak is the average long period (Lp) of the shish-kebab system.^[17] The average long period of shish-kebabs and average thickness of kebabs are listed in Table 1.

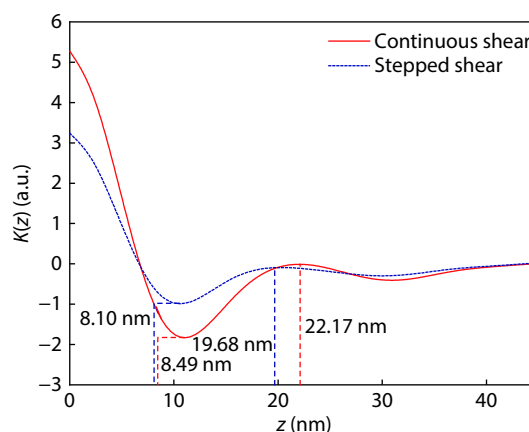


Fig. 11 $K(z)$ curve of pipes with different shear modes.

Table 1 Average long period of shish-kebab and average thickness of kebabs in samples with two shear modes.

Mode	Average long period/thickness (nm)	
	Shish-kebab	Kebab
Continuous	22.17	8.49
Stepped	19.68	8.10

In order to better characterize the specific size of shish-kebabs, the average lateral length of kebabs is necessary. Consequently, the SAXS data analysis was performed. Fig. 12 was obtained by integrating the diffractive intensity along the q direction (as shown in Fig. 12).

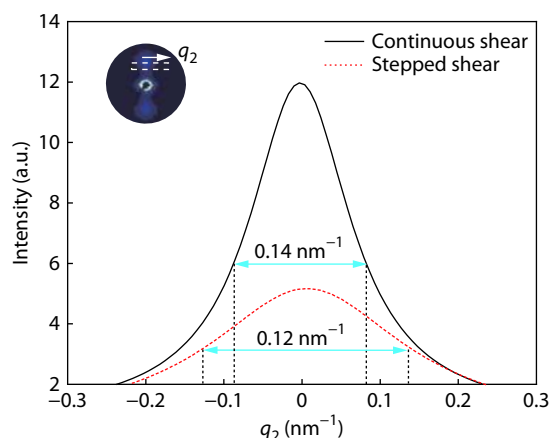


Fig. 12 One-dimensional scattering intensity distribution curve of pipes under different shear modes.

For isotropic samples, Lorentz correction of scattered intensity is needed, but it is not necessary for perfectly oriented samples.^[57] However, there is no unified processing method in the transition stage between the two. In this study, owing to the high degree of orientation (see Fig. 9), Lorentz correction was not performed. The lateral size of kebabs (L_{SAXS}) can be obtained from Fig. 12.^[55,56,58,59]

$$L_{\text{SAXS}} = \frac{2\pi}{\Delta q_2} \quad (6)$$

where Δq_2 is the width of the peak at half height in the I/q_2 curve. Combined with Eq. (6), the $L_{\text{SAXS}} = 43.84$ nm of the sample with continuous shear and the $L_{\text{SAXS}} = 29.66$ nm of the sample with stepped shear can be obtained. Overall, the data of SAXS is consistent with SEM images.

Analysis of crystallinity (DSC)

The results of the orientation and crystallization analysis suggest the formation of different size shish-kebabs. In order to further quantify the crystallinity of *i*PP under different shear modes, DSC was performed. The melting temperature and melting enthalpy of the samples obtained by DSC curve are presented in Table 2.

Table 2 Comparison of DSC test results of *i*PP pipe.

Mode	Melting peak temperature (°C)			Melting enthalpy (J/g)		
	Inner	Core	Outer	Inner	Core	Outer
Continuous	164.53	163.26	164.29	101.7	102	103
Stepped	165.77	165.38	165.48	102	103.5	101.1

Combined with the above Eq. (1), and according to the data in Table 2, the crystallinity of the sample was calculated. The results obtained from the preliminary analysis of DSC are summarized in Table 3.

It can be obtained from Table 3 that, with a certain allow-

Table 3 Comparison of crystallinity of each layer of *i*PP pipe.

Mode	Crystallinity		
	Inner	Core	Outer
Continuous	57.46%	57.63%	58.19%
Stepped	57.65%	58.54%	57.18%

able error, except for the outer layer, the crystallinity of samples prepared by stepped shear is higher than the other. For the inner layer of the pipe, the stepped shear provides a large shear stress with less shear heat, part of the molecular chains are quickly frozen by the cooling system before the orientation, resulting in about the same crystallinity. For core melt, the molecules are stacked more closely, the oriented molecules are hard to recover due to the larger shear stress and lower shear heat, resulting in the formation of dense and small clusters of crystals. However, for outer melt, due to less shear heat and lower processing temperature, the molecular relaxation time increased, and the crystallization rate decreased. This also leads to a lower crystallinity of *i*PP in the outer layer.

Combined with morphology analysis, the reasons for the differences in mechanical properties of samples under different shear modes have surfaced. Better hoop mechanical properties of samples prepared by stepped shear correspond to the highly oriented shish-kebabs along the hoop direction. Furthermore, obtained from Fig. 4(a), the shish-kebab with smaller size but denser kebabs can improve the tensile strength of pipes to a greater extent. The results might be explained by the interlocking structure of the shish-kebab (see Fig. 13). In the stage of slip deformation of the lamella after yielding in the amorphous region, the interlocked shish-kebabs make the slip deformation between the lamella and the lamella more difficult.^[60,61] It is reasonable to hypothesize that the small and dense shish-kebabs produce more interlock structures, which makes the hoop lamellar slip more difficult, and then improves the hoop tensile properties of the pipes. Furthermore, the elongation at break of the pipe was drastically decreased while the hoop strength of the pipe was increased owing to the higher orientation structure under stepped shear.^[62]

Moreover, a hypothesis is also proposed for the improvement of axial mechanical properties of samples prepared by shear. Combined with the analysis of orientation and crystallization, we suggest that the small and dense kebab lamellae produced in the hoop direction may lead to the arrangement of shish-kebabs closer to each other (see Fig. 13). Moreover, there are random lines running through each other in the kebabs on different shishs, resulting in a more compact "shish-kebab interlock" structure. When stretching in the axial direction, it is equivalent to stretching the shish-kebabs arranged along the hoop direction in the direction of vertical shish. It is the interaction force between shish-kebab that leads to a great increase in the axial tensile strength. Additionally, the elongation at break of the samples prepared by shear decreased greatly. Under the action of axial tension, the isotropic lamella of the conventional sample will go through the process of lamella rotation and lamella slip to respond to the tensile action. However, the distribution of kebabs in the

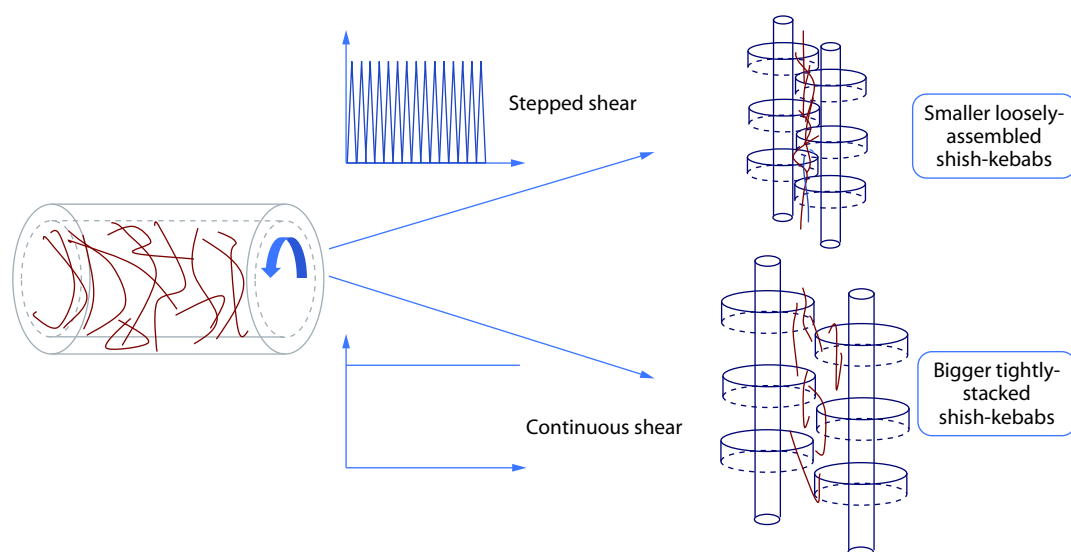


Fig. 13 Schematic diagram of shish-kebab structure under different shear modes.

tensile direction of the dynamic sample was regular and difficult to move, resulting in micro-deformation difficulty and brittle fracture.

CONCLUSIONS

This paper has argued the difference between morphologies and mechanical properties of *i*PP pipes prepared under different shear modes. The shear modes in the experiment were precisely controlled due to the self-made rotational shear system (RSS). By means of SEM, SAXS and DSC tests, it was found that samples prepared under both shear modes contained shish-kebab structure, but the size and density of shish-kebabs were different. Moreover, through WAXD, the molecular chains of *i*PP had a higher degree of orientation under stepped shear, and shish-kebabs were easier to be produced. Due to the combined effect of the shear heat and the cooling rate, the small and dense shish-kebabs were produced under stepped shear and large and loose ones were produced under continuous shear. Owing to the special morphology, the sample prepared by stepped shear shows better mechanical properties in both axial and hoop directions. This study provides a deeper insight into the relationship between the shear modes during processing and the morphology-property of polymer.

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