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Control of Rotation Extrusion over Shish-Kebab Crystal Alignment in Polyethylene Pipe and Its Effect on the Pipe's Crack Resistance

Min Nie, Qi Wang
State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University,
Chengdu 610065, China
Correspondence to: Q. Wang (E-mail: poly.nie@gmail.com)

ABSTRACT: A self-designed rotation extrusion system was adopted to extrude polyethylene (PE) pipe. The experimental results showed that when the mandrel and die rotated in the same directions during the PE pipe extrusion, apart from the axial stress, all polymer melts in PE pipes were also subjected to the hoop stress so that the formed shish-kebab crystal in the whole pipe deviated from the axial direction greatly, which was further fixed by the double cooling on both inner and outer walls. As a result, the PE pipe with better resistance to slow crack growth was prepared. As compared to the PE pipe produced by the convention extrusion, the crack initiation time of the PE pipe manufactured by the novel method increased from 27 to 174 h, by 544%. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Polyethylene (PE) pipes have been widely used as gas or water transport pipes owing to their comprehensive advantages, such as lightweight, low cost, corrosion resistance, and easy processing.[1,2] However, in the convention extrusion of PE pipes, due to the strong axial drag force of traction device, the molecules orient along the axial direction and subsequently the formed shish-kebab crystals also parallel to the axial direction,[3,4] so the axial performance of the pipe is much higher than the hoop. Unfortunately, the pressurized pipe mostly is subjected to a hoop stress in its application, resulting in that a kind of failure mode named slow crack growth (SCG) often happens in the convention extruded PE pipe, i.e., a crack often propagates through the pipe wall, parallel to the axis.[5]

Up to now, many efforts have been devoted to improving PE pipe's resistance to SCG and many technologies also have been developed, such as the solid deformation processing,[6] die-drawing,[7] vibration extrusion,[8] rotation extrusion,[9–11] etc. Among the above approaches, rotation extrusion has attracted much attention. Compared with the convention extrusion, during the plastic pipe's rotation extrusion, a hoop stress was generated by die or mandrel rotation except the axial stress to induce the shish-kebab crystals apart from the axial direction so that the pipe's properties in the axial and hoop directions was balanced and its resistance to SCG was enhanced.[10,12] However, the previous studies focused on mandrel rotation extrusion where the inner layer of the pipe rotated together with the mandrel while the outer layer remained stationary, so the hoop stress imposed by the mandrel rotation was gradually decreased from the inner to the outer layer. As a result, there was no effect on the molecular orientation and crystal morphology in the outer layer. Moreover, the formation of the shish-kebab crystal resulted from the competition between stress-induced molecular stretching and subsequent relaxation.[13] A higher temperature quickened the molecular relaxation and thus was not favorable to retain the oriented molecules and the resulting shish-kebab crystals. The above pipe's cooling method was to cool the outer surface by water to slow the inner surface cooling rate, so it was very difficult for the inner layer to maintain the shish-kebab crystals obtained by rotation extrusion due to very fast relaxation. Therefore, the convention rotation extrusion was of little efficacy on improving PE pipe's performance.[14,15]

On the basis of polymer crystallization's sensitivity to stress and temperature, we have designed and constructed a novel rotation extrusion processing system,[16] which could achieve the independent or integrated rotation of both mandrel and die as well as the double cooling of both inner and outer walls, so as to control the stress and temperature field during the PE pipe extrusion. In this way, the crystallization and orientation of PE could be adjusted to produce the PE pipes with higher performances.[17–19] This article further focused on the effects of the mandrel-die-same direction-rotation extrusion on the obtained PE pipe's microstructure and resistance to SCG and studied the relationship among the stress, cooling rate, and final structure, so as to prepare the PE pipe with better resistance to SCG.

EXPERIMENTAL

Materials

A commercially available HDPE pipe resin TR480 provided by Sinopec JinFei Petrochemical, Shanghai, China, was used in this study. Its melt flow index, measured at 190°C under 2.16 kg, was 140 mg/10 min, and the weight average molecular weight was 450,000 g/mol and the molecular weight distribution (M_w/M_n) was about 6.54. Arkopal OP-10, a detergent, was purchased from Kelong Chemical Agents, Chengdu, China to accelerate the SCG tests.

Sample Preparation

In this study, the self-designed rotation extrusion system was used to prepare PE pipes. This system has the following features: firstly, both the mandrel and the die could rotate, either separately or integratedly, in the same direction or in the opposite directions; the rotation speed and direction could be easily adjusted by the motor and gear reduction system, so as to change the hoop stress imposed on the melt. Secondly, the system has a hollow mandrel, through which a cooling media, such as the air and water, can be transmitted to cool the interior surface of the pipe. As a result, its inner and outer wall can simultaneously cool down, and their cooling rate and temperature gradient cross the pipe can be adjusted by changing the temperature and flow rate of the cooling medium. In this study, when the mandrel and die rotated in the same direction at the speed of 5 rpm, besides water cooling on the outer wall of PE pipes, the cool compressed air was introduced through the pipe to achieve the quick cooling of the inner wall. The extruded PE pipe was named as SPE. For the purpose of comparison, the convention extrusion was also carried out under the same processing conditions but without mandrel and die rotation, and the extrudate was named as TPE. The outer diameter and wall thickness of the final PE pipes obtained in this experiment were $\sim$32 and $\sim$3 mm, respectively.

The prepared PE pipe was equally divided into three layers along the thickness direction, that is, inner layer, middle layer, and outer layer. The thickness of each layer was $\sim$1 mm.

Characterization

DSC Analysis. Q20 differential scanning calorimetry apparatus (TA instrument, USA) was explored to conduct the thermal analysis of the samples. Temperature calibration was carried out with indium and zinc standards. The 6–8 mg specimens from each layer of the PE pipe were heated in nitrogen atmosphere from 40 to 160°C and the heating rate is 10°C/min.

SEM Observation. The crystal structure of the PE pipes and the fibrils morphology in the fracture surfaces after the cone test for various pipes were observed by an Inspect F (FEI) SEM instrument at 0.5 Torr and 20 kV. Prior to the observation, the SEM samples were cut from the pipes and put into the 50°C permanganic etchant for 3 h to remove the amorphous phase, and then were carefully washed by diluents sulfuric, hydrogen peroxide, and distilled water. Finally, the SEM samples were gold-sputtered for observation.

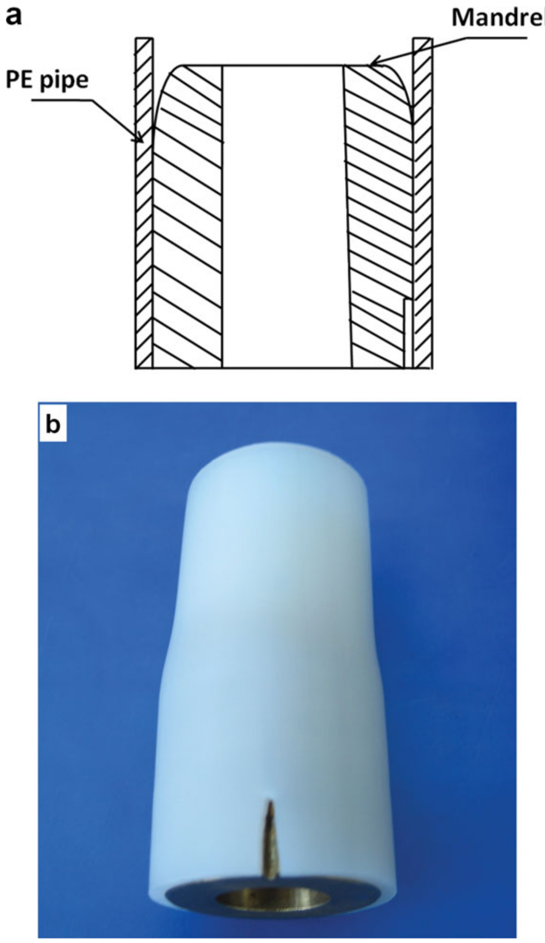

Figure 1. The schematic diagram (a) and photo (b) for PE pipe's cone test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Shrinkage. The strips of $\sim$2 cm length were cut along the axial direction from the prepared PE pipes and the ring was cut along the hoop direction of the rotation extruded PE pipe, then they were put into glycerol and kept in 145°C until no further dimensional changes occurred. The shrinkage was then measured based on the ratio of the length of the samples before to after heating.

Two-Dimensional Wide-Angle X-Ray Scattering. The two-dimensional wide-angle X-ray scattering experiment was carried out at synchrotron radiation X-ray scattering station (U7B, $\lambda = 0.154$ nm) in National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The sample was cut along the axial direction and was placed with the PE pipe's axial direction perpendicular to the beams.

Cone Tests for SCG. The PE pipe's resistance to SCG was evaluated by an environmental stress crack test called cone test according to ISO 13480: 1997. The schematic diagram and photo for PE pipe's cone test were shown in Figure 1. In this test, a 15 cm long length of the pipe was cut from the prepared PE pipes and inserted by a metallic cone with 1.12 times bigger diameter than the nominal internal diameter of the pipes.

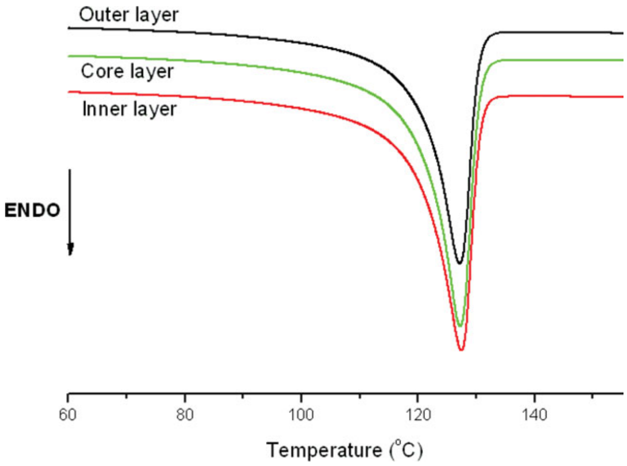

Figure 2. DSC curves of each layer along the wall thickness for the rotation extruded PE pipe. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A single 10 mm long notch was cut by a fresh razor blade along the axial direction on one end of the pipe. Then the assembly was immersed in 5 wt % aqueous solution of Arkopal OP-10 at a well controlled temperature of 80°C. The crack length increment was measured at regular time intervals and then the curve of the crack length increment versus time was plotted and extrapolated to the time axis. Their intersection point was defined as the crack initiation time.

RESULTS AND DISCUSSION

Effect of the Mandrel-Die-Same Direction-Rotation Extrusion on the Morphological Structure of Polyethylene Pipe

The changed crystal structure along the wall thickness for the rotation extruded PE pipe could be demonstrated by DSC experiment. From Figure 2, it was seen that their melting temperatures of the three layers were nearly same, about 127°C. During the rotation extrusion, the polymer melts were subjected to the hoop stress by the rotation of the mandrel and die as well as the axial stress by axial traction. The resulting stress would induce molecular orientation and the formation of shish-kebab crystals. Fast cooling was favorable to the fixation of shish-kebab crystals with more thermostatically stable orientation structure. Therefore, higher cooling rate of outer layer would cause the imperfect crystal to reduce the melting temperature, which yet could be compensated by the fixation effect of higher cooling on the stress-generating shish-kebab crystals during the rotation extrusion. As a result, the melting temperatures of the samples along the wall thickness did not change nearly.

Figure 3 further showed the crystal morphologies at different zones for the rotation extruded PE pipe. Clearly, all zones were covered with the shish-kebab crystals which did not align along the axial direction but at an angle relative to the axial direction. The angle relative to the axial direction from the outer to inner layer were 50°, 52°, and 45°, respectively. As compared with the shish-kebab parallel to the axial in the convention extruded PE pipe,[17] the shish-kebab structure was more suitable for improving PE pipe's performance.

The alignment direction of the shish-kebab crystals depended on the orientation direction of the molecules, which was always consistent with the direction of the external stress,[20] so

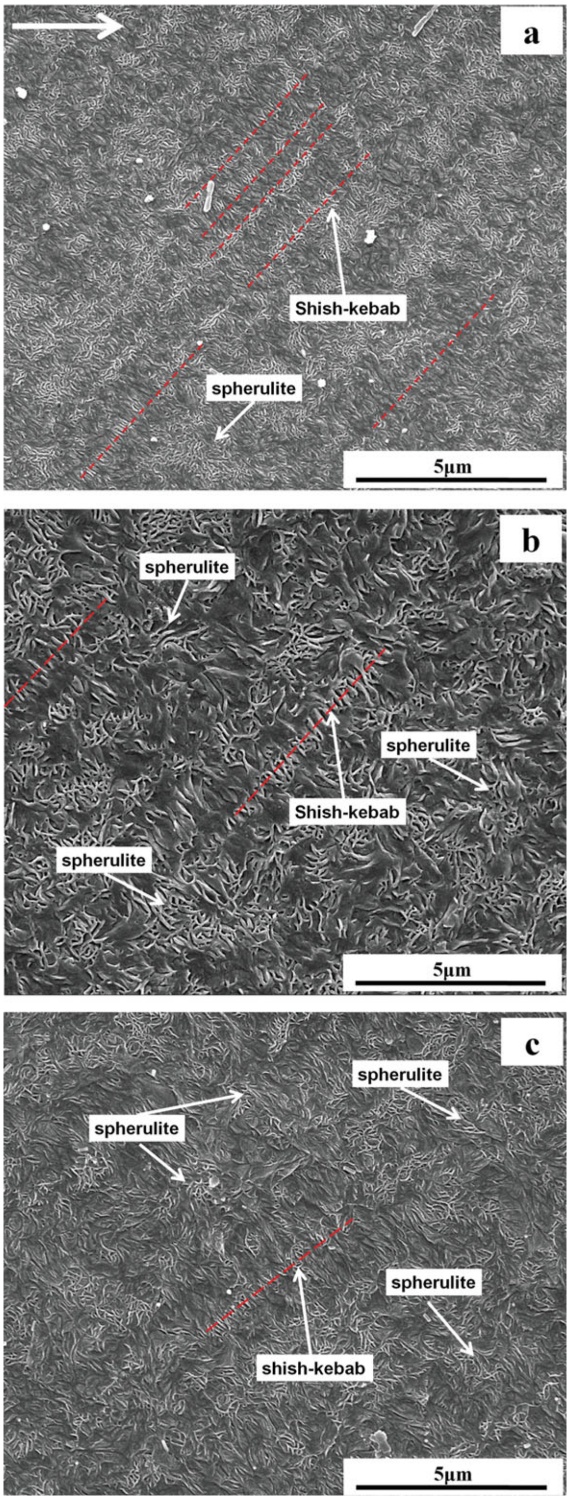

Figure 3. SEM photos of the rotation extruded PE pipe. (a) outer layer, ×20,000; (b) core layer, ×20,000; (c) inner layer, ×20,000; The direction of arrow showed the axial direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

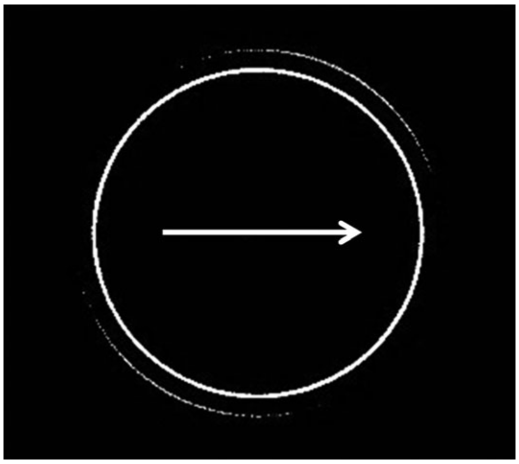

Figure 4. Two-dimensional WAXS pattern of the PE pipe by rotation extrusion. The direction of arrow showed the axial direction.

controlling the direction of the stress imposed on the melt was expected to adjust the directions of the shish-kebab crystals in PE pipe. During the mandrel-die-same direction-rotation extrusion, besides the axial stress, all melts in the PE pipe were subjected to the hoop stress by mandrel and die rotation. As a result, the direction of the resultant force deviated from the axial direction, so the molecular orientation direction changed. Good evidence came from 2D WAXS pattern of SPE in Figure 4. One observed strong reflection of (200) plane of SPE sample and its direction deviated from the axial direction, indicating the preferential orientation was not along the axial direction. As a result, the formed shish-kebab crystals aligned at an angle relative to the axial direction.

Thermal shrinkage also was carried out to investigate the effect of the mandrel-die-same direction-rotation extrusion on PE pipe's orientation. When the sample of the orientation structure was heated above its melting temperature, the oriented molecular chains in the sample would go back to the random orientation state due to the intense thermal motion, usually reducing the sample's length along the orientation direction.[21] For the sample with a higher degree of orientation, its shrinkage ratio would be lower, which was an indicator of the orientation degree of molecular chains in the PE pipe. Figure 5 was the photographs of the strips cut from PE pipe along the axial direction after 30 min annealing at 145°C, and their original length was 2 cm. Clearly, the size of TPE along the axial direction decreased significantly, indicating for the convention extrusion PE pipe there was a preferred orientation of molecular chains along the axial direction. In the conventional extrusion process, the pipe was only subjected to the axial force, so that the molecular chains always tended to orient along the axial direction. When both of the die and mandrel were rotated synchronously, the hoop stress was imposed on the melt to induce the orientation direction of the molecular chains unparallel to the extrusion direction, which also had been proved by the results of SEM. As a result, the orientation degree along the extrusion direction decreased and the axial length of SPE hardly changed. For further confirming rotation extrusion induced the hoop orientation of molecular chains, a ring was cut along the hoop direction of the rotation extruded PE pipe and then was heated above the melting temperature. From Figure 6, it was seen that the diameter of the rotation extruded PE pipe was smaller than its original size of 32 mm, which marked the hoop orientation of molecular chains.

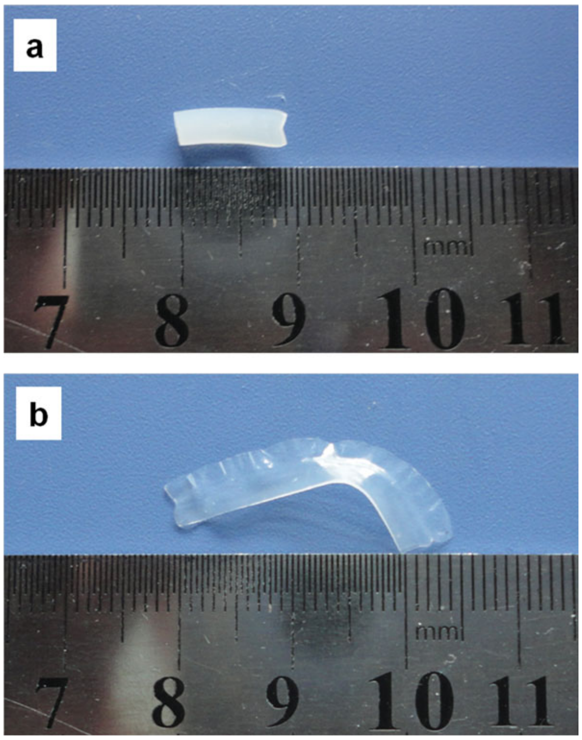

Figure 5. The photographs of the strips from the convention extruded pipe (a) and the rotation extruded pipes (b) along the extrusion direction after 30 min annealing at 145°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the comparison of the amount of shish-kebab between the outer and inner layer in Figure 3, it was found that the inner layer was covered mainly by spherulites and a small

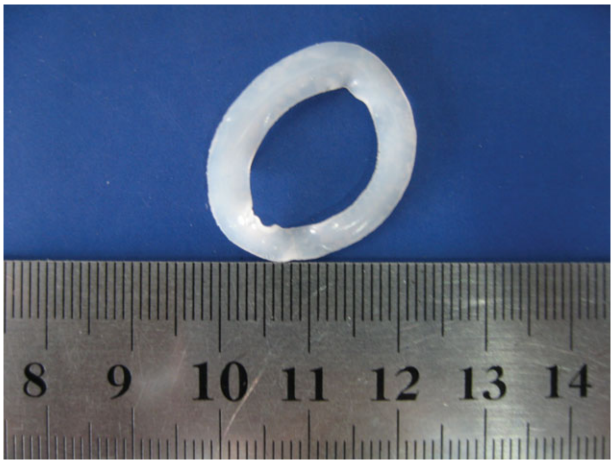

Figure 6. The photograph of the ring cut from the rotation extruded pipe after 30 min annealing at 145°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

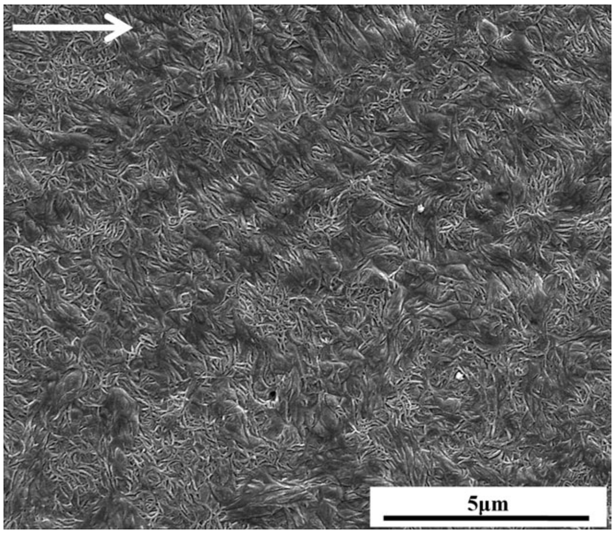

Figure 7. SEM photos of the inner layer of the rotation extruded PE pipe with the inner cooling rate 2.0°C/s, ×10,000. The direction of arrows showed the axial direction.

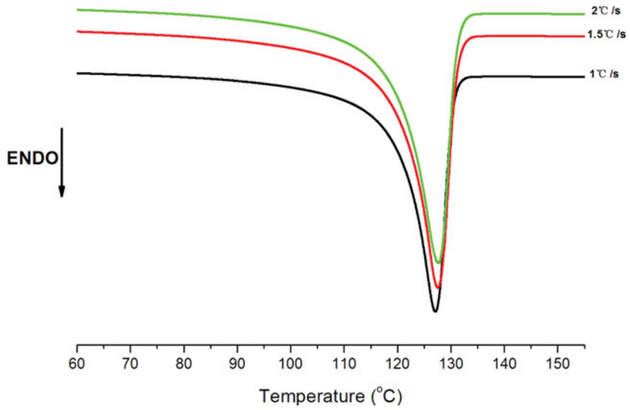

Figure 8. DSC curves of the rotation extruded PE pipes obtained at different inner wall cooling rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of the shish-kebab crystals. The formation of the shish-kebab crystals resulted from the competition between stress-induced chain stretching and subsequent relaxation.[22] A faster cooling rate was expected to slow down the molecular relaxation, which was favorable to retain the oriented molecules. In the subsequent crystallization process, the oriented molecules were bundled in the form of the nucleation spot to promote the epitaxial growth of folded chain lamellae. As a result, the resulting shish-kebab crystals were generated. During the above extrusion, the extruded pipe was cooled by water on its outer surface, resulting in much faster cooling rate, lower temperature, and higher amount of shish-kebab crystals retained in the outer layer of the pipe than those in the inner layer with slow cooling. Therefore, during the rotation extrusion, an effective method to improve the number of the shish-kebab crystals in the inner layer was to increase the inner wall's cooling rate. To get this goal, compressed air as a cooling medium was introduced through their interior to achieve the quick cooling of the inner wall. Compared with Figure 3(c)it could be seen from Figure 7 that the shish-kebab crystals in the inner layer were more dense and compact with the increasing inner cooling rate.

The effect of the different inner wall's cooling rates on the crystal structure of SPE samples was further demonstrated by DSC experiment. Figure 8 showed the DSC curves from the first heating run of the samples. Obviously with the increasing cooling rate, the melting temperature of the samples had a tendency to increase. It was evidenced that high cooling rate could decrease the thickness of the lamellar crystals and cause the imperfect crystal so as to reduce the melting peak. Comparing SEM photos in Figures 3(c) and 7, it was seen that the lamellae thickness of the rotation extruded PE pipe produced by fast cooling rate indeed was lower. This effect was opposite to the results obtained from Figure 8. This could be ascribed to the formation of more thermostatically stable oriented molecular chains during the rotation extrusion, which could increase the melting temperature of the sample. The cooling and stress involved during processing were two key factors for the formation of the oriented molecular chains. The shear stress could induce the high orientation of molecular chains, while the cooling may slow down the molecular relaxation to facilitate the fixation of the oriented molecules. The combined effects improved the molecular orientation degree. During the rotation extrusion, the effects of the melting temperature increase induced by the cooling-fixing orientation structure were higher than those of the melting temperature decrease by cooling-decreasing lamellae thickness. As a result, with the increasing cooling rate the number of the oriented molecular chains went up, so did the melt temperature. This was consistent with the results of SEM.

Effect of the Mandrel-Die-Same Direction-Rotation Extrusion on the Resistance of Polyethylene Pipe to SCG

The changes of direction and amount of the shish-kebab crystals in the PE pipe would exert direct influence on its resistance to SCG. Figure 9 depicted the resistance to SCG for the

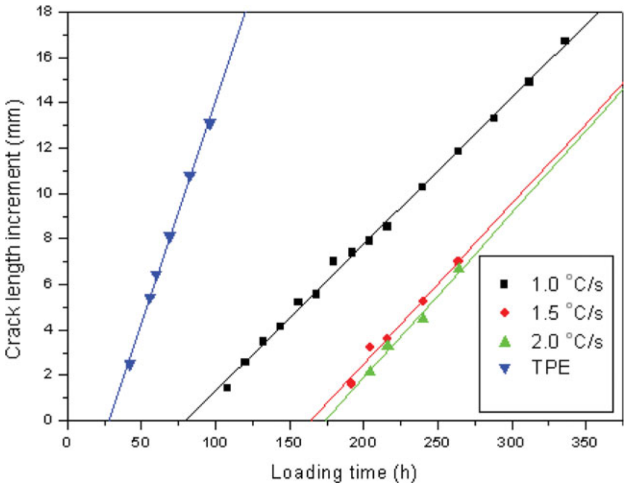

Figure 9. Crack length increment during cone testing for TPE and the PE pipes prepared by different inner wall cooling rate when the speed of die and mandrel rotation was 5 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

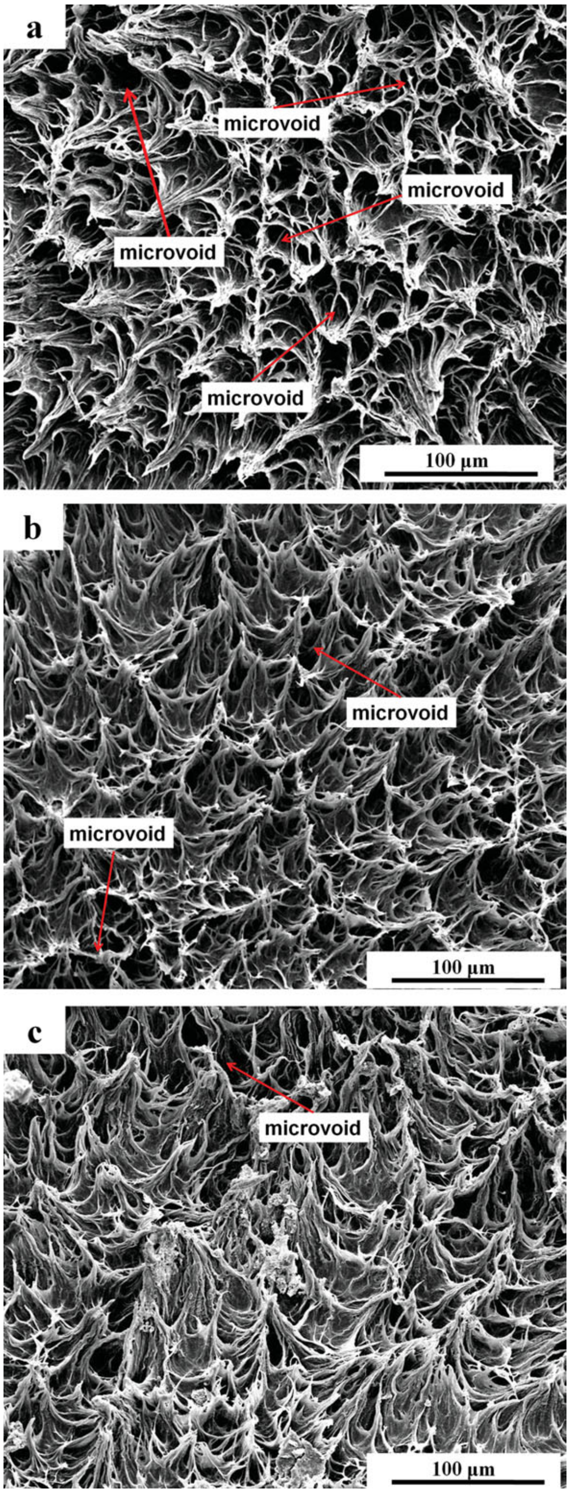

Figure 10. (a) SEM micrographs of fracture zone from the convention extruded pipe, (b) the rotation extruded pipes with the inner cooling rate 1.0°C/s, and (c) 1.5°C/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

convention extruded PE pipe and the rotation extruded PE pipes. It was seen that the crack initiation time of TPE was 27 h. However, when the mandrel and die rotated in the same direction, this time was enhanced and increased rapidly with the increasing cooling rate, even up to the maximal 174 h, indicating that the resistance of the PE pipe to SCG was improved.

Figure 10 showed the fracture morphology of TPE and SPE after the cone testing. Clearly, the fracture morphologies of the rotation PE pipes and the conventional PE pipe were similar, and the fracture zones were highly fibrillated. However, the fractured surface morphologies of the three PE pipes were different. Obviously, for TPE sample, the fracture region was covered with numerous microvoids and the fibrils were slender. Compared to the conventionally extruded PE pipe, fewer microvoids appeared in the fracture region of the PE pipe prepared when both of mandrel and die were rotated and the inner wall's cooling rate was 1°C/s. That is, the fibrils became denser. Garcia et al. confirmed that the denser fibrils could more effectively curb the crack growth within the material,[23] so it was concluded that the rotation extruded PE pipe had better resistance to SCG. This was consistent with longer crack initiation time. However, due to the lower cooling rate of inner cooling rate, the inner layer was covered only by a small amount of the shish-kebab crystals. Therefore, its resistance to SCG was not improved significantly. With the increasing cooling rate, the increase of the amount of the shish-kebab crystals could improve a lot. As a result, Figure 10(c) looked different from Figure 10(b). As shown in Figure 10(c)fibrils in the fracture region of the PE pipe turned to be denser and thicker.

The Relationship Among the Processing Condition, the Morphological Structure and Properties of the PE Pipes

Brown showed the oriented molecule chains parallel to the applied stress could bear larger stress than the ones perpendicular.[21,24] The internally pressurized pipe was subjected to a hoop stress twice as high as the axial stress in its application.[25] However, during the convention extrusion of PE pipe, the

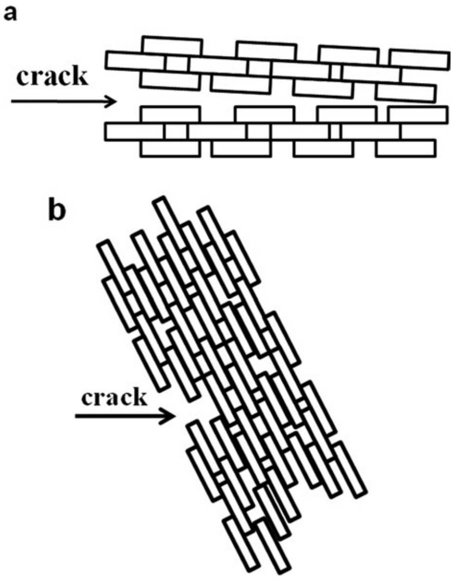

Figure 11. Schematic models for the relation between the direction of shish-kebab and crack growth. (a) shish-kebab crystals parallel to the axial direction; and (b) shish-kebab crystals deviated from the axial direction.

shish-kebab crystals paralleled the axial and the molecules oriented perpendicular to the hoop direction, which was disadvantageous to its resistance to SCG, so the crack easily grew along the axial direction. During the rotation extrusion, a hoop stress imposed on the polymer melt led to the shish-kebab crystal direction deviated from the axial direction and the multiaxial orientation of the molecules, resulting in the increase of the orientation of the molecular chains along the hoop direction. This was favorable to resist the hoop stress in the PE pipe's application and curb the crack growth. Schematic models for the relation between the direction of shish-kebab and crack growth were shown as Figure 11. As a result, the resistance to SCG was perfected. And a fast cooling rate slowed down the molecular relaxation and increased the amount of the shish-kebab crystals. Therefore, the oriented molecule along the hoop direction became more with the increasing cooling rate and the PE pipe became more excellent.

CONCLUSION

During the PE pipe extrusion, through the mandrel and die rotation at the same direction a hoop stress was imposed on all the melt in the pipe to have the shish-kebab crystal in the whole pipe deviate from the axial direction. When introducing the double cooling mode of both inner and outer walls into rotation extrusion, the molecular relaxation could be slowed down and the shish-kebab crystal in the PE pipe could be fixed. As a result, the PE pipe with better resistance to SCG was prepared.

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