

# Effect of the Inner Wall Cooling Rate on the Structure and Properties of a Polyethylene Pipe Extruded at a High Rotation Speed

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**ABSTRACT:** A novel rotation extrusion processing system was self-designed to prepare high-performance polyethylene (PE) pipes. In this study, during the extrusion of the PE pipes at a high mandrel rotation speed, compressed air, as a cooling medium, was introduced through their interior to achieve the quick cooling of the inner wall and the effects of the inner wall cooling rate on the microstructure and mechanical properties of the obtained PE pipes were investigated. The experimental results showed that in contrast to conventional extrusion, the molecular orientation deviated from the axial direction under a high mandrel rotation speed and was fixed by the inner wall cooling; with increasing cooling rate, the orientation degree also increased. On the other hand, cooling promoted the augmentation of spherulites. So when the cooling rate reached a

certain high point, the effect of cooling on the formation of spherulites was stronger than that on the fixation of the orientation. A much higher cooling rate decreased the orientation degree, which was closely related to the performance of the PE pipe. As a result, there was an optimal cooling rate of the inner wall during the rotation extrusion for better performance of the PE pipe. When the cooling rate was  $1.5^{\circ}\text{C}/\text{s}$ , the hoop strength of the PE pipe produced by the novel extrusion method increased from the original 24.1 MPa up to 37.1 MPa without a decrease in the axial strength, and the pipe's crack initiation time increased from 27 to 70 h. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1659–1666, 2011

**Key words:** extrusion; orientation; polyethylene (PE); structure–property relations

## INTRODUCTION

High-density polyethylene (HDPE) pipes have been widely used as gas- or water-transport pipes because of their comprehensive advantages, including their light weight, low cost, corrosion resistance, and easy processing and welding.<sup>1,2</sup> However, because of the strong drag force of the traction device during the conventional extrusion process of polyethylene (PE) pipes, the molecular chains orient along the axial direction, so their axial strength is much higher than the hoop strength.<sup>3</sup> Unfortunately, the hoop stress imposed on internally pressurized pipes is twice as high as the axial stress in their application, the result of which is that a crack splits easily along the axial direction and grows quickly.<sup>4,5</sup> Therefore, changing the molecular orientation direction in plastic pipes is an important approach for enhancing the performance of PE pipes. Many scientists and engineers have made great contri-

butions to this field, and many approaches are available for changing the molecular orientation in plastic pipes, such as solid deformation processing,<sup>6</sup> die drawing,<sup>7</sup> vibration extrusion,<sup>8</sup> and rotation extrusion.<sup>9–11</sup>

Among these approaches, rotation extrusion has attracted much attention because of its simple equipment and easy implementation. Compared with conventional extrusion, rotation extrusion can eliminate the weld line.<sup>12</sup> More importantly, a hoop stress imposed on the polymer melt by the rotational mandrel can have the direction of the resulting force deviate from the axial direction so the molecular chains do not orient along the axial direction. Also, by changing the rotation speeds, one can adjust the orientation direction, and the physical and mechanical properties in the axial and hoop directions of the plastic pipe can be balanced.<sup>13</sup> However, the orientation of the molecular chains results from competition between the stress-induced orientation and subsequent relaxation.<sup>14</sup> A higher temperature determines shorter relaxation times of the molecular chains and, thus, is not favorable for retention of the oriented molecular chains. In the existing rotation extrusion process of plastic pipes, the pipe's outer wall in the immediate vicinity of the die is normally cooled with water, whereas the slowly cooled inner wall, which is exposed to the quiescent air, retains a higher

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temperature.<sup>15</sup> As a result, a higher orientation is retained in the outer wall of the pipe, whereas it is very difficult to maintain the oriented molecular chains obtained by rotation extrusion for the inner wall because of very fast relaxation. Therefore, conventional rotation extrusion is not effective for improving the performance of plastic pipes.<sup>16,17</sup>

Thus, increasing the cooling rate in the inner wall of PE pipes during rotation extrusion is very important for slowing relaxation and reserving the orientation. To obtain this goal, our research group designed and constructed a novel rotation extrusion processing system<sup>18</sup> that could cool the pipe's inner wall quickly. In this way, the relaxation of the oriented molecules was slowed, and the orientation structure was reserved in the PE pipes. Therefore, the performance of the obtained PE pipes was enhanced.<sup>19–22</sup> Previous studies on rotation extrusion have mainly focused on the low rotation speed, in which the hoop orientation degree in the PE pipes was lower. In this study, we further examined the effects of the inner wall cooling rate on the structure and properties of the PE pipes obtained through fast mandrel rotation to optimize the processing conditions for the high-performance PE pipes.

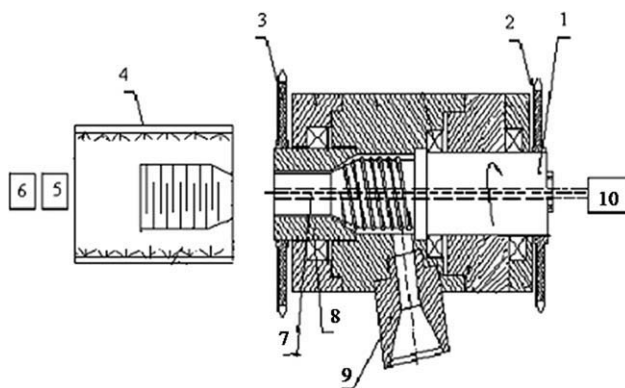
## EXPERIMENTAL

### Materials

The material used in our experiment was a commercially available HDPE pipe resin (TR480) of Sinopec JinFei Petrochemical Co., Ltd. (Shanghai, China), supplied in pellets with a weight-average molecular weight of 450,000 g/mol. Its melt flow rate was 0.14 g/10 min, measured at 190°C under 2.16 kg. Arkopal OP-10, a detergent, was purchased from Kelong Chemical Agents Co., Ltd. (Chengdu, China), to accelerate the slow crack growth (SCG) tests.

### Apparatus and sample preparation

To adjust the molecular orientation and retain the orientation result generated by rotation extrusion, novel plastic pipe extrusion equipment was designed and manufactured by our research group; its schematic diagram is shown in Figure 1, and more details were described elsewhere.<sup>18</sup> In this study, when the mandrel rotated at a high speed of 10 rpm, the cool compressed air, which was introduced through the PE pipe during its extrusion, could achieve quick cooling of the inner wall, and the cooling rate of the inner wall could be changed by adjustment of the air flow velocity, even up to the maximal 2.5°C/s, which was measured by the fixing of fast-response thermocouples on the polymer melt and the recording of its temperature change at regular intervals. The extruded PE pipe



**Figure 1** Schematic diagram of the pipe rotation extrusion equipment: (1) mandrel, (2) drive system, (3) drive system, (4) vacuum sizing box, (5) traction device, (6) cutting device, (7) flow route of the cooling medium, (8) die, (9) adapter block, and (10) inlet of the cooling medium.<sup>18</sup>

was named MPE<sub>x</sub>, where  $x$  refers to the cooling rate in the inner wall. For comparison, conventional extrusion was also carried out under the same processing conditions but without mandrel rotation, and this extruder was named TPE. The diameter and wall thickness of the final PE pipes obtained in this experiment were about 32 and 3 mm, respectively.

### Characterization

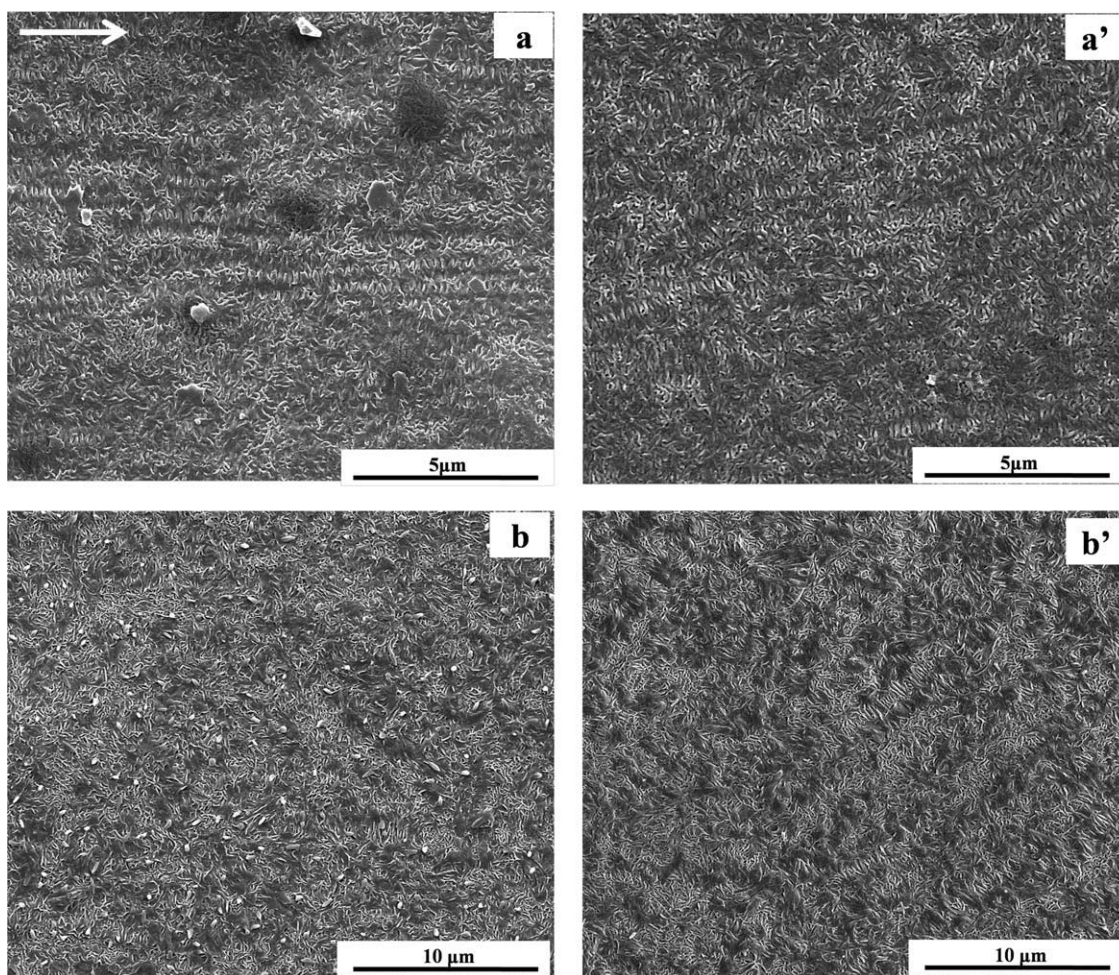
#### Cone tests for SCG

The PE pipe's resistance to SCG was evaluated by an environmental stress crack test called the *cone test* according to ISO 13480: 1997. In this test, a 15 cm long pipe was cut from the prepared PE pipes and inserted by a metallic cone at a constant rate. Because the diameter of the metallic cone used in the cone test was 1.12 times the nominal internal diameter of the pipes, the driving force for crack propagation was generated after the cone insertion. Under this condition, 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 into a 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 increment versus time was plotted and extrapolated to the time axis. Their intersection point was defined as the crack initiation time.

#### Measurement of the mechanical properties

For axial strength testing, dumbbell-shaped specimens were cut from the extruded pipe along the axial direction according to GB/T 8804-2003 (China), and then, a universal testing machine (model RG L-10, Shenzhen Reger Instrument Co., Ltd.) was used for tensile testing at room temperature with a 50 mm/min constant crosshead movement. The specimens of





**Figure 2** SEM micrographs of the etched PE pipe from (a,b) TPE and (a',b') MPE<sub>1</sub>: (a,a') the external surface (20,000 $\times$ ) and (b,b') the interior surface (10,000 $\times$ ). The arrow shows the extrusion direction.

the hoop strength tests were cut from the extruded pipe in the hoop direction into 10 mm wide rings and then tested under the same testing conditions used for the axial specimens. The axial and hoop tensile strengths of the pipe were the maximum the specimens could be subjected to before failure. Five specimens were measured for each process condition.

#### Differential scanning calorimetry (DSC) analysis

The thermal analysis of the specimens was conducted by a Q20 DSC apparatus (TA Instruments), which was calibrated according to indium and zinc standards. The slices were cut from the inner wall of the PE pipe, and the 5–8 mg specimens for each test were heated from 50 to 160°C at a 10°C/min heating rate under the protection of the nitrogen.

#### Scanning electron microscopy (SEM) observation

The crystal structure of the PE pipes and the fibril morphology in the fracture surfaces after the cone test for various pipes were observed with an FEI

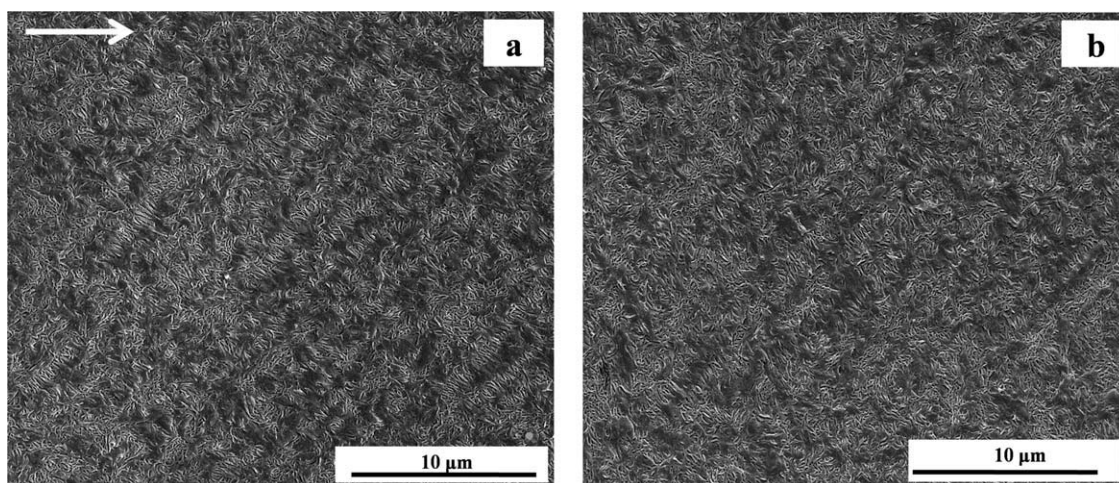
Inspect F SEM instrument at 0.5 Torr and 10 kV. The SEM samples were gold-sputtered before observation. To investigate the crystal structure, the SEM samples were cut from the pipes along the axial direction and were etched by a 1% solution of potassium permanganate at 50°C for 3 h to remove the amorphous phase.<sup>23</sup> Then, the etched samples were carefully washed by diluents sulfuric, hydrogen peroxide, and distilled water. Finally, the SEM samples were gold-sputtered for observation.

## RESULTS AND DISCUSSION

### Effect of the inner wall cooling rate on the morphological structure of the PE pipe extruded at a high mandrel rotation speed

In the conventional extrusion process, the pipe is generally longitudinally drawn so that the large axial tensile stress is imposed on the polymer melt by the traction device. As a result, the molecular chains in the pipe are oriented along the axis direction. Figure 2 shows the SEM micrographs of TPE's etched surface parallel to





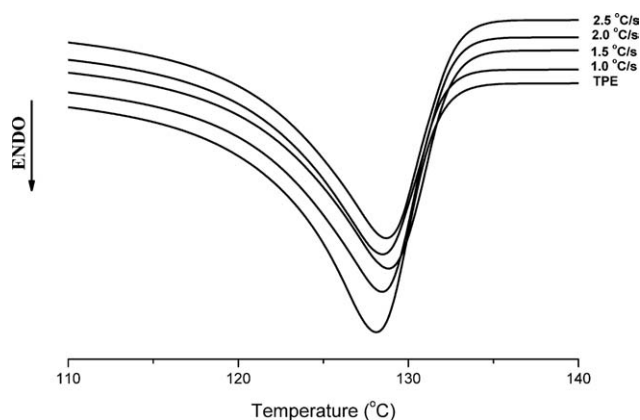
**Figure 3** SEM micrographs of the etched inner surface in the PE pipe obtained when the speed of the mandrel rotation was 10 rpm and the inner cooling rate was (a) 1.5 or (b) 2.5°C/s (10,000 $\times$ ). The arrow shows the extrusion direction.

the extrusion direction. Although the interior surface is typically covered with spherulites, exhibiting a random arrangement with no orientation, the external surface is studded with some clusterlike crystallites, which orient along the axial direction. This results from the different cooling rates across the pipe wall.<sup>24</sup> In the conventional extrusion process, the outer wall is cooled with water, and the inner wall of the pipe is exposed to quiescent air so that the cooling rate of the polymer melt in the outer wall is higher than that in the inner wall. The oriented molecular chains may relax due to the molecular motion.<sup>25</sup> The higher the temperature of the polymer melts is, the faster the molecular chains relax. When the oriented molecular chains cool before it is back to its random orientation, its orientation is reserved. Therefore, the molecular chains orient along the axial direction in the outer wall with a high cooling rate, and there is no preferred orientation structure found in the slowly cooled inner wall.

When the mandrel rotated at a high speed of 10 rpm and the inner wall cooling rate was 1°C/s, the morphology in the PE pipes changed. As shown in Figure 2, not only the molecular chains in the outer wall of MPE<sub>1</sub> happened to orient but also some oriented molecules were reserved in the inner wall. This occurred because a certain amount of compressed air introduced into the PE pipe increased the inner wall cooling rate to restrain the relaxation of the oriented molecular chains. At the same time, the orientation direction was not the axial direction but an angle relative to the extrusion direction. The orientation angles relative to the axial direction in the outer and inner walls were 17 and 50°, respectively. The oriented direction of the molecular chains was always consistent with the direction of the external stress,<sup>26</sup> so controlling the direction of the stress imposed on the melt was expected to adjust the orientation directions of the molecular chains in the PE pipes. During the rotation extrusion, a macroscopic hoop

stress by the mandrel's rotation was imposed on the PE melt to have the direction of the resulting force deviate from the axial direction, so the orientation direction changed. Because the inner wall adhered to the mandrel during the rotation extrusion, the hoop stress was maximal in the inner wall and gradually decreased apart from the inner wall. Therefore, at constant axial drag force, the resulting force in the inner wall leaned to the hoop direction more markedly, and the orientation angle relative to the axial direction was bigger in the inner wall. Meantime, with increasing rotation speed of the mandrel, the hoop stress imposed on the melt became bigger, so compared with the results at the low mandrel rotation,<sup>22</sup> the orientation angle in the outer and inner walls increased from 12 and 43° to 17 and 50°, respectively, which was more suitable for the improvement of the PE pipes' performance.

The orientation of the molecular chains resulted from the competition between the stress-induced orientation, chain stretching, and subsequent relaxation.<sup>27</sup> As is well known, the high cooling rate shortened the crystallization time to slow down the relaxation of the oriented molecules and to reserve the oriented molecular chains. Thus, to increase the orientation degree of the inner wall, a faster cooling was expected to be an effective method. Figure 3 describes how the cooling rate affected the orientation of the molecular chains in the inner wall; the morphologies in the outer wall are not shown because they were very similar to that of MPE<sub>1</sub>. It was clear that when the cooling rate increased to 1.5°C/s, the oriented molecules deviating from the axial direction in the inner wall were most dense and compact; that is, the high inner wall cooling rate increased the amount of the oriented molecular chains. However, a too-high cooling rate suppressed the increase. As shown in Figure 3(b), not only was the inner surface of MPE<sub>2.5</sub> studded by the oriented



**Figure 4** DSC curves of TPE and the PE pipe obtained with different inner wall cooling rates when the speed of the mandrel rotation was 10 rpm.

lamellae, but also, many spherulites occurred there. When the effect of the cooling rate on the crystallization behavior of a polymer is studied, a fact that should be considered is the effect of the cooling rate on the crystallization rate in addition to the fixation of the orientation of the molecular chains. Crystallization is a typical process, including nucleation and growth.<sup>28</sup> A fast cooling rate could decrease the crystallization activation energy so that more crystal nuclei are produced; this would result in an increase in the formation probability of spherulites in the bulk polymer melt.<sup>29</sup> So the final morphology in the PE pipe depended on two factors, the fixation of the orientation and the formation of spherulites. At a low mandrel rotation speed, the stress was weak so that the orientation effect generated by the mandrel rotation was low, and the oriented molecular chains easily happened to disorient because of molecular motion. If the orientation was not frozen-in in time, the oriented molecular chains returned to their random orientation state. As a result, the fixation of the cooling was dominant among all of the cooling rates, and the orientation degree in the inner wall always mounted up with the enhancement of the inner wall cooling rate.<sup>22</sup> However, at a high mandrel rotation speed, the stress was high enough to have the molecular chains orient so the orientation effect was distinct, and the resistance of the oriented molecules to disorientation was stronger compared with that at the slow mandrel rotation. Consequently, with the increasing cooling rate, the formation of spherulites played an increasing role. When the cooling rate was low, the effect of the cooling on the fixation of the orientation was stronger than that on the formation of spherulites, so the amount of the oriented molecular chains went up with increasing cooling rate. At a too-high cooling rate, more crystal nuclei in the bulk polymer melt were generated; as a result, the formation of spherulites overwhelmed the ori-

ented precursor by the external stress. As a result, the amount of oriented molecular chains decreased.

The DSC experiment also demonstrated the changed crystal structure in the samples. Figure 4 shows the DSC curves of the PE pipe by the conventional extrusion and the pipe obtained at the different inner wall cooling rates when the mandrel rotated at 10-rpm speeds. With increasing cooling rate, the melting temperature of the samples had a tendency to increase, but at the high cooling rate, it decreased.

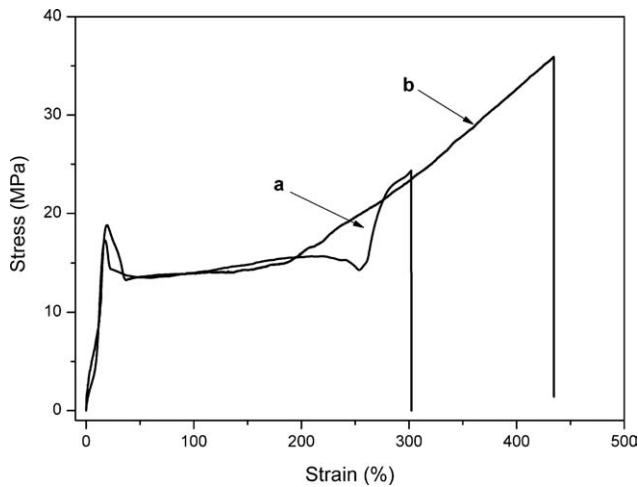
The formation of the oriented molecular chains was governed by the combined effect of cooling and stress involved during processing, which were of a more thermostatically stable structure and increased the melting temperature of the sample. The external stress led to a high orientation of molecular chains, whereas the cooling facilitated the fixation of the oriented structure. However, a higher cooling rate decreased the thickness of the lamellar crystals and caused the imperfect crystal, which may have reduced the melting peak. At the low cooling rate, the leading function of cooling was the fixation of the orientation. Therefore, the amount of oriented molecular chains increased with increasing cooling rate and so did the melt temperature. However, at a too-high cooling rate, the formation of spherulites may have increased, so the melting temperature went down. This was consistent with the results of SEM.

As discussed previously, during the rotation extrusion, the cooling rate played an important role in the formation of the oriented molecular chains. The orientation degree in the inner wall mounted up with the enhancement of the inner wall cooling rate, but too high a cooling rate in the inner wall promoted the formation of spherulites and decreased the amount of oriented molecular chains. The change of the special morphology induced by cooling affected the mechanical properties of the obtained PE pipe, as shown later.

#### Effect of the inner wall cooling rate on the mechanical properties of the PE pipe extruded at a high mandrel rotation speed

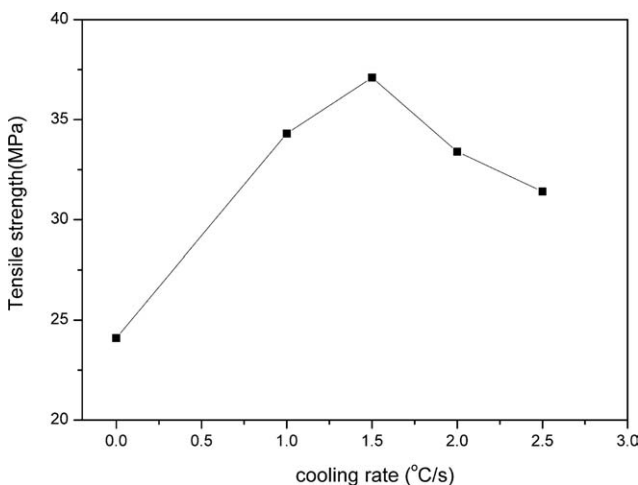
Figure 5 illustrates the typical stress-strain curves of the PE pipe produced by conventional extrusion. The tensile strength was defined as the maximum stress the samples could be subjected to before failure. The results clearly confirm that the hoop strength was only 24.1 MPa, which was lower than its axial strength, 36.8 MPa. Unfortunately, the hoop stress imposed on the internally pressurized pipe was twice as high as the axial stress in its application, so the low hoop strength was disadvantageous to the application.

At a high mandrel rotation speed, the hoop and axial strengths of the prepared PE pipes changed,

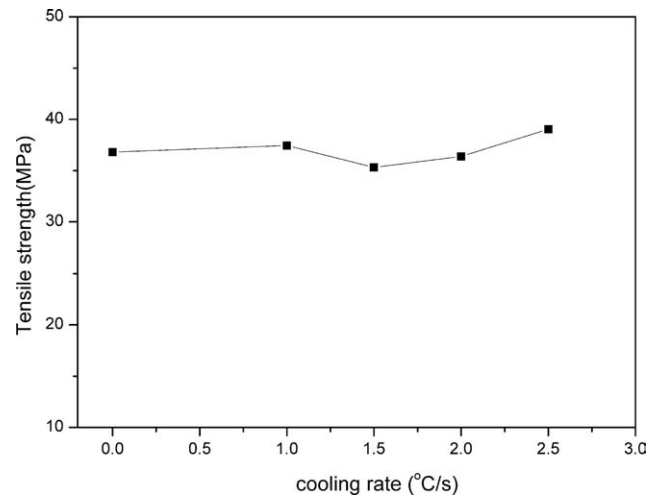


**Figure 5** Stress–strain curves of the PE pipe produced by conventional extrusion: (a) along the hoop direction and (b) along the axial direction.

and the results are shown in Figures 6 and 7. When the cooling rate was  $0^{\circ}\text{C/s}$ , the value of the corresponding point was the result of the conventional pipe. The experimental results show that rotation extrusion enhanced the hoop strength of the PE pipe, and there was an optimized cooling rate for the enhancement of the hoop strength. When the cooling rate was less than  $1.5^{\circ}\text{C/s}$ , the hoop strength increased with increasing cooling rate. However, a further increase led to a decrease in the hoop strength. However, it still was higher than that of TPE. The maximum hoop strength of the PE pipe increased from 24.1 MPa (the conventional pipe) to 37.1 MPa, and the increase was 54%. As shown in Figure 7, there was nearly no change in the tensile strength in the axial direction for the rotation pipes compared with that of the conventional pipe; this indicated that the tensile strength in the hoop direc-



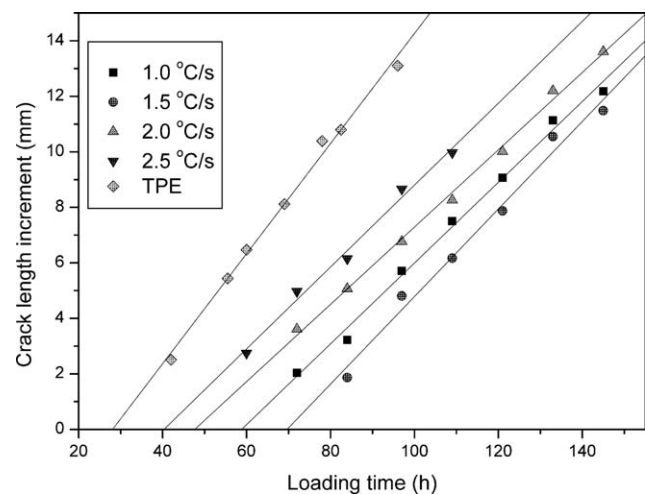
**Figure 6** Hoop tensile strength of TPE and the PE pipes prepared with different inner wall cooling rates when the speed of the mandrel rotation was 10 rpm.



**Figure 7** Axial tensile strength of TPE and the PE pipes prepared with different inner wall cooling rates when the speed of the mandrel rotation was 10 rpm.

tion was improved without a decrease in the tensile strength in the axial direction.

Additionally, the cone test specified in ISO 13480: 1997 was adopted to measure the PE pipe's resistance to SCG in this study. Figure 8 depicts the crack length increase versus time for the rotation pipes and the conventional pipe in the cone test, and the corresponding crack initiation times are summarized in Table I. The crack initiation time of TPE was 27 h. However, when the mandrel was in rotation, this time was enhanced and increased rapidly with increasing cooling rate, even up to the maximal 70 h; a further increase in the cooling rate showed no more increase but a decrease, as the hoop strength did. The longer crack initiation time indicated that the resistance of the PE pipe to SCG was improved.



**Figure 8** Increments of the crack length during cone testing for TPE and the PE pipes prepared with different inner wall cooling rates when the speed of the mandrel rotation was 10 rpm.



**TABLE I**  
**Crack Initiation Times for TPE and the Rotation Pipes**

	TPE	MPE <sub>1.0</sub>	MPE <sub>1.5</sub>	MPE <sub>2.0</sub>	MPE <sub>2.5</sub>
Crack initiation time (h)	27	59	70	48	40

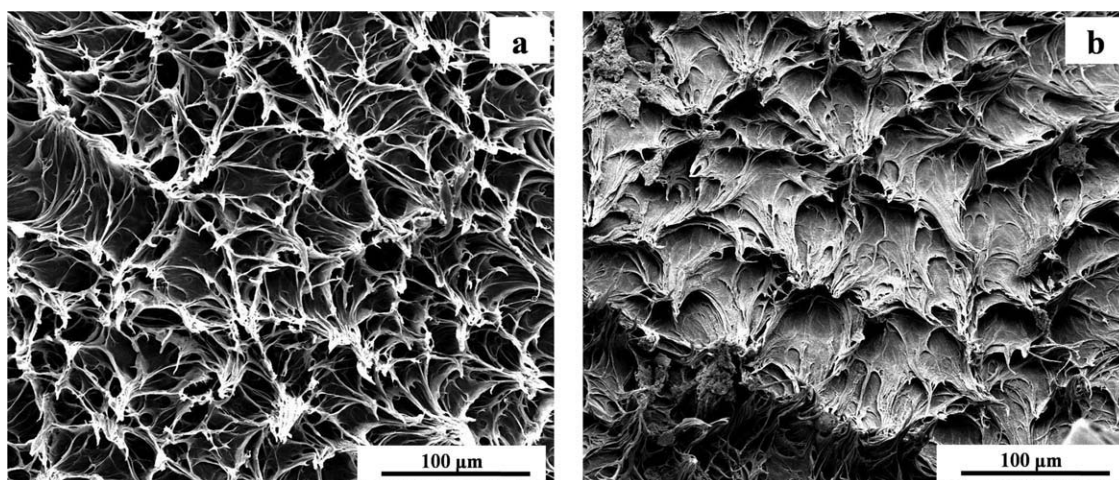
In PE pressure pipe applications, SCG is one of the principal failure modes that determines the pipe service lifetime. Therefore, this better resistance to such failure was of great significance for the PE pipe's high performance. Moreover, the enhancement was confirmed by the fracture morphology of the inner wall ahead of the notch, too. As Figure 9 clearly shows, the fibrils were slender, and numerous microvoids appeared in the fracture region of TPE. However, when the mandrel was rotated and the inner wall cooling rate was 1.5°C/s, the fracture region was covered with fewer microvoids, and its fibrils were in clusters and became denser and thicker compared to those of the conventional pipe; this suggested that the fibrils could withstand the applied stress for a longer time. Therefore, the pipe had better resistance to SCG. This was consistent with the suggestion of a longer crack initiation time.

#### Relationship between the processing conditions, the morphological structure, and the mechanical properties of the PE pipes

Because polymer crystallization is a kinetic event, variations in the processing conditions, stress, and cooling rate, in particular, have great influence on its crystallization behavior to affect the final morphology of a polymer in the products, which, in turn, exert a direct influence on its mechanical properties.<sup>30</sup> It is well known that the orientation of molecular chains can facilitate the improvement of the strength along the orientation direction.<sup>31</sup> During the rotation extrusion, the orientation direction of the

molecular chains deviated from the axial direction. Therefore, the multiaxial orientation of the molecular chains was achieved; this implied that the orientation of the molecular chains along the hoop direction increased compared with the conventional extrusion. Moreover, as shown by the results of DSC and SEM, the orientation degree depended on the competition between the fixation of the oriented molecular chains and the formation of spherulites. As a result, with increasing cooling rate, the orientation degree in the inner wall decreased after an increase, and so did the hoop strength. Also, it was true that the department of the molecular orientation from the axial direction decreased the orientation degree along the axial direction. However, in the conventional extrusion, the molecular chains oriented along the axial direction only existed in the outer wall because of the slow cooling rate of inner wall. Because the inner wall adhered to the mandrel, the hoop stress was lower in the outer wall during the mandrel rotation; this resulted in the departure from the axial direction in the outer wall being small, and the orientation angle only was 17°. Accordingly, no great changes took place in the axial tensile strength.

Additionally, the resistance to SCG was primarily governed by the disentanglement rate of the fibrils at the base of the craze.<sup>32</sup> The extensive research of Brown and his coworkers<sup>33,34</sup> showed that there were more molecules that bore the applied stress in the fibrils when the orientation direction of molecular chains was parallel to the applied stress than that when the original structure was perpendicular to the applied stress, and therefore, the average force per molecule might decrease. Consequently, the disentanglement rate of the fibrils decreased, and the resistance to SCG increased with increasing orientation degree. The internally pressurized pipe was subjected to a hoop stress twice as high as the axial stress in its application. The orientation of the molecular chains along



**Figure 9** SEM micrographs of the fracture zone in (a) TPE and (b) MPE<sub>1.5</sub>.

the hoop direction was expected to improve the pipe's resistance to SCG, and more improvement could be achieved at the higher hoop orientation degree. Therefore, for the resistance to SCG, there was an optimal cooling rate where the orientation degree reached the maximal value.

### CONCLUSIONS

In this study, the mandrel was rotated at high speed so that a hoop stress was imposed on the polymer melt to have the molecular orientation deviate from the axial direction. At the same time, compressed air as a cooling medium was introduced through the PE pipe to quicken its inner wall cooling rate. The results showed that the cooling rate played an important role in the formation of the oriented molecular chains. At the low cooling rate, the effect of the cooling rate on the fixation of the orientation was dominant so that the relaxation of the oriented molecule was slowed to reserve the orientation structure. Consequently, with increasing cooling rate, the orientation degree went up. However, too high a cooling rate produced more crystal nuclei to promote the formation of spherulites. As a result, the amount of oriented molecular chains went down. Therefore, there was an optimal cooling rate of the inner wall during the rotation extrusion for higher amounts of oriented molecular chains and better PE pipe performance.

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