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Structure and performance of polybutene-1 pipes produced via mandrel rotation extrusion

Abstract: In this article, a new rotational extrusion processing system was adopted for manufacturing of polybutene-1 (PB-1) pipes, and the effects of mandrel rotation speed on their structures and mechanical performances were studied. The experimental results showed that besides the conventional axial extrusion flow field, a hoop shear stress field imposed to the melt, which was generated by the introduction of mandrel rotation, could lead the combined stress apart from the axial direction of the pipes to induce the molecular orientation deviated from the axial direction. Thus, the axial orientation of PB-1 was restrained, which was revealed by thermal shrinkage measurements and polarized infrared spectra. Moreover, it was also found and confirmed by scanning electron microscopy and two-dimensional wide-angle X-ray diffraction that orientation mainly existed in the amorphous region rather than the crystal region. Differential scanning calorimetry tests showed that the mandrel rotation could facilitate the formation of more perfect crystals and higher crystallinity. As a result, compared with the PB-1 pipe produced by conventional extrusion, the hoop strength of the PB-1 pipes manufactured at a mandrel rotation speed of 8 rpm increased from 20.2 to 24.9 MPa, achieving a mechanical balance in both axial and hoop directions.

Keywords: mechanical properties; molecular orientation; polarized infrared spectra; polybutene-1; rotation extrusion.

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1 Introduction

Isotactic polybutene-1 (PB-1) is a semicrystalline polyolefin possessing superior creep resistance and heat resistance

in comparison with other polyolefins, such as polyethylene (PE) and polypropylene, so that PB-1 pipes are widely used to convey gas, hot water, and sewage [1–3].

Like other polymers, PB-1 can also form an oriented structure with the induction of a stress field such as shear, stretch, etc. [4, 5]. It is convincing that the orientation significantly affects the mechanical performance of polymer products, noted as the highly promoted mechanical properties along the orientation direction, while the lessened performances are perpendicular to that [6]. During the conventional extrusion process of plastic pipes, the polymer melts flow along the axial direction and the axial stress generated by the extrusion-traction devices forces the molecular chains to orient parallel to the axial direction, which results in a much higher strength in the axial direction than that in the hoop direction. However, the hoop stress imposed on the pressurized pipes is twice as high as the axial stress in their actual uses. Therefore, the cracks easily generate and propagate along the axial direction to finally induce the failure of polymer pipes [7–9]. Obviously, erasing the axial molecular orientation and balancing the strength in both hoop and axial directions would be the keys to gain polymer pipes with better mechanical performance.

Numerous techniques have been developed to improve the pipe's mechanical properties of a given polymer through manipulating the molecular orientation in extruded pipes, by optimizing pipe processing conditions or inducing external fields such as vibration plasticating extrusion [7], spiral flowing extrusion [10], flow-forming process [11], die drawing process [12], and rotational extrusion [13–15]. Among these approaches, rotational extrusion is a relatively efficient processing route for polymer pipe mass manufacturing. Not only can it erase the weld line generated by the spider supporting the mandrel, but it also changes the molecular orientation from the axial direction so as to enhance the hoop strength of pipes [16]. Zachariades and Chung [17] prepared a glass fiber-filled polypropylene pipe with improved hoop strength through die rotation extrusion. By adjusting the extrusion rate and the rotation speed of die, the hoop and axial mechanical performance can be balanced. To further study the morphological evolution and properties during rotational extrusion under the

complicated field of flow, temperature, or combined, our group developed a novel rotational extrusion processing system, which could impose proper hoop shear stress on both the inner and outer walls of the polymer melt, and then boost the inner wall cooling rate of the pipes in the later cooling stage [18]. A previous work has confirmed that the mandrel rotation speed and inner wall cooling rate could adjust the formation and orientation angle of the shish-kebab structure effectively in PE pipes [19] so as to improve their mechanical performances.

Although rotational extrusion of PE pipes has already been reported, its effect on PB-1 is still yet to be investigated. PB-1 differs from PE in various aspects such as molecular structure, crystal transition, and the relatively slow crystallization rate [20]. Moreover, their crystallization behaviors under the condition of complex stress and temperature field would vary distinctly. Hence, in seeking techniques to produce PB-1 pipes with improved mechanical performance, it is crucial to further study the microstructural evolution of PB-1 pipes during mandrel rotation extrusion, especially the molecular orientation and the crystal structure. As a part of systematical investigations, this article focused on the effect of mandrel rotation speed on the structures and mechanical performances of PB-1 pipes.

2 Materials and methods

2.1 Materials

The raw material used in this study was isotactic PB-1 (PB4235), a commercial PB-1 piping resin manufactured by Lyondell-Basell (Brussels, Belgium). Its melt flow index was 0.4 g/10 min (190°C/2.16 kg).

2.2 Sample preparation

A self-designed polymer pipe rotational extrusion equipment was used to extrude the PB-1 pipe. The schematic mechanical drawing of this equipment is shown in Figure 1. More detailed information about this equipment has been described in previous work [15, 18, 19]. This equipment can achieve rotation of the mandrel so as to adjust the stress direction during the polymer pipe extrusion. In this study, raw materials were plasticized in a single-screw extruder with a length/diameter ratio of 28:1 and extruded into the rotation die, and the PB-1 pipes were produced at different mandrel rotating speeds. The prepared pipe was named as N_x , where x stands for the

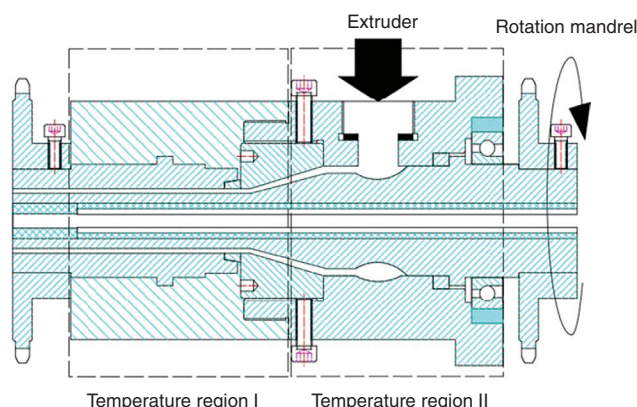


Figure 1 Schematic of the polymer pipe's rotational extrusion apparatus.

mandrel rotation speed (rpm). For example, N_4 represents a pipe extruded with a mandrel rotation speed of 4 rpm. N_0 refers to PB-1 pipes produced by conventional extrusion, during which the mandrel stayed motionless. The screw speed was maintained at 35 rpm. The temperatures of the extruder were set at 160°C, 180°C, and 190°C (from hopper to die, respectively), and the temperatures of the rotation die were set at 190°C (temperature region I) and 190°C (temperature region II), as illustrated in Figure 1. After aging for more than a week at room temperature to erase the metastable tetragonal forms, the diameter and wall thickness of the obtained PB-1 pipes were 20 and 2 mm, respectively.

2.3 Mechanical properties measurement

A universal testing machine (model RG L-10; Shengzhen Reger Instrument Co., Ltd.) was used to measure the tensile strength at room temperature with a cross-head speed of 20 mm/min. As illustrated in Figure 2A, the ring-shaped specimens for hoop strength test were cut from the prepared pipes along the hoop direction with a width of 10 mm, while the dog-bone-shaped specimens for the axial strength test were cut along the axial direction according to GB/T 8804-2003. The tensile strength was defined as the maximum stress that the specimens could bear before failure. For each processing condition, five specimens were tested.

2.4 Thermal shrinkage measurement

The stripes with a length of 25 mm and a width of 1.5 mm were cut along the axial direction of the

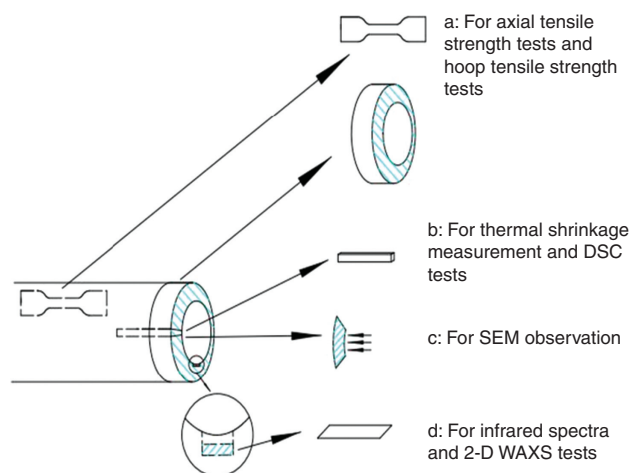


Figure 2 Illustration of sample preparation.

prepared pipes (seen in Figure 2B) and placed in glycerol at 175°C for >30 min until no further dimensional changes occurred. Then, the thermo-shrunk stripes were stored at room temperature for a week. The shrinkage ratio was then measured according to the length of the strip before and after thermal treatment, which was defined as the ratio of the initial length divided by the final length of the samples.

2.5 Infrared spectra (P-IR)

A Nicolet 6700 infrared spectrometer with an infrared polarizer was used in this study to characterize the molecular orientation. Thin slices of ca. 20 μm in thickness were cut off from the inner wall of the prepared pipes by using an ultrathin slicer (as illustrated in Figure 2D). By adjusting the direction of the polarizer, the electric vector direction of infrared light was set to be parallel or perpendicular to the axial direction of PB-1 tubes. Characteristic absorption intensities were measured in both polarization directions.

2.6 Differential scanning calorimetry (DSC) analysis

Thermal analysis of the prepared pipes was done using a Q20 DSC apparatus (TA Instruments), calibrated using indium and zinc standards. The 0.5-mm-thick slices were cut from the inner wall of the PB-1 pipes, and 6–7 mg specimens for each test were heated from 40°C to 190°C at a rate of 10°C/min under the protection of nitrogen. To calculate the crystallinity of the sample, a standard melting

enthalpy of 125 J/g was used, as proposed by Hussein and Strobl [21].

2.7 Scanning electronic microscope (SEM) observations

Specimens cut off from PB-1 pipes (see Figure 2C) were etched for 12 h with a etchant containing 2.9 wt.% potassium permanganate (KMnO_4), 32.4 wt.% concentrated sulfuric acid, and 64.7 wt.% concentrated phosphoric acid, according to the procedure proposed by Olley and Bassett [22]. After gold-sputter treatment, an Inspect F(FEI)SEM instrument was used for crystal structure observation at 0.5 Torr and 20 kV.

2.8 Synchrotron two-dimensional wide-angle X-ray diffraction (2D-WAXD) measurement

The synchrotron 2D-WAXD experiments were carried out on the U7B beam line at Shanghai Synchrotron Radiation Facility, Shanghai, China, with the wavelength of X-ray being 0.235 nm. Each 2D-WAXD diagram was recorded by a detector at a sample-to-detector distance of 98 mm with exposure time of 60 s, at room temperature. The samples were cut from the prepared pipes for testing, as shown in Figure 2D.

3 Results and discussion

3.1 Effect of mandrel rotation on the orientation and crystalline structure of the prepared PB-1 pipes

When temperature increases to above the melting temperature due to the thermal motion of molecules, extended molecules will disorient and coil to the random state, resulting in dimensional shrinkage along the orientation direction. Hence, comparing the samples' dimensional change along the orientation direction before and after heating could be a simple but effective way to characterize orientation. The bigger thermal shrinkage ratio reflects the higher degree of molecular orientation [23]. Figure 3 is a photograph of thermal shrunk stripes cut from conventionally extruded and rotationally extruded pipes, and the thermal shrinkage ratio is shown in Figure 4, where N0 refers to conventionally extruded PB-1 pipes. Apparently, compared with

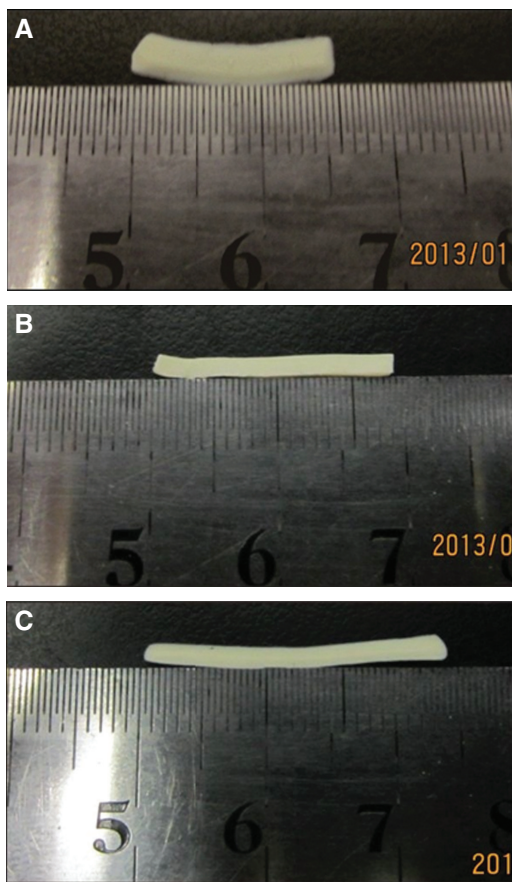


Figure 3 Photographs of thermal shrunk stripes axially cut off from PB-1 pipes produced at different mandrel rotation rates. The initial length of the strip was 25 mm. (A) N0; (B) N4; (C) N12.

conventional extrusion, PB-1 pipes produced by rotational extrusion exhibit a lower thermal shrinkage ratio, indicating a lower degree of axial orientation for rotationally

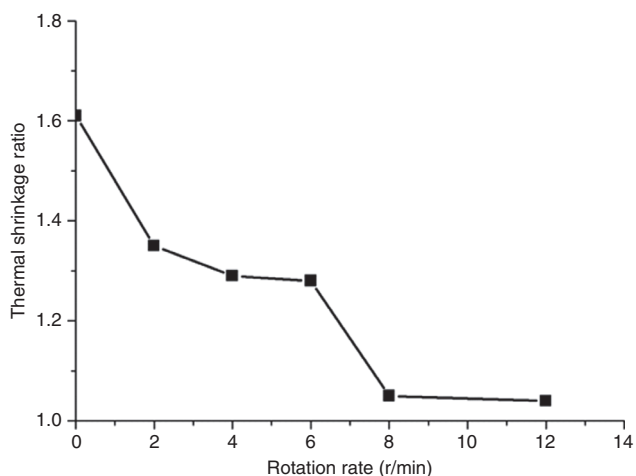


Figure 4 Shrinkage ratio of PB-1 pipes produced at different mandrel rotation rates.

extruded pipes. Moreover, the thermal shrinkage ratio tends to decrease further with the increasing mandrel rotation speed. During conventional extrusion, due to strong axial extrusion flow and longitudinal stress imposed by the traction device, the molecular chains of PB-1 oriented along the extrusion direction, reflected as a relatively high thermal shrinkage ratio. When the mandrel rotated, hoop stress was imposed to the melt so the direction of the combined stress in the melt was off the axial direction. Thus, the melt flow of PB-1 could be highly changed from an axial extensional flow to a combination of axial extensional flow and hoop shearing flow, so as to diverge the orientation of molecular chains from the axial direction. As a result, the rotationally extruded PB-1 exhibits less axial thermal shrinkage after heating treatment. With the increasing rotation speed, stronger hoop stress was imposed on the polymer melt, inducing the resulting stress apart from the axial to a greater extent to further suppress the axial orientation, resulting in further decreasing thermal shrinkage ratio. When the rotation speed reaches 8 rpm, the thermal shrinkage ratio approximates to 1, indicating that the axial orientation was eliminated completely.

The orientation measured by thermal shrinkage could result from the oriented molecules in both crystalline and amorphous regions. For distinguishing their effects separately, orientation degrees in the crystalline and amorphous regions were characterized by infrared spectra, SEM, and two-dimensional wide-angle X-ray diffraction (2D-WAXD).

Infrared spectra analysis is also an effective technique for characterizing orientation [24, 25]. The absorption peak at the wave number of 760 cm^{-1} corresponds to the rocking vibration of C-C bond on the PB-1's side-chain methine in the amorphous region [26]. Given that its vibration vector direction is perpendicular to the molecular orientation direction of PB-1, it can be used to determine the molecular orientation. It is well known that an isotropic sample has equal absorbances in both directions, whereas for an oriented one the absorbance would be related to the vibration vector direction with respect to the electric field vector direction, and the absorbance would be minimum when the two directions are perpendicular to each other (otherwise, the maximum). Thus, infrared dichroism, which was defined as the absorption intensity of the 760 cm^{-1} peak when the electric vector direction of infrared light was perpendicular to extrusion direction divided by its intensity when the electric vector was parallel to the extrusion direction, can reveal the axial orientation degree in the amorphous region: a larger infrared dichroism indicates a higher degree of molecular orientation. Figure 5 shows the polarized infrared absorption spectra

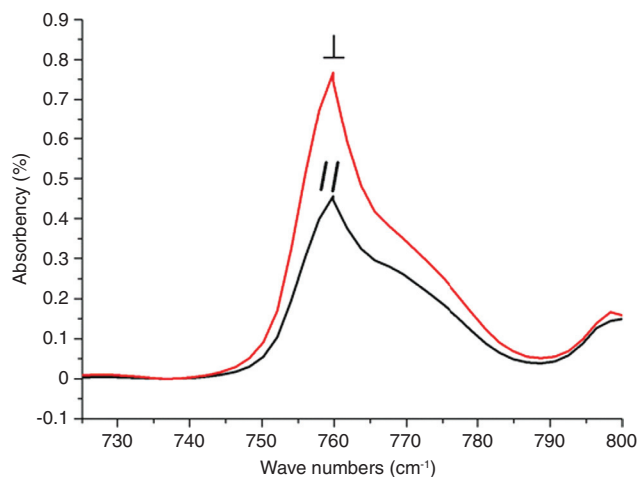


Figure 5 Polarized FTIR spectra of the PB-1 pipe produced by conventional extrusion.

from 730 to 800 cm^{-1} when the electric field vectors of the incident light were perpendicular and parallel to the extrusion direction of the PB-1 pipe, with \perp and \parallel as their respective absorbance; the relative infrared dichroism of all samples are shown in Figure 6. In Figure 5, for the conventionally extruded PB-1 pipe, \perp was stronger than \parallel , indicating a preferred hoop orientation of the side chains' rocking vibration in the amorphous region, i.e., the chain of PB-1 oriented along the axial direction. With the introduction of mandrel rotation, the single axial extensional flow was combined with a hoop flow, which would diverge the combined stress field off the axial direction, thus restraining axial orientation. Therefore, the infrared dichroism decreased. The continuing speeding up of mandrel rotation resulted in lower infrared dichroism. After the rotation speed reached 8 rpm, infrared dichroism approached 1, which indicates that the axial orientation was minimum. This tendency of decreasing orientation degree with increasing rotation rate is in accordance with the thermal shrinkage results.

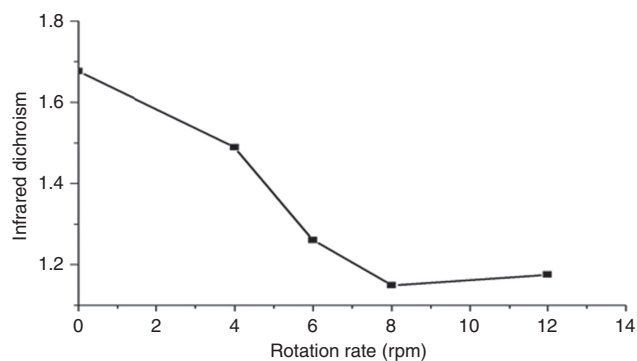


Figure 6 Infrared dichroism of the PB-1 pipes as a function of the mandrel rotation rate.

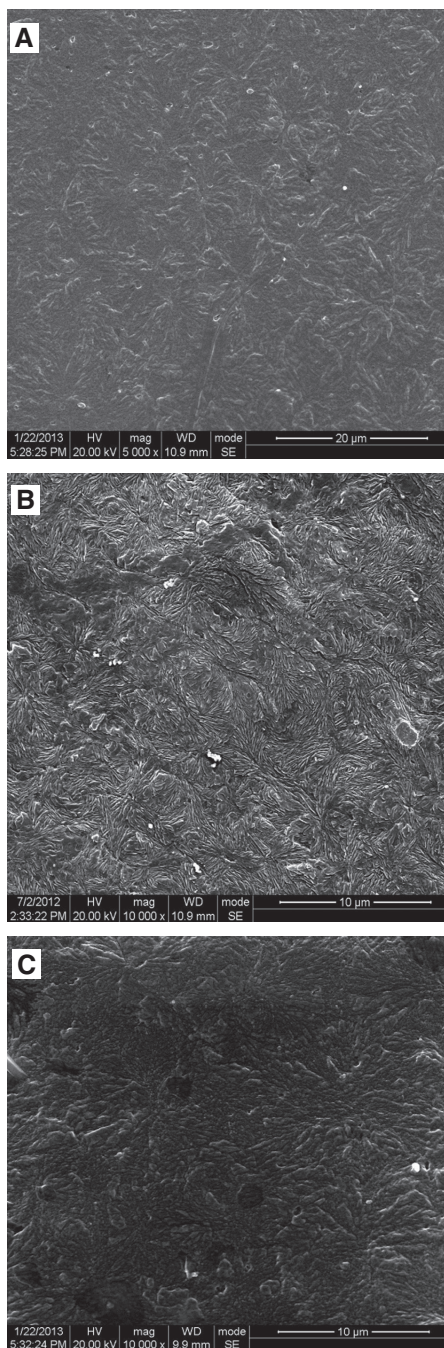


Figure 7 SEM photographs of the etched inner wall of PB-1 pipes. (A) N0; (B) N4; (C) N8.

To further reveal the crystalline morphologies in PB-1 pipes, SEM observation was carried out. As shown in Figure 7, the inner wall of PB-1 pipes produced via both rotational extrusion and conventional extrusion were covered with spherulites, and even when the rotation speed reached a level as high as 8 rpm, there existed no anisotropic shish-kebab structure as reported in PE pipes prepared by rotational extrusion earlier [15, 19]. The reasons for the absence of this oriented crystals could be two: first,

longer and larger ethyl side chains increased the relatively steric barrier for the formation of the extended molecule shish, which was a precursor for shish-kebab; however, the crystallization rate of PB-1 was relatively slow, so it was very difficult to fix the extended molecule shish also through epitaxial crystallization. Thus, the molecular orientation cannot be fixed in the crystalline region but can be preserved in the amorphous region, in which case the crystal region of PB-1 acted as physical cross-linking points [27]. This was also confirmed by 2D-WAXD, for isotropic diffraction rings were observed in Figure 8.

DSC tests were carried out to investigate the crystal structure formed under different processing conditions. Figure 9 shows the DSC curves of PB-1 pipes produced at different mandrel rotation speeds, and the melting temperature and crystallinity data are listed in Table 1. It is noteworthy that both the melting temperature (T_m) and crystallinity of rotationally extruded PB-1 pipes were always higher than that of the conventionally extruded one, and their values increased with the increasing rotation speed. When rotation speed reached 12 rpm, the T_m and crystallinity increased to 130.46°C and 61.20%, while those of N0 were 127.8°C and 56.14%. As a matter of fact, it is evident that stress can promote the extension of polymer

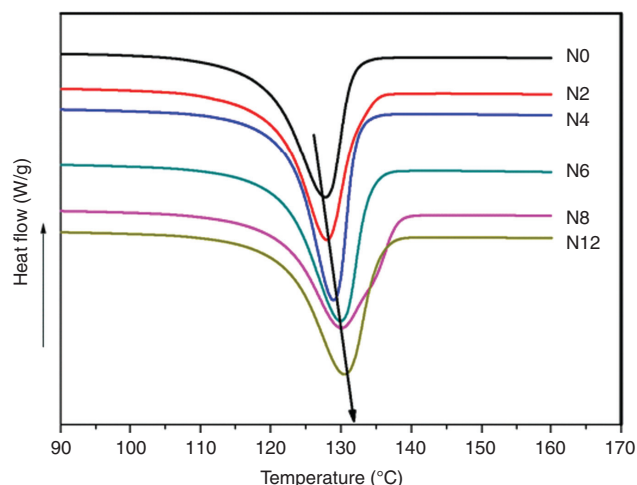


Figure 9 DSC curves of PB-1 pipes produced at different rotation speeds.

molecules and overcome the nucleation barrier to form more crystal nuclei during crystallization, thus producing a thicker lamellar system and more perfect crystals, which can be reflected as higher melting temperatures and crystallinity. The stronger the stress, the more obvious this effect. During the rotational extrusion, besides the axial stress, the hoop stress was imposed on the polymer melts by mandrel rotation. The resulting stress was stronger and increased further with increasing mandrel rotation. As a result, it was easily understood that the PB-1 pipe prepared by rotational extrusion had a thicker lamellar system and more perfect crystals.

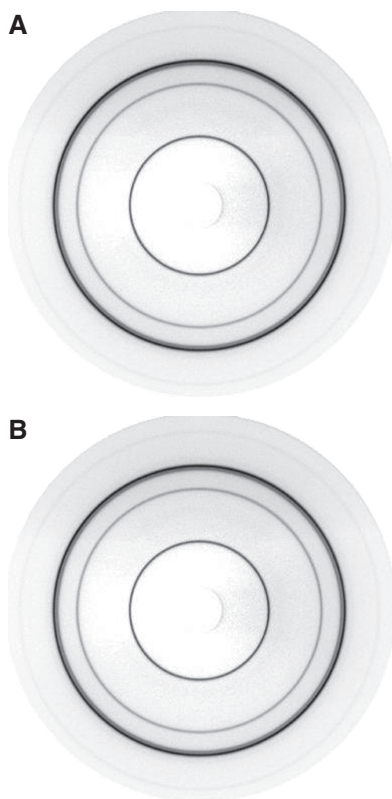


Figure 8 2D-WAXS patterns of PB-1 pipes. (A) N0; (B) N8.

3.2 Effect of mandrel rotation extrusion on the mechanical properties of the prepared PB-1 pipes

As mentioned above, the introduction of mandrel rotation could restrain axial orientation and endow PB-1 to form more perfect crystals and higher crystallinity, thus affecting the mechanical properties of the prepared pipes. As can be seen in Figure 10, significant changes in

Table 1 Melting temperature and crystallinity of PB-1 pipes produced at different mandrel rotation speeds.

Samples	T_m (°C)	Crystallinity (%)
N0(CEP)	127.8	56.14
N2	127.96	59.11
N4	128.94	60.58
N6	129.96	60.25
N8	130.04	60.77
N12	130.46	61.20

mechanical property occurred. In conventional extrusion, the strong axial molecular orientation formed by axial stress field results in much higher axial strength (39.2 MPa) than hoop strength (20.2 MPa). Unfortunately, this is an unwanted outcome as the required hoop strength in pressurized pipes is twice as high as that in axial direction, as mentioned above. The axial orientation would cause crack generation and propagation, and eventual failure, in the service of pressurized PB-1 pipes.

During rotational extrusion of the PB-1 pipe, a hoop stress generated by the introduction of mandrel rotation leads the combined stress to deviate from the original axial direction. Thus, the orientation was apart from the axial, i.e., the axial orientation direction decreased while the hoop orientation increased. Therefore, the prepared PB-1 pipe exhibits enhanced hoop strength and lessened axial strength. The faster mandrel rotation speed will further suppress the axial orientation to improve its hoop strength (Figure 11). When mandrel rotation reaches a certain level (8 rpm), the axial orientation could be erased. Therefore, the hoop strength was enhanced to 24.9 MPa (increased by 23.3% compared with the conventionally extruded PB-1 pipe) with the axial strength decreasing to 30.9 MPa. The balance of mechanical performance in both directions is achieved.

However, when rotation speeds were too high, e.g., 12 rpm, the hoop strength of the PB-1 pipe decreased. This can be attributed to defects between crystal regions. As shown in Figure 12, an interesting and unique finding was that there were nanosized holes (marked in white circles) in the inner wall of N12, whereas these did not appear in other samples at lower rotation speeds (Figure 7). PB-1 is a polymorphic polymer with tetragonal and trigonal forms. During the crystallization, PB-1 is first crystallized into the

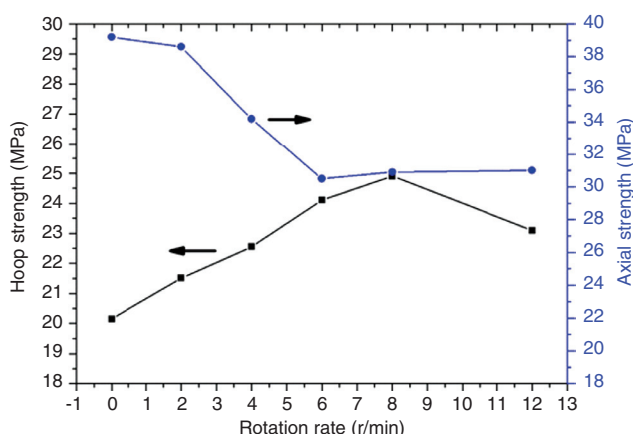


Figure 11 Tensile strength at hoop and axial directions of PB-1 pipes produced at different mandrel rotation speeds.

tetragonal form, which is metastable and would transform into the more stable trigonal form fast after aging. As the density of the tetragonal form was 0.907 g/cm^3 , lower than that of the trigonal form, 0.95 g/cm^3 [28], the modification transformation can induce the volume contraction and the hole will be formed in the PB-1 matrix. This contraction turns out to be even more notable in the highest crystallinity and thickest lamellar system, resulting in a voiding space between crystal regions. Hence, PB-1 pipes prepared at a mandrel rotation speed of 12 rpm had lower strength.

4 Conclusion

In this present study, a rotational extrusion system was adopted to produce PB-1 pipes, and the effects of the

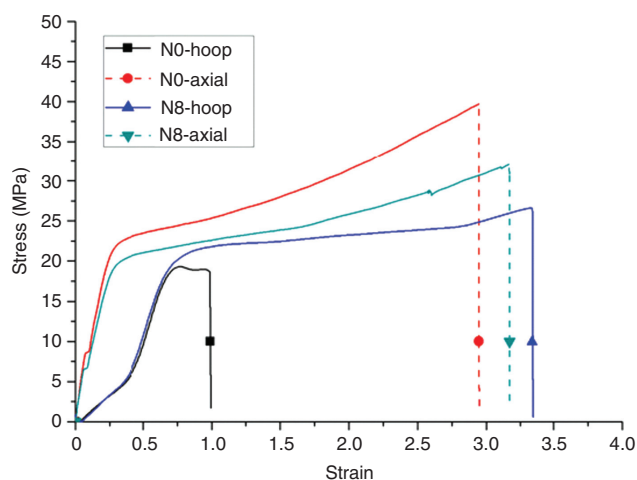


Figure 10 Representative axial (dot line) and hoop stress-strain of PB-1 pipes produced by conventional extrusion and rotational extrusion.

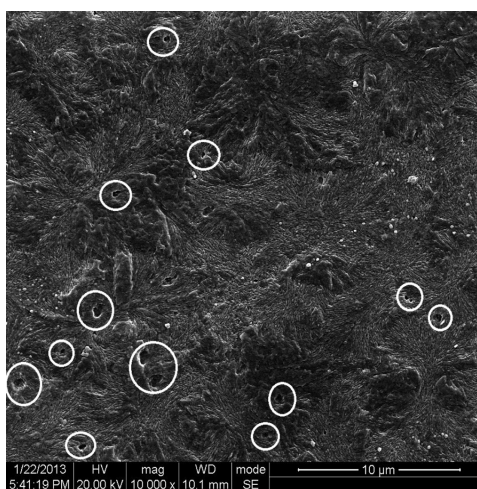


Figure 12 SEM photographs of the etched inner wall of PB-1 pipes (N12).

mandrel rotation speed on their structure and mechanical performance were studied. Results showed that the mandrel rotation could impose a hoop shearing field on the melt so that the resulting stress is not axially oriented, bringing changes to the orientation direction of the molecular chains; that is, the axial orientation in the amorphous phase of PB-1 pipes was restrained. Furthermore, more perfect crystals and higher crystallinity were also formed with the induction of hoop shear stress. As a result, the performances of the PB-1 pipe were greatly enhanced. However, high rotation speeds may generate some defects due to crystal modification transformation. Therefore, there was an optimal mandrel rotation speed during the rotational extrusion for better performance of

the PB-1 pipe. When the mandrel rotation speed was 8 rpm, the PB-1 pipe produced by the novel extrusion method showed the best hoop strength of 24.9 MPa, 23.3% higher than that of the conventionally extruded one, achieving a mechanical balance in both the axial and hoop directions.

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