

HIGH SPEED INJECTION MOLDING OF HIGH DENSITY POLYETHYLENE — EFFECTS OF INJECTION SPEED ON STRUCTURE AND PROPERTIES*

Kun Jiang, Fei-long Yu, Run Su, Jing-hui Yang, Tian-nan Zhou, Jian Gao, Hua Deng^{**}, Ke Wang,
Qin Zhang, Feng Chen and Qiang Fu^{**}

*College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering,
Sichuan University, Chengdu 610065, China*

Abstract Thin wall samples of high density polyethylene (HDPE) were prepared *via* injection molding with different injection speeds ranging from 100 mm/s to 1200 mm/s. A significant decrease in the tensile strength and Young's modulus was observed with increasing injection speed. In order to investigate the mechanism behind this decrease, the orientation, molecular weight, molecular weight distribution, melt flow rate, crystallinity and crystal morphology of HDPE were characterized using two-dimensional wide-angle X-ray diffraction (2D-WAXD), gel permeation chromatography (GPC), capillary rheometry and differential scanning calorimetry (DSC), respectively. It is demonstrated that the orientation, molecular weight, molecular weight distribution, melt flow rate and crystallinity have no obvious change with increasing injection speed. Nevertheless, the content of extended chain crystals or large folded chain crystals was found to decrease with increasing injection speed. Therefore, it is concluded that the decrease in tensile properties is mainly contributed by the reduced content of extended chain crystals or large folded chain crystals. This study provides industry with valuable information for the application of high speed injection molding.

Keywords: High speed injection molding; High density polyethylene; Tensile properties; Extended chain crystals structure; Large folded chain crystals.

INTRODUCTION

Injection molding is the most important manufacturing technology for the production of plastic products with various shapes and dimensions. With the increasing demand for products of high additional value; thinner, lighter and smaller products become essential^[1–3]. High speed injection molding (HSIM) is one of the most useful methods for the manufacture of these thin wall products. Furthermore, high speed injection technology leads to better transcription ratio^[4], lower strain and more accurate dimension^[3]. Good tensile performance is an important criterion for industrial applications. It is well known that the injection speed is one of the most important factors affecting the tensile properties. Several studies about the effect of injection speed on the tensile properties have been carried out. Chen *et al.*^[5] investigated nylon 6-clay nanocomposites under different injection speeds and indicated that tensile strength increased with increasing injection speed. However, Narh *et al.*^[6] reported the tensile properties of PET/LCP blends decreased with increasing injection speed, which was due to the fact that thickness of the skin layer decreased with increasing injection speed. Similarly, Govaert *et al.*^[7] observed a slight decrease in yield stress with increasing injection speed for polycarbonate samples. The

* This work was financially supported by the National Natural Science Foundation of China (No. 51073111).

** Corresponding author: Hua Deng (邓华), E-mail: huadeng@scu.edu.cn

Qiang Fu (傅强), E-mail: qiangfu@scu.edu.cn

Received May 26, 2010; Revised August 23, 2010; Accepted August 31, 2010

doi: 10.1007/s10118-011-1049-3

main cause is that the flow shear process lasts longer time at low injection speed. Nevertheless, most of the previous works focus on the relatively low injection speed (0–200 mm/s) and the standard injection molded bars. Few papers have reported studies on tensile properties of thin wall samples by HSIM^[8].

High density polyethylene (HDPE) is one of the most widely studied semi-crystalline polymers, as concerns the plasticity phenomena, owing to its simple crystalline structure and well-characterized physical properties^[9]. Therefore, this paper aims to investigate the effect of injection speed on the tensile properties of thin wall HDPE samples manufactured by HSIM. The tensile properties of samples were investigated in detail, and the results were discussed regarding to the polymer chain orientation, molecular weight, molecular weight distribution, melt flow rate, crystallinity and crystal morphology, with the aid of two-dimensional wide angle X-ray diffraction (2D WAXD), gel permeation chromatography (GPC), capillary rheometry and differential scanning calorimetry (DSC), respectively.

EXPERIMENTAL

Materials and Sample Preparation

HDPE (trade marked: F600) used in this study was supplied by the Korea Petrochemical Ind. Co., Ltd. It has a melt flow index (MFI) of 0.035 g/10min (190°C, 2.16 kg) and a density of 0.957 g/cm³.

A mould in rectangular shape with a size of 80 mm × 60 mm, and thickness of 0.45 mm was used. The samples for the tests were cut from the plates produced from injection molding (as shown in Fig. 1). Furthermore, another cavity after the rectangular plate is set-up (shown as the shadowed part in Fig. 1) in order to achieve high injection speed before the mould is completely filled by polymer melt.

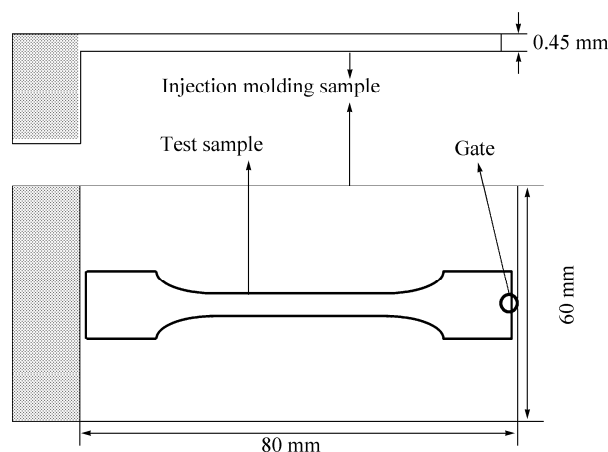


Fig. 1 The schematic representation of sample preparation for tensile properties testing

The specimens were injection molded at different injection speeds of 100, 200, 500 and 1200 mm/s, respectively. Injection molding machine with a screw diameter of 25 mm and barrel temperature of 180°C was used to produce samples in current study.

Tensile Experiments

The tensile properties were measured using a SANS universal testing machine with a crosshead speed of 20 mm/min at a temperature of 23°C. The values were calculated as averages over five specimens for each processing condition.

2D WAXD Measurements

The synchrotron 2D-WAXD experiments were conducted using the U7B beam line in the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The wavelength used was 0.1409 nm and the transmission mode was used. The orientation level of various planes could be calculated by the orientation parameter f , and the

methods for calculation were described in detail elsewhere^[10].

Differential Scanning Calorimetry (DSC)

Thermal analysis of the samples was conducted using a Perkin-Elmer pyris-1 DSC. In order to exam the melting behavior layer by layer, the slices were cut from the surface to the core along sample thickness. The test samples were heated from 20°C to 180°C at a heating rate of 10 K/min and held there for 10 min, then cooled to 20°C at a rate of 10 K/min and again heated to 180°C at a heating rate of 10 K/min for the second heating curves. During the measurement, dried nitrogen was purged at a constant flow rate. The crystallinity index X_c was calculated using the following equation.

$$X_c = \Delta H_m / \Delta H_m^0 \quad (1)$$

where ΔH_m , the melt enthalpy of the samples, and ΔH_m^0 , the theoretical melt enthalpy is 293 J/g for HDPE^[11].

Gel Permeation Chromatography (GPC)

GPC was employed to determine the molecular weight and the molecular weight distribution of the samples produced at different injection speeds. GPC analysis was performed on a high temperature PL-GPC220. The samples were dissolved in 1,2,4-trichlorobenzene, and the GPC runs were carried out at 160°C.

Capillary Rheometry

Capillary rheometry could serve as a fast and easy way to determine the melt flow rate (MFR) of a polymer. A capillary rheometer (CFT-500D Shimadzu) was used to study the MFR of the injection molded samples produced at different injection speeds. Experiments have been conducted with a temperature of 190°C and piston pressure of 9.8 MPa. A capillary with a length $L = 10$ mm and diameter $D = 1$ mm was used.

RESULTS AND DISCUSSION

Tensile Properties

The stress-strain curves of samples with different injection speeds are shown in Fig. 2. There is no obvious necking and the fracture mode is brittle, with an ultimate elongation of around 8%. High molecular orientation of semi-crystalline polymers could be one of the reason responsible for this^[12]. The tensile strength and Young's modulus of samples with different injection speeds are shown in Fig. 3. The highest tensile strength and Young's modulus reach as high as 130 MPa and 4380 MPa, respectively. It should be noted that all the strength and modulus values of thin wall samples in this paper are higher than those of conventional injection molding (around 20–40 MPa)^[13], but they decrease sharply with increasing injection speed. For semi-crystalline polymers, there are many factors can affect the tensile properties^[1, 14–19]. In this paper, we focus on the orientation, molecular weight, molecular weight distribution, melt flow rate, crystallinity and crystal morphology.

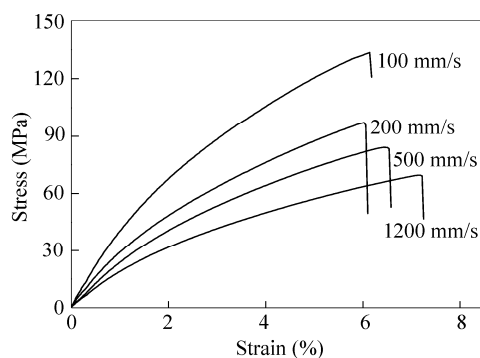


Fig. 2 Selective stress-strain curves of samples with different injection speeds

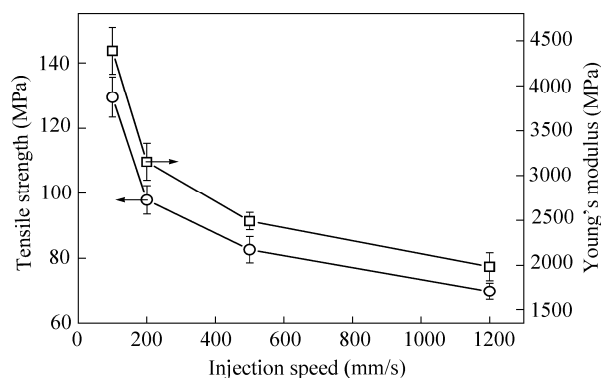


Fig. 3 Modulus and tensile strength of samples with different injection speeds

Orientation of Thin Wall Samples

Orientation plays an important role in the tensile properties of polymer materials. In our previous work, it was shown that relatively high tensile strength and modulus were obtained for specimens with high degree of orientation^[12]. Figure 4 shows the 2D WAXD patterns of HDPE samples with different injection speeds. The diffractions of (110) and (200) planes in orthorhombic PE along the equatorial direction indicate a preferential orientation along the injection flow direction, and the oriented structure is found in all samples. The degree of orientation obtained from 2D WAXD patterns is 66%, 63% and 69% for the samples produced at the injection speed of 100, 500 and 1200 m/s, respectively. There is no obvious difference between them, which demonstrates that the variation of tensile properties may not be caused by different orientation.

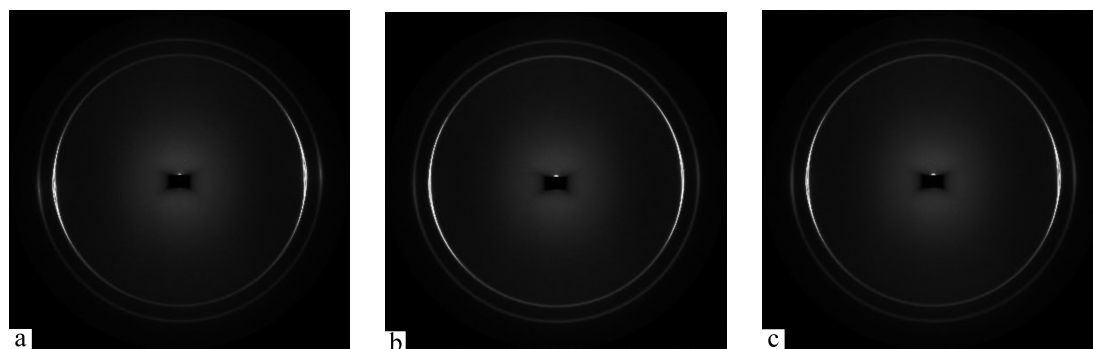


Fig. 4 2D WAXD patterns of samples with different injection speeds: 100 mm/s (a), 500 mm/s (b) and 1200 mm/s (c)

GPC Measurements

It is thought that the decrease in mechanical properties might be caused by degradation of polymer molecules, which could be a consequence of ultra high injection molding speeds. Therefore, GPC was used to determine the molecular weight and the molecular weight distribution of the samples produced under different injection speeds. The GPC chromatograms for the samples with injection speed of 100 mm/s is shown in Fig. 5. The others are not shown here, which have the same graphic structure. The distribution of HDPE used in this experiment is bimodal and the detail results of the molecular weight are listed in Table 1. By increasing the injection speed, the weight average molecular weight (M_w) and polydispersity index (PDI) of the samples have no obvious variation. It indicates that high speed injection molding does not induce degradation of polymer molecules, and the decreasing of tensile properties in this experiment should not have any relationship with molecular weight and molecular weight distribution.

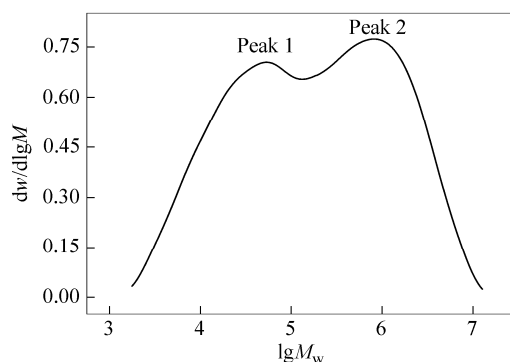


Fig. 5 GPC curve of a sample with injection speed of 100 mm/s

Table 1. Weight average molecular weight and polydispersity index of samples with different injection speeds

Injection speed (mm/s)	M_w of peak 1	M_w of peak 2	PDI of peak 1 (M_w/M_n)	PDI of peak 2 (M_w/M_n)
100	1.57×10^6	5.46×10^4	2.35	3.71
500	1.58×10^6	5.22×10^4	2.44	3.64
1200	1.57×10^6	5.32×10^4	2.43	3.77

Melt Flow Rate

Many studies have been carried out to investigate the effect of entanglement density on tensile properties^[20, 21]. It was reported that the entanglement density could play an important role in the final tensile properties. For this reason, the melt flow rate of the samples fabricated by different injection speeds has been investigated *via* capillary rheometer. The HDPE used in this experiment has a relatively low MFI of 0.035 g/10min (190°C, 2.16 kg). In order to reduce fluctuation in measurement and avoid instability flow in rheologic testing process, a moderated piston pressure (9.8 MPa) was used in this experiment.

Figure 6 shows the MFR values of samples melted at 190°C, held for 2 min and 10 min, respectively. Almost a constant MFR is observed for all of the samples. This indicates that there is no difference in entanglement density between the samples, and the decrease in tensile properties with increasing injection speed may have no relationship with entanglement density.

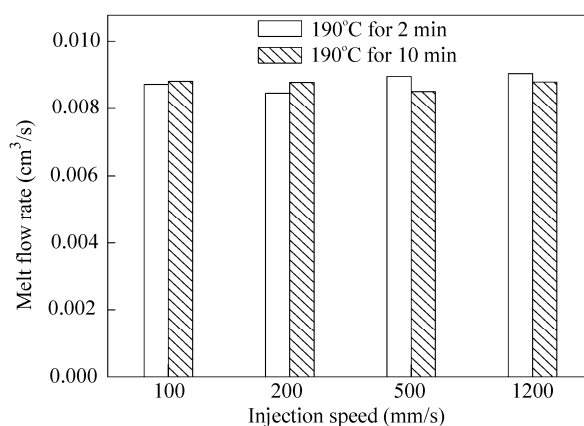


Fig. 6 MFR values of samples fabricated by different injection speeds

DSC Analysis

It is well known that crystallinity and crystalline forms are influential factors for tensile properties^[16, 22]. Kalay *et al.*^[13] investigated the enhancement of mechanical properties of HDPE and indicated that the crystal

structure of shish-kebab had noticeable effect on the tensile properties. Here, the DSC measurement is utilized to investigate the crystallinity, crystal structure and melting temperature. The first heating DSC thermograms of the samples from different locations along the sample thickness with different injection speeds are shown in Fig. 7. In the skin layer (0–25 μm), there are two peaks for all the samples with different injection speeds. The main peaks are around 127.8°C, and the another peaks are around 134°C. There is about a 6°C difference between them. For the second heating curve of sample with injection speed of 100 mm/s at layer of 0–25 μm (Fig. 8), there is only one peak. This means that the two peaks in these injection molded samples were induced by the special processing method but not the special property of the HDPE. The peaks at higher temperatures can be considered as the melting of extended chain crystalline structure^[13] or larger folded chain crystalline structure. It is shown in the figures that the content of extended chain crystals or larger folded chain crystals decreases with increasing injection speed. One of the features from the melting behavior of skin layer of samples produced at low injection speed (100 mm/s) is that the width of the peaks is broader than that of the others. Shear induced crystalline thick lamellae are responsible for the high melting temperature, shearing also results in a broader distribution of crystal size and thus broadening the melting peaks^[10]. For the middle layer (75–100 μm), the location of peaks is the same with these peaks from skin layer. From Fig. 7(c), one can observe only one peak for all except the sample with low injection speed (100 mm/s), which shows another peak at higher temperature. It indicates the presence of extended chain crystals or large folded chain crystals in the core layer (200–225 μm) of samples produced at low injection speed (100 mm/s). However, the melt temperature peak of the second heating curve is between that of the two peaks of the first heating curve. This can be understood as a consequence of the fast cooling rate of thin wall injection molded samples. It results in a smaller crystal size and decrease in the melting temperature. It should be noted that DSC results alone are not enough to prove the formation of extended chain crystal, 2D SAXS is needed to verify the result.

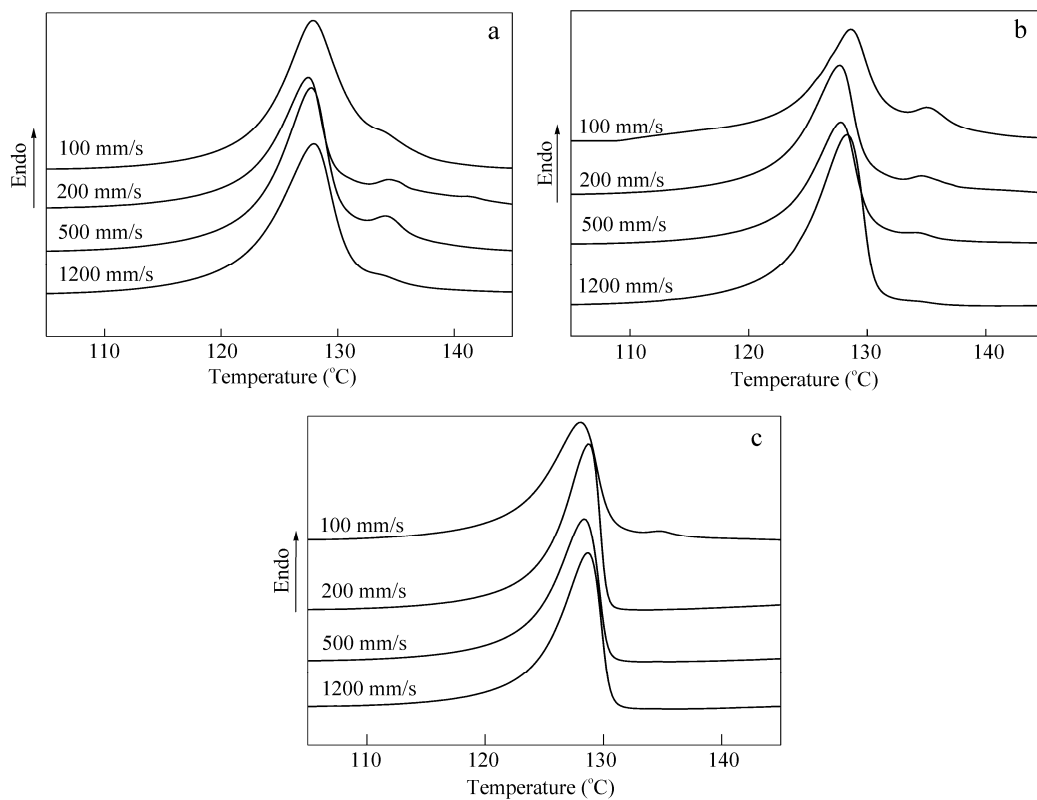


Fig. 7 The first DSC heating curves of samples with various injection speeds from different sample layers: (a) 0–25 μm , (b) 75–100 μm and (c) 200–225 μm

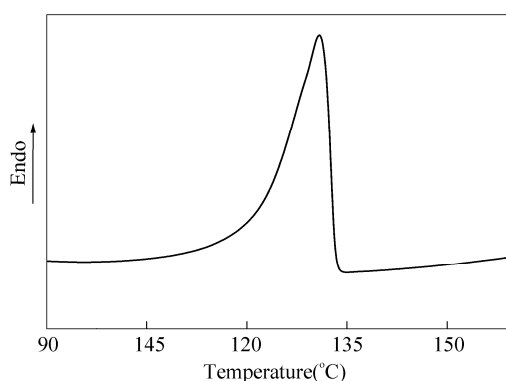


Fig. 8 The second DSC heating curve of sample with injection speed of 100 mm/s at layer of 0–25 μm

The crystallinity of samples is listed in Table 2. A similar crystallinity is obtained for the samples fabricated at injection speeds between 200 mm/s to 1200 mm/s. Interestingly, a slightly higher crystallinity was obtained for the sample produced at low injection speed (100 mm/s). And this is corresponding with the broader melting peaks of the samples produced at low injection speed. The difference in crystallinity among different layers is caused by the difference in shear rate and temperature distribution along the thickness direction.

Table 2. Crystallinity of samples with different injection speed at each layer

Injection speed (mm/s)	Hierarchical layer (μm)	Crystallinity (%)
100	0–25	53
	75–100	55
	200–225	48
200	0–25	48
	75–100	47
	200–225	51
500	0–25	49
	75–100	45
	200–225	51
1200	0–25	49
	75–100	47
	200–225	51

In summary, the content of extended chain crystals or large folded chain crystals decreases with increasing injection speed. For neat HDPE, the extended chain crystals can affect tensile properties significantly. There are many reports about the improvement in tensile properties of the self-reinforced polyethylene caused by the formation of extended chain crystal structure^[23, 24]. Djurner and co-workers^[24] investigated the development of extended chain crystals by high pressure injection molding and found the higher content of extended chain crystal resulted in higher tensile strength and Young's modulus. In current study, similar orientation and crystallinity is obtained for the samples fabricated under different injection speeds. The content of the extended chain crystals or large folded chain crystals has important influence on the tensile properties. The continuous decrease of tensile strength and Young's modulus with increasing injection speed is due to the decreased content of extended chain crystals or large folded chain crystals.

Furthermore, to understand such a behavior, the flow stability was investigated. It is well known that the unstable flow widely exists in polymer processing^[25]. In current study, flow instability was studied by extrusion with an injection molding machine. The pictures of extruded rods are shown in Fig. 9. The roughness of the sample surface increases with increasing injection speed. The increase in roughness with increasing injection speed is due to the increased instability of melt flow and shear stress. Therefore, the decreased tensile properties could be also due to the increased instability of melt flow with increasing of injection speed. More work is needed on the melt instability at high injection speed, which is important for industrial application.

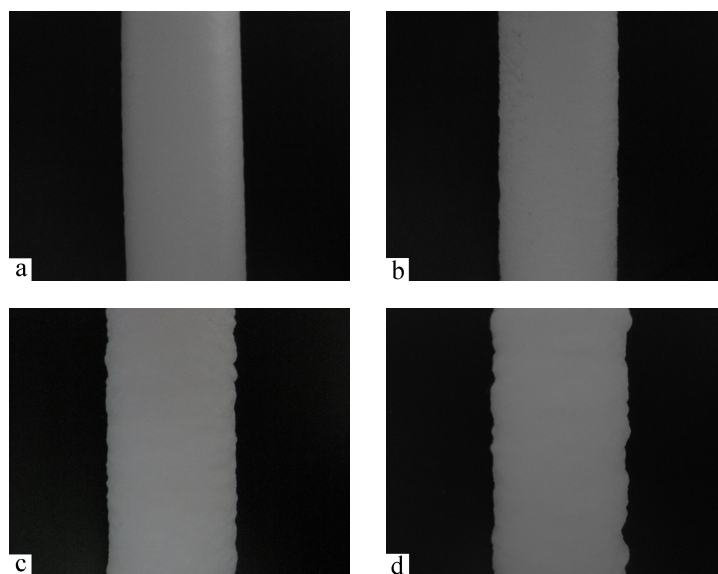


Fig. 9 Photographs of the extruded rods through injection molding machine with different injection speed: (a) 100 mm/s, (b) 200 mm/s, (c) 500 mm/s and (d) 1200 mm/s

CONCLUSIONS

Thin wall samples of HDPE were prepared through injection molding of different injection speeds. The effect of injection speed on the tensile properties was investigated in detail by examining the orientation, crystallinity and the crystal structure of the specimens. It was found that the overall orientation, molecular weight, molecular weight distribution, melt flow rate and crystallinity had no obvious change with increasing injection speed. A hierarchy structure with varied crystal structure along the thickness direction of samples was obtained due to the difference in shear rate and shear stress from the skin to the core. The gradual decrease in the content of extended chain crystals or large folded chain crystals with increasing injection speed was induced by difference in shear rate and stability of melt flow. The decrease in tensile strength and Young's modulus with increasing injection speed is mainly due to the decrease in the content of extended chain crystals or large folded chain crystals. Other factors, such as orientation, molecular weight, molecular weight distribution, entanglement density and crystallinity, seem to have little contribution to the mechanical property changes in this case. More research is needed to make sure the reasons which cause the tensile strength decrease with increasing injection speed. For example, 2D SAXS is needed to verify the extended chain crystals; the 2D WAXD of the samples from different locations along the sample thickness with different injection speeds is needed to confirm whether the orientation of different samples has no obvious difference. The tensile properties of the HDPE samples was decreased with increasing of injection speed, but the mechanism for this decrease should be carefully investigated based on the structure change and melt instability.

ACKNOWLEDGEMENT We would like to express our sincere thanks to Prof. Liangbin Li and Guoqiang Pan of National Synchrotron Radiation Laboratory (NSRL) in University of Science and Technology of China for their help in synchrotron WAXD experiments.

REFERENCES

- 1 Chen, S.C., Peng, H.S., Huang, L.T. and Chung, M.S., *J. Reinf. Plast. Compos.*, 2003, 22(5): 479
- 2 Chien, R.D., Chen, S.C., Peng, H.S., Su, P.L. and Chen, C.S., *J. Reinf. Plast. Compos.*, 2004, 23(6): 575
- 3 Kamal, M.R., Isayev, A.I. and Liu, S.J., "Injection molding technology and fundamentals", Hanser, Ohio, 2009

- 4 Yokoi, H., Han, X., Takahashi, T. and Kim, W.K., *Polym. Eng. Sci.*, 2006, 46(9): 1140
- 5 Chen, S.C., Chen, H.L. and Hsu, P.M., *J. Reinf. Plast. Compos.*, 2008, 27(13): 1381
- 6 Narh, K.A. and Li, Z.G., *Polym. Compos.*, 2000, 21(5): 751
- 7 Engels, T.A.P., Govaert, L.E. and Meijer, H.E.H., *Macromol. Mater. Eng.*, 2009, 294(12): 821
- 8 Hasegawa, S. and Yokoi, H., *Int. Polym. Process.*, 2006, 21(5): 464
- 9 GaucherMiri, V. and Seguela, R., *Macromolecules*, 1997, 30(4): 1158
- 10 Yang, J.H., Wang, K., Deng, H., Chen, F. and Fu, Q., *Polymer*, 2010, 51(3): 774
- 11 Wunderlich, B., "Thermal analysis", Academic Press, New York, 1990
- 12 Na, B., Wang, K., Zhang, Q., Du, R.N. and Fu, Q., *Polymer*, 2005, 46(9): 3190
- 13 Kalay, G., Sousa, R.A., Reis, R.L., Cunha, A.M. and Bevis, M.J., *J. Appl. Polym. Sci.*, 1999, 73(12): 2473
- 14 Ye, Z.B., Feng, W., Zhu, S.P. and Yu, Q., *Macromol. Rapid Commun.*, 2006, 27(11): 871
- 15 Pakhomov, P.M., Khizhnyak, S., Reuter, H., Galitsyn, V. and Tshmel, A., *Polymer*, 2003, 44(16): 4651
- 16 Daver, F. and Cherry, B.W., *J. Appl. Polym. Sci.*, 1995, 58(13): 2429
- 17 Phillips, R., Herbert, G., News, J. and Wolkowicz, M., *Polym. Eng. Sci.*, 1994, 34(23): 1731
- 18 Nitta, K. and Odaka, K., *Polymer*, 2009, 50(16): 4080
- 19 Cermak, R., Obadal, M., Ponizil, P., Polaskova, M., Stoklasa, K. and Heckova, J., *Eur. Polym. J.*, 2006, 42(9): 2185
- 20 Men, Y.F., Rieger, J. and Strobl, G., *Phys. Rev. Lett.*, 2003, 91(9): 4
- 21 Bartczak, Z., *J. Polym. Sci. Part B-Polym. Phys.*, 2010, 48(3): 276
- 22 Kubáut, J. and Manson, J.A., *Polym. Eng. Sci.*, 1983, 23(16): 869
- 23 Prox, M., Pornnimit, B., Varga, J. and Ehrenstein, G.W., *J. Therm. Anal.*, 1990, 36(5): 1675
- 24 Djurner, K., Kubat, J. and Rigdahl, M., *Polymer*, 1977, 18: 1068
- 25 Wang, S.Q. and Drda, P., *Macromol. Chem. Phys.*, 1997, 198(3): 673