

Vibration Assisted Extrusion of Polypropylene*

Fang-zhen An^a, Xue-qin Gao^{a**}, Jun Lei^{a**}, Cong Deng^b, Zhong-ming Li^a and Kai-zhi Shen^a

^aDepartment of Polymer Science and Materials, State Key Laboratory of Polymer Materials Engineering,
Sichuan University, Chengdu 610065, China

^bAnalytical and Testing Center, Sichuan University, Chengdu 610065, China

Abstract A new homemade apparatus, *i.e.* vibration assisted extrusion equipment, is employed to extrude polypropylene. Vibration assisted extrusion is based on the application of a specific macroscopic shear vibration field. Reduction of apparent melt viscosity as a function of vibration frequency is measured at different screw speeds and die temperatures. The effect of the process is investigated by performing mechanical tests, differential scanning calorimetry studies, polarized light microscopy and wide-angle X-ray diffraction. It is found that, compared with conventional extrusion, vibration assisted extrusion could effectively improve the rheological properties of PP melt by incorporating an extra shear vibration field. Both the tensile strength and elongation at break increased under the shear vibration field. For vibration assisted extrusion samples, both the melting temperature and crystallinity increased, accompanied by remarkable grain refinement. Vibration assisted extrusion induced a significantly enhanced bimodal orientation with a high fraction of a^* -oriented α -crystallites, while only a limited improvement in the flow direction orientation. A structural model, *i.e.* bimodal c -axis and a^* -axis orientation of PP macromolecular chains, was adopted to explain the experimental results.

Keywords: Vibration assisted extrusion; Polypropylene; Mechanical properties; Microstructure.

INTRODUCTION

The processing conditions affect the microstructure of polymeric materials, which then affects the properties of the final products. Introducing specific external fields into polymer processing is one of the most attractive approaches for structuring the microstructure and improving the properties of polymeric materials. Many new processing technologies have been proposed and intensively studied in recent years. For example, Casulli *et al.*^[1] superimposed longitudinal and transverse oscillations on the die section at the exit of an extruder. The results showed that the mechanical properties of the extrudate were improved and the die swell reduced. Shear controlled orientation in injection molding, based on the application of a macroscopic shear stress field to a solidifying melt in a mold cavity, was studied by Guan *et al.*^[2] and Kalay *et al.*^[3]. It was found that the mechanical properties were greatly enhanced, on account of perfect spherulites, the existence of shear-induced shish-kebab crystals, and a remarkably enhanced molecular orientation. Guo *et al.*^[4, 5] investigated the effect of ultrasonic oscillations, which are in the direction parallel to the flow of polymer melts, on the morphology and properties of polymeric materials. They found that the die pressure and apparent viscosity decreased, the mechanical properties were improved, and the dispersion of the dispersed phase or nano-filler was more uniform. Isayev *et al.*^[6, 7] imposed a perpendicular superposition of ultrasonic oscillations, and found that the complex

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51033004 and 51121001) and China Postdoctoral Science Foundation (No. 2013M540711).

** Corresponding authors: Xue-qin Gao (高雪芹), E-mail: gxqsnow@163.com

Jun Lei (雷军), E-mail: lei jun@scu.edu.cn

Received August 17, 2014; Revised August 30, 2014; Accepted September 10, 2014

doi: 10.1007/s10118-015-1617-z

viscosity, storage and loss moduli were increased, mechanical properties increased, and the dispersion of filler was improved. Li *et al.*^[8] and Zhang *et al.*^[9] superimposed a pulsing pressure on the melt during the injection and packing stages, *i.e.* the so-called vibration assisted injection molding, and investigated the effects of vibration frequency and pressure amplitude. The results showed that, through melt vibration, the spherulitic morphology in the core was changed into parallel lamellae perpendicular to the melt flow direction, and shish-kebab crystals and row-nucleated lamellae were obtained in the shear layer. Besides, crystal size became smaller, and a change of crystal structure of PP from α -form to β -form and γ -form was achieved. Jiang *et al.*^[10] and Nie *et al.*^[11, 12] prepared PE pipe with improved hoop mechanical properties *via* rotational extrusion. They found that the molecular orientation deviated from the axial direction following the rotation of the mandrel and die, and the resistance to slow crack growth was considerably improved.

To investigate the effects of the application of an extra shear vibration field on the processing, mechanical properties and microstructure of polymer, we developed a hydraulic vibration extrusion apparatus with a frequency of 0–93.3 Hz. The results showed that the effects of the shear vibration field were more effective at lower vibration frequency and bigger vibration amplitude in the range of our experiment, So once more we design a new vibration assisted extrusion apparatus with optimized parameters. In the present study, PP extruded samples were prepared *via* conventional extrusion and vibration assisted extrusion, and microstructure analysis was performed.

EXPERIMENTAL

Equipment

A schematic diagram of the equipment of mechanical vibration assisted extrusion is shown in Fig. 1. The apparatus composed of four parts, namely, an extruder, an extrusion head, a crank vibration system, a pressure and temperature measurement and control system. The temperatures of the extrusion head and die were controlled individually. Moreover, the vibration frequency, which was in the range of 0–3.3 Hz, was also continuously adjustable by adjusting motor rotation speed. The main feature of vibration assisted extrusion is that an extra shear vibration field is applied to the polymer melts by two vibration rods that vibrate asynchronously with the same frequency. We also carried out conventional extrusion by using the same processing parameters but in the absence of vibration for comparison purpose.

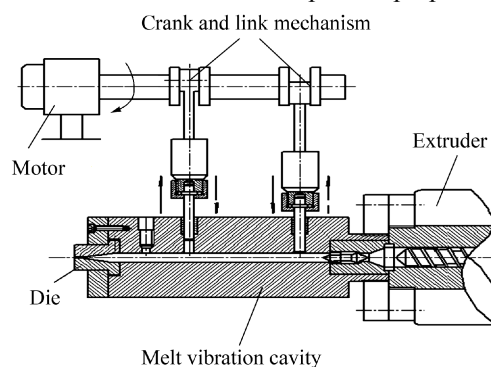


Fig. 1 Schematic diagram of vibration assisted extrusion equipment

Material and Sample Preparation

Polypropylene (PP) under trade name T30s was used. The PP, a commercial product of Lanzhou Petroleum Chemical Co. (China), had a melt index of $0.25 \text{ g} \cdot \text{min}^{-1}$ at 230°C and a density of $0.91 \text{ g} \cdot \text{cm}^{-3}$.

The PP was extruded in the special mechanical vibration assisted extrusion equipment developed in our laboratory, in the presence or absence of vibration at different screw speeds ($4, 8, 12 \text{ r} \cdot \text{min}^{-1}$), die temperatures ($180, 190, 200^\circ\text{C}$), and vibration frequencies ($0\text{--}3 \text{ Hz}$). The temperatures from hopper to vibration zone were $160, 180, 200$, and 200°C . The die in the extruder was a slit die with 50 mm width and 1 mm thickness. The extrudates were cooled in air.

Characterizations

Analysis of the apparent viscosity

To compare the rheological properties of the PP melt under vibration extrusion and under conventional extrusion, the apparent viscosity was calculated.

According to the theoretical analysis of the flow of liquids through rectangular channels, if the width/height ratio of the rectangular cross section of the slit is greater than 10/1, the apparent viscosity could be calculated according to the following equation^[13, 14]:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{h\Delta P}{2L} \bigg/ \frac{6Q}{wh^2} = \frac{wh^3\Delta P}{12QL} = \frac{wh^3\Delta P\rho t}{12LM} \quad (1)$$

where τ is the shear stress, $\dot{\gamma}$ is the apparent shear rate, ΔP is the differential pressure, Q is the volume output rate, h is the height of the die, w is its width, L is its length, ρ is the density of material, t is the interval of time, and M is the weight of the sample.

Because the purpose of analyzing the apparent viscosity was only to compare the differences between the apparent viscosities under vibration extrusion and under conventional extrusion, the formula with a non-Newtonian exponential was not adopted. It would not influence the comparative results.

Tensile property measurements

Dumbbell-shaped tensile test specimens were obtained from extrudates by simple cutting. A REGER-3010 universal electronic testing machine was employed for tensile testing at room temperature (23 °C); the crosshead speed was 50 mm·min⁻¹. Four specimens with the same processing conditions were tested to guarantee the precision of experimental results.

Differential scanning calorimetry (DSC)

The DSC measurements were carried out on a NETZSCH DSC 204 F1 differential scanning calorimeter (Germany). Scans were recorded at a heating rate of 10 K·min⁻¹ over a temperature range between 40 and 200 °C. The weight of the samples for each test was about 5 mg. During the measurements, dried nitrogen gas was purged at a constant flow rate.

The degree of crystallinity (X_c) for each specimen was evaluated by using the following formula:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (2)$$

where ΔH_m is the measured fusion enthalpy and ΔH_m^0 is the fusion enthalpy of 100% crystalline PP. The value of ΔH^0 was selected as 207 J·g⁻¹^[15].

Polarizing light microscopy (PLM)

In order to investigate the microstructure of the samples, thin slices with a thickness of 10 μm cut along the flow direction of extrudates were analyzed by PLM. PLM observations were performed with a DX-1 (Jiang-Xi Phoenix Optical Co. China.) microscope. The photographs were recorded by a Nikon 500D digital camera.

Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray scattering experiments (WAXD) were conducted using a Philips X'Pert Pro MPDX diffractometer. The tube voltage and current were set at 40 kV and 40 mA, respectively. Scans were conducted with Cu K α radiation ($\lambda = 0.15406$ nm) in the range of 10°–35° in 2θ with a scanning rate of 0.03 deg·min⁻¹. The samples were placed with the flow direction perpendicular to the beams.

For quantitative evaluation of the data, the PP α -phase orientation indices were derived by comparing the intensities of different reflections (for definitions of parameters see Table 1)^[16–18].

(a) The orientation index A_{110} , and a similarly defined orientation index A_{130} : The definition of both indices is based on a decrease in intensity of reflections (111) and ($\bar{1}$ 31 + 041) in equatorial measurements when the

crystallites orientate with their *c*-axis along the flow direction. These indices thus give an indication of the degree of orientation parallel to the *c*-axis of crystallites corresponding to the flow direction in our samples.

(b) An index C_{040} : It serves as a measure of the epitaxially induced double orientation of α -PP crystallites (that means the crystallographic axis *c* and also the crystallographic axis a^* may form a fiber axis in the flow direction). This index is based on the fact that in the equatorial measurement both a^* - and *c*-oriented crystallites contribute to the (040) reflection, but only *c*-oriented crystallites contribute to the (110) and (130) reflections.

Table 1. Parameters derived from the WAXD pattern

Orientation parameters:	
$A_{110} = \frac{I_{110}}{I_{110} + I_{111} + I_{131+041}}$	(3)
$A_{130} = \frac{I_{130}}{I_{130} + I_{111} + I_{131+041}}$	(4)
$C_{040} = \frac{I_{040}}{I_{110} + I_{040} + I_{130}}$	(5)

RESULTS AND DISCUSSION

Rheological Behavior

The apparent melt viscosity at different screw speeds and die temperatures was calculated, and the results are shown in Figs. 2 and 3, respectively, as a function of vibration frequency. As can be seen in Figs. 2 and 3, the apparent viscosity under the conditions of vibration extrusion decreases substantially compared with that under conventional extrusion conditions. The apparent viscosity first decreases sharply with the increase of vibration frequency, and then begins to decrease slowly and fluctuate slightly. Furthermore, the rate and magnitude of change in apparent viscosity with vibration frequency are different under different screw speed and temperature conditions. As shown in Fig. 2, the higher the screw speed is, the lower the apparent viscosity is, but accompanied by a smaller decrement in apparent viscosity with vibration frequency. The maximum decrement is 33.1%, from 2180 Pa·s to 1460 Pa·s, at a screw speed of 4 r·min⁻¹. This is because the lower the screw speed is, the longer the vibration time is and the greater the effect is. As for the effect of die temperature, at a high value, the molecular chains have high mobility, thus enabling the chains to disentangle or slip past each other easily and resulting in a low viscosity. On the other hand, the application of an extra shear vibration field didn't result in a much larger decrement in the apparent viscosity at a higher die temperature.

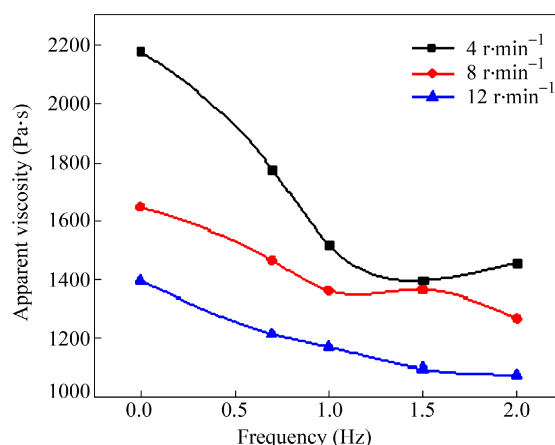


Fig. 2 Effects of vibration frequency on the apparent viscosity at different screw speeds (Die temperature = 180 °C)

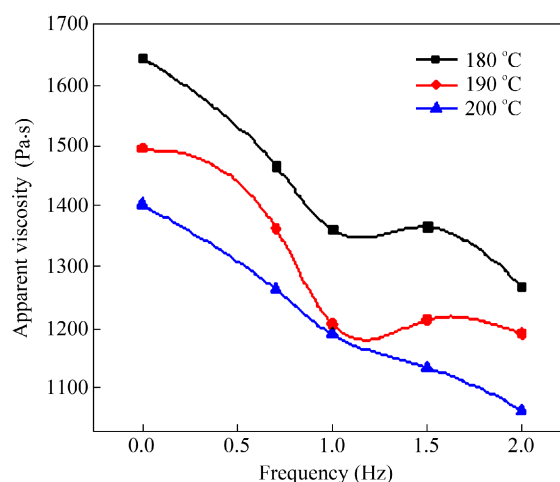


Fig. 3 Effects of vibration frequency on the apparent viscosity at different die temperatures (Screw speed = 8 r·min⁻¹)

Mechanical Properties

Based on the above analysis, a lower screw speed, 2 r·min⁻¹, and a die temperature of 200 °C were chosen to investigate the effect of vibration extrusion on microstructure and properties of PP. Since the apparent viscosity keeps decreasing in the frequency range 0 Hz to 2 Hz at a die temperature of 200 °C, the vibration frequency was set to 2, 2.5 and 3 Hz respectively.

According to the stress-strain curves, not presented here, all tensile specimens deformed by necking and cold drawing followed finally by fracture, indicating a typical ductile fracture. Figure 4 presents the tensile strength and elongation at break of PP samples, derived from the stress-strain curves, as a function of vibration frequency. Obviously, both tensile strength and elongation at break of samples processed by vibration assisted extrusion were improved compared with those processed by conventional extrusion. The largest improvement in both tensile strength and elongation at break was obtained at a vibration frequency of 2.5 Hz. Although the tensile strength shows only a limited improvement following the application of the shear vibration field, from 39.2 MPa to 41.5 MPa, the elongation at break shows a very significant increase, from 550% to 840%. Furthermore, it shows that when the vibration frequency is 3 Hz, the mechanical performances show relative decreases, but still higher than those of conventional samples. We speculate that when the vibration frequency is 3 Hz, there may be a lag for the molecular chains to response to the shear vibration field, thus resulting in a less significant improvement in the mechanical properties.

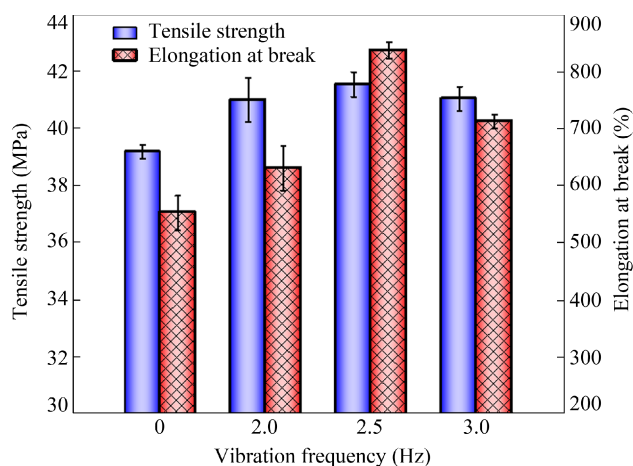


Fig. 4 Tensile strength and elongation at break versus vibration frequency

DSC Analysis

The DSC thermograms were investigated to study the melting behavior of PP samples prepared *via* vibration assisted extrusion as compared to conventional samples in shown in Fig. 5. And the analytical data are listed in Table 2. It shows that the conventional sample exhibits three melting peaks at 131.3 °C, 149.5 °C and 165.4 °C, respectively. The melting peak at 149.5 °C is attributed to the β -form crystals of PP and that at 165.4 °C belongs to the α -form crystals. The source of the melting peak at 131.3 °C is not clear yet. After the application of vibration during extrusion, only the major α melting peak exists. As is well known, a decrease of the β -crystal fraction is favorable to improve the tensile strength^[19]. Moreover, both the melting temperature and crystallinity of vibration assisted extrusion samples increase and show the largest increment at a vibration frequency of 2.5 Hz. The increase in melting temperature is correlated to an increase in lamellae thickness and indicates the perfection of crystals improved with the application of the shear vibration field. Generally, an increase in crystallinity or increase in lamellae thickness increases the tensile strength^[20, 21]. The change tendency of the β -crystal content and crystallinity is similar to that reported by Kalay and Bevis^[22] for PP processed under a shear field applied during injecting molding.

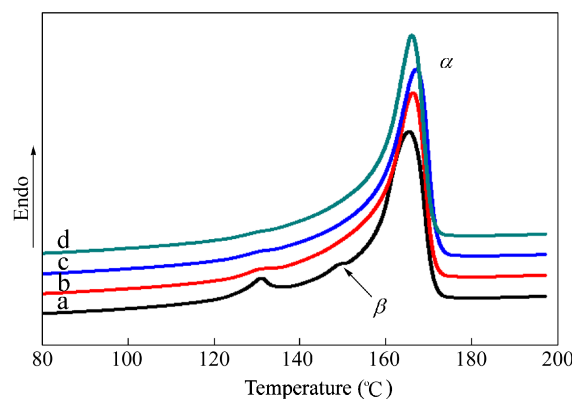


Fig. 5 DSC curves of PP samples obtained at different vibration frequencies: (a) $F = 0$ Hz, (b) $F = 2.0$ Hz, (c) $F = 2.5$ Hz and (d) $F = 3.0$ Hz

Table 2. DSC results of PP samples extruded at different vibration frequencies

Vibration frequency (Hz)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
0	165.4	87.2	42.1
2.0	166.3	91.1	44.0
2.5	167.0	92.5	44.7
3.0	166.0	91.8	44.3

PLM Observation

According to our experimental results presented above, here we select PP samples processed by conventional extrusion and vibration assisted extrusion at a vibration frequency of 2.5 Hz (the optimum condition), to present the change of the microstructure.

The PLM micrographs of PP samples obtained at different frequencies are shown in Fig. 6. It indicates that the crystal structure of both conventional and vibration assisted extrusion samples is typical spherulites. Besides, the spherulites in conventional sample are not of the same birefringence, suggesting that they are of different crystalline modifications. According to the previous studies^[23] and the results of DSC analysis, we believe that these two crystalline modifications correspond to α -form and β -form crystals respectively, as shown in Fig. 6. In the meantime, it shows an obvious decrease in the spherulite size for the vibration assisted extrusion sample compared to that of the conventional sample. According to previous reports, a reduction in the size of spherulites generally reduces the tensile strength, but increases the elongation at break under a ductile fracture mode^[24–26]. These fine spherulites are one of the major reasons for the substantial increase in elongation at break. On the

other hand, the molecular orientation has a significant influence on the mechanical performances, and hence will be discussed in detail below.

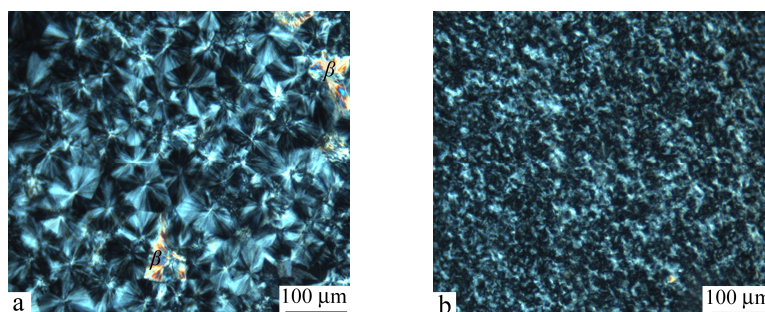


Fig. 6 PLM micrographs of PP samples obtained at different vibration frequencies: (a) $F = 0$ Hz and (b) $F = 2.5$ Hz

WAXD Analysis

The diffraction patterns of WAXD are shown in Fig. 7 as typical examples. Each profile was vertically shifted for clarity. It presents seven strong crystalline diffraction peaks at $2\theta = 14.0^\circ$, 16.8° , 18.4° , 21.0° , 21.7° , 25.3° , and 28.5° corresponding to the (110), (040), (130), (111), ($\bar{1}31 + 041$), (060), and (220) crystal planes, respectively. It also shows that the β -form or γ -form crystal doesn't exist or too little to be detected in both samples except for the existence of α -form crystal.

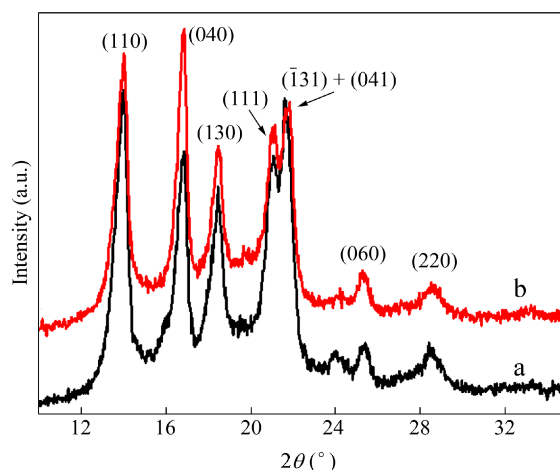


Fig. 7 WAXD diffraction patterns of PP samples obtained at different frequencies: (a) $F = 0$ Hz and (b) $F = 2.5$ Hz

The application of the shear vibration field induced changes in the crystal structure of PP. In Fig. 7, the peak intensities of (110), (130), (111) and ($\bar{1}31 + 041$) crystal planes decrease following the application of vibration. Another important feature is the increase of the ratio of the (040) reflection intensity, $I(040)$, to that of the (110) reflection, $I(110)$, under the shear vibration field. This behavior implies that the shear vibration field applied to polymer melt changes the crystal orientation, inducing a preferential orientation in the (040) direction and a higher degree of crystal orientation^[27, 28]. Costantino *et al.*^[18] also reported similar phenomenon for PP samples processed by shear controlled orientation in injection molding. Their WAXD data showed typical XRD patterns as shown in Fig. 7 of our study.

The orientation parameters, estimated from the WAXD patterns, are shown in Table 3. It shows that all these orientation parameters increase in the presence of vibration. A_{110} and A_{130} show slight increases of about 6.6% and 2.7%, which indicates that the degree of orientation in the flow direction is enhanced, though limited in extent. On the other hand, C_{040} shows a significant 31.0% increase, thus indicating a significantly enhanced bimodal orientation in which the crystallographic c - and a^* -axes are mixed oriented to the flow direction.

Considering A_{110} , A_{130} and C_{040} increase to very different extents, it was concluded that the application of the shear vibration field led to a high fraction of a^* -oriented α -crystallites.

Table 3. Orientation parameters derived from the WAXD patterns

Vibration frequency (Hz)	A_{110}	A_{130}	C_{040}
0	0.397	0.258	0.310
2.5	0.423	0.265	0.406

Summarizing the above results, here we adopted a model proposed by Clark and Spruiell^[29], as shown in Fig. 8, to interpret our experimental results. The structural model was proposed as a structure of skin layer in injection-molded polypropylene, based on previous studies on the mixed c -axis and a^* -axis orientation seen in such as melt-spun polypropylene fiber and skin layer in injection-molded polypropylene. In this model, the primary component consists of a planar row structure of lamellae with c -axis parallel to the flow direction, interconnected by tie molecules. The secondary component consists of small interlamellar crystallites with a^* -axis parallel to the flow direction. They thought the formation mechanism was that the c -axis-oriented component was formed first and the a^* -oriented component was formed by epitaxial overgrowth on the c -oriented substrate.

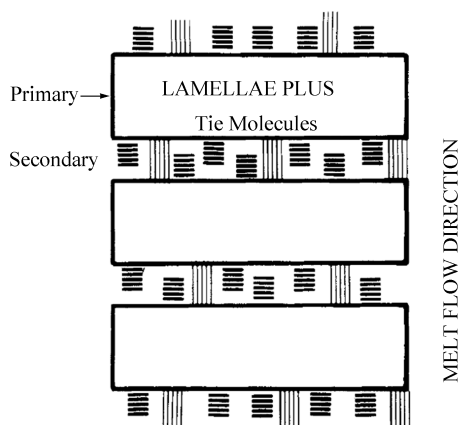


Fig. 8 Morphology of polypropylene with bimodal orientation, showing primary and secondary crystallization stages^[29]
(Reprinted with permission from Ref. [29]; Copyright (1976) of John Wiley and Sons)

In our experiment, the application of the shear vibration field induced a more substantial a^* -orientation and a slightly enhanced c -orientation. As for implications for mechanical properties, the tensile strength and elongation at break were both improved, but to different extent. Combining with the aforementioned structural model, this is understandable. In the model, the principal matrix, the portion with c -axis orientation, provides strength and cohesion, and the secondary component, the portion with a^* -orientation, acts as a “morphological plasticizer”, absorbing much of the deformation of the total structure and distributing stress relatively uniformly to the connecting links of the matrix^[29]. Considering the a^* -oriented crystallites are small, imperfect, nonuniform and not connected, they thus contribute little to yield stress^[30]. Moreover, the prominent grain refinement contributes to the pronounced increase in elongation at break. On the other hand, an increase of crystallinity, a decrement of the β -crystal content, and an improvement in crystalline perfection are responsible for the increase in tensile strength.

CONCLUSIONS

A new vibration assisted extrusion apparatus was developed in this work and its effects on the rheological, mechanical properties and microstructure of PP were studied. We found that, compared with conventional extrusion, vibration assisted extrusion can effectively improve the rheological properties of polymer melts by

incorporating an extra shear vibration field. The higher the screw speed, the lower the apparent viscosity, but accompanied by a smaller decrement in apparent viscosity with vibration frequency. Data on mechanical properties showed that both the tensile strength and elongation at break of PP samples increased under the shear vibration field. The maximum increments in both tensile strength and elongation at break were obtained at a vibration frequency of 2.5 Hz, from 39.2 MPa and 550% to 41.5 MPa and 840%, respectively. Both the melting temperature and crystallinity of PP samples processed *via* vibration assisted extrusion increased as compared with those of conventional samples, while the content of β -form crystal decreased. The application of the shear vibration field led to a remarkable grain refinement. As for the effect of the process on molecular orientation, vibration assisted extrusion induced a significantly enhanced bimodal orientation with a high fraction of a^* -oriented α -crystallites, while only a limited improvement in the flow direction orientation. A structural model, *i.e.* bimodal c -axis and a^* -axis orientation of PP macromolecular chains, was adopted to explain the experimental results.

In summary, vibration assisted extrusion can effectively improve the rheological and mechanical properties, and change the microstructure morphology of PP.

REFERENCES

- 1 Casulli, J. and Clermont, J.R., *Polym. Eng. Sci.*, 1990, 30: 1551
- 2 Guan, Q., Zhu, X.G., Chiu, D., Shen, K.Z., Lai, F.S. and McCarthy, S.P., *J. Appl. Polym. Sci.*, 1996, 62: 755
- 3 Kalay, G. and Kalay, C.R., *J. Appl. Polym. Sci.*, 2003, 88: 814
- 4 Chen, G.S., Guo, S.Y. and Li, H.L., *J. Appl. Polym. Sci.*, 2001, 86: 23
- 5 Zhao, L.J., Li, J., Guo, S.Y. and Du, Q., *Polymer*, 2006, 47: 2460
- 6 Swain, S.K. and Isayev, A.I., *Polymer*, 2007, 48: 281
- 7 Isayev, A.I., Kumar, R. and Lewis, T.M., *Polymer*, 2009, 50: 250
- 8 Li, Y.B., Liao, Y.C., Gao, X.Q., Yuan, Y., Ke, W.T. and Shen, K.Z., *J. Polym. Sci., Part B: Polym. Phys.*, 2005, 43: 13
- 9 Zhang, J., Shen, K.Z., Na, S. and Fu, Q., *J. Polym. Sci., Part B: Polym. Phys.*, 2004, 42: 2385
- 10 Jiang, L., Shen, K.Z., Ji, J.L. and Guan, Q., *J. Appl. Polym. Sci.*, 1998, 69: 323
- 11 Nie, M., Bai, S.B. and Wang, Q., *Polym. Bull.*, 2010, 65: 609
- 12 Nie, M. and Wang, Q., *J. Appl. Polym. Sci.*, 2013, 128: 3149
- 13 Wales, J.L.S., Den Otter, J.L. and Janeschitz-Kriegl, H., *Rheol. Acta*, 1965, 4: 146
- 14 Gao, X.Q., Zhang, J., Chen, C.S. and Shen, K.Z., *J. Appl. Polym. Sci.*, 2007, 106: 552
- 15 van der Wal, A., Mulder, J.J. and Gaymans, R.J., *Polymer*, 1998, 39: 5477
- 16 Zipper, P., János, A., Geymayer, W., Ingolic, E. and Fleischmann, E., *Polym. Eng. Sci.*, 1996, 36: 467
- 17 Zhu, P.W. and Edward, G., *Macromol. Mater. Eng.*, 2003, 288: 301
- 18 Costantino, A., Pettarin, V., Viana, J., Pontes, A., Pouzada, A. and Frontini, P., *Procedia. Mater. Sci.*, 2012, 1: 34
- 19 Luo, F., Wang, K., Ning, N.Y., Geng, C.Z., Deng, H., Chen, F., Fu, Q., Qian, Y.Y. and Zheng, D., *Polym. Adv. Technol.*, 2011, 22: 2044
- 20 Tanniru, M., Yuan, Q. and Misra, R.D.K., *Polymer*, 2006, 47: 2133
- 21 Yuan, Q. and Misra, R.D.K., *Polymer*, 2006, 47: 4421
- 22 Kalay, G. and Bevis, M.J., *J. Polym. Sci. B Polym. Phys.*, 1997, 35: 265
- 23 Li, Q.T., Zheng, G.Q., Dai, K., Xie, M.C., Liu, C.T., Liu, B.C., Zhang, X.L., Wang, B., Chen, J.B., Shen, C.Y., Li, Q. and Peng, X.F., *Mater. Lett.*, 2011, 65: 2274
- 24 Way, J.L., Atkinson, J.R. and Nutting, J., *J. Mater. Sci.*, 1974, 9: 293
- 25 Campbell, D. and Qayyum, M.M., *J. Mater. Sci.*, 1977, 12: 2427
- 26 Chan, C.M., Wu, J.S., Li, J.X. and Cheung, Y.K., *Polymer*, 2002, 43: 2981
- 27 Rybníkář, F., *J. Appl. Polym. Sci.*, 1989, 38: 1479
- 28 Choi, W.J. and Kim, S.C., *Polymer*, 2004, 45: 2393
- 29 Clark, E.S. and Spruiell, J.E., *Polym. Eng. Sci.*, 1976, 16: 176
- 30 Fujiyama, M., Wakino, T. and Kawasaki, Y., *J. Appl. Polym. Sci.*, 1988, 35: 29