Structure Memory Effects and Rheological Behaviors of Polyethylenes in Processing Temperature Window

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ABSTRACT: In this work, both hexene copolymerized polyethylene of TR-571 and homopolymerized polyethylene of 5000s were ram extruded using a temperature window effect. The rheological results show that the extrusion pressures abruptly drops at very narrow extrusion temperature windows for the two types of polyethylenes, but the window range (150–155°C) of TR-571 are higher about 6°C than that of 5000s, and the threshold melt velocity value (where the window effect set in) for TR-571 is remarkably lower than that of 5000s. Besides, the differential scanning calorimeter experiments indicate that the melting points (T_m) of the extrudates obtained inside the temperature window are lower 3.74–4.56°C than those obtained outside, whereas the crystallization peak temperatures (T_c) of the former are higher 3.29–3.57°C than those of the later. The crystal orientation, shown in the photographs of wide-angle x-ray diffraction and scanning electron microscope, indicates that the chain alignment induced by elongational flow in the temperature window can at least be partially maintained and leave a structure memory in the melt state. Successive self-nucleation and annealing fractionation results suggest that these well-aligned chains as the result of structure memory effect can act as a nucleating agent in the crystallization process. Thus, the number of the lamellae increases and the thickness decrease, which finally leading to higher T_c and lower T_m of extrudates obtained inside a temperature window. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 354–361, 2013

INTRODUCTION

Effectively processing polyethylene with low pressure and temperature is of great significance for reducing degradation, decreasing energy consumption, and improving product quality. Generally, conventional processing of polyethylene is usually carried out at temperatures far above its melting point, both to ascertain that the material is completely molten and also to reduce the viscous flow resistance.[1] High processing temperature, however, will increase energy consumption and aggravate polymer degradation.

In the 1960s, Wunderlich and Arakawa[2] as well as Rees and Bassett[3] discovered the extended-chain hexagonal crystal phase of polyethylene. Due to the enhanced chain mobility of this phase, numerous theoretical and experimental investigations were elicited in both industry and academia. However, the extremely high pressure (>360 MPa) and temperature (>230°C) associated with the formation of hexagonal crystals make it almost impossible for processing polyethylene in this phase.

In 1989, Waddon and Keller[4] first recognized a temperature window effect while studying the melt rheological behavior of linear polyethylene by batch capillary rheometer experiments, at temperatures right above those at which flow-induced crystallization is expected. Within the narrow temperature window of the studied polyethylene, a sharp minimum extrusion pressure (p) and flow resistance at around 150°C (as opposed to the expected increase, leading to blockage as in preceding works[5]) were observed together with the associated disappearance of flow instabilities and extrudate distortions. Subsequently, Kolnaar and Keller[6–8] systematically investigated the effects of various parameters, such as piston velocity and molecular weight, on temperature window of high-density polyethylene (HDPE).

The mechanisms of unexpected melt flow behavior within temperature window of HDPE were independently or collaboratively studied by Keller, Hsiao, Hikosaka, and Fang.[9–19] They reported that the reduced flow resistance was attributed to the formation of mobile hexagonal mesophase by flow-induced chain alignment which is critical to molecular weight and melt
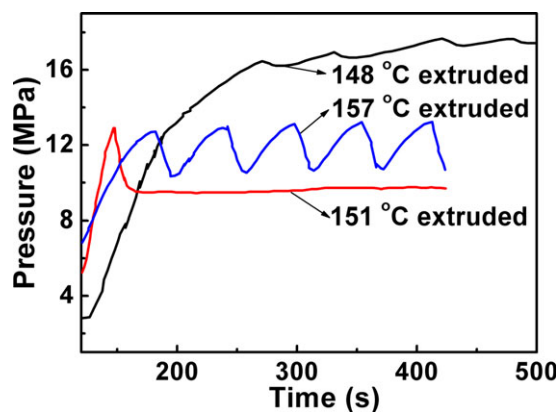
Figure 1. Time evolution of extrusion pressure at different extrusion temperatures with the extrusion of TR-571 at $v = 1$ mm/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flow velocity. This hypothesis was confirmed by the observation of the transformation from an orthorhombic phase to a hexagonal phase through *in situ* wide-angle X-ray diffraction (WAXD).[20–22]

The discovery of temperature window effect has potential significance for polymer processing at low pressures and temperatures. Presently, the correlated studies on temperature window effect are mostly concerning HDPE, especially its melt rheological behavior.[1] However, various copolymerized polyethylenes, such as copolymer of ethylene with α-olefin, are being widely used due to its uniquely controllable structures and performance. Besides, previous research indicated that crystallization behavior of polymer can significantly affect its various properties, especially mechanical performance.[23,24]

In this work, we first determined whether copolymerized polyethylene TR-571 has temperature window effect by its melt rheological behavior under various processing parameters. Then, the effect of temperature window on the micro-morphologies and rheological behaviors has been studied by successive self-nucleation and annealing (SSA) fractionation method. Besides, the corresponding rheological behavior and thermal properties of homopolymerized polyethylene have also been studied for comparing with those of copolymerized polyethylene.

EXPERIMENTAL SECTION

Materials
Homopolymerized HDPE of 5000s with the melt flow index (MFI) of 1.08 g/10 min (190°C, 2.16 kg), molecular weight of 3.3 $\times 10^5$, and the density of 0.95 g/cm^3 was supplied by Lanzhou Chemical Industry Factory (China). Ethylene-hexene copolymer HXM TR-571 with MFI of 0.02 g/10 min (190°C, 2.16 kg), molecular weight of 8.2 $\times 10^5$, and the density of 0.95 g/cm^3 was supplied by Singapore Petroleum Co. (Singapore). E143 as an example is the abbreviation of the extrudates obtained at 143°C.

Rheological Experiments
A capillary rheometer of Rosand RH7 (Malvern Co., England) was used to study the rheological behaviors of various polyethylenes. The capillary diameter and length are 1 and 30 mm,

respectively. In view of the large length-to-diameter ratio, entrance pressure losses were assumed to be negligible, and consequently, no Bagley corrections were made. The barrel diameter is 7.5 mm, and the volume of melt reserve is 44.2 cm^2. Piston speed varies from 1.0 to 8.0 mm/min, and stainless steel die is used, having an entrance angle of 180°. Besides, the pressure transducer is positioned before and close to the die. The extrusion processes comprise the following steps: (1) The resin was melted at a given temperature of 200°C and pressured for 30 min; (2) the melt was cooled to a given extrusion temperature and was kept constant for about 15 min; (3) extrusion was carried out at a fixed extrusion velocity and temperature. The majority of the experiments are consisted of measuring pressure (p) as a function of temperature (T) or time (t) at a constant piston velocity (v).

Thermal Analysis
All the calorimetric experiments were carried out using a Mettler Toledo DSC1 differential scanning calorimeter (DSC) under nitrogen atmosphere (50 mL/min). Calibration for the temperature scale was performed using indium as a standard to ensure reliability of the data obtained. The measurements were carried out as follows: samples were kept at 200°C for 8 min to erase any previous thermal history. Then, they were cooled to 25°C for 8 min with the rate of 10°C/min and subsequently heated to 200°C with the same rate. T_m and T_c were the peak temperatures of the heating curve and the subsequent cooling curve, respectively.

SSA fractionation method[25,26] is described as follows: (1) Erasure of the crystalline thermal history by heating the sample to 200°C and holding for 8 min; (2) cooling the sample to 50°C and holding for 1 min; (3) reheating the sample to a partial melting temperature denoted T_s; (4) maintaining the sample at T_s for 5 min; (5) cooling samples from T_s to 50°C and holding for 1 min, where the effects of the thermal treatment will be reflected in the crystallization of the samples; (6) repeating from the third step to fifth step at a gradually lower T_s, which were varied from 140°C to 105°C with 5°C intervals for a total self-nucleation/annealing
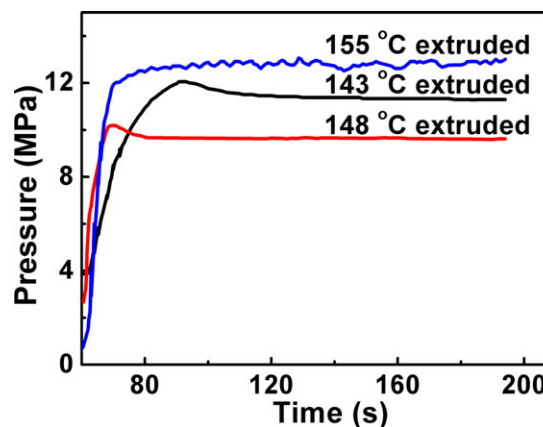
Figure 2. Time evolution of extrusion pressure at different extrusion temperatures with the extrusion for 5000s at $v = 8$ mm/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
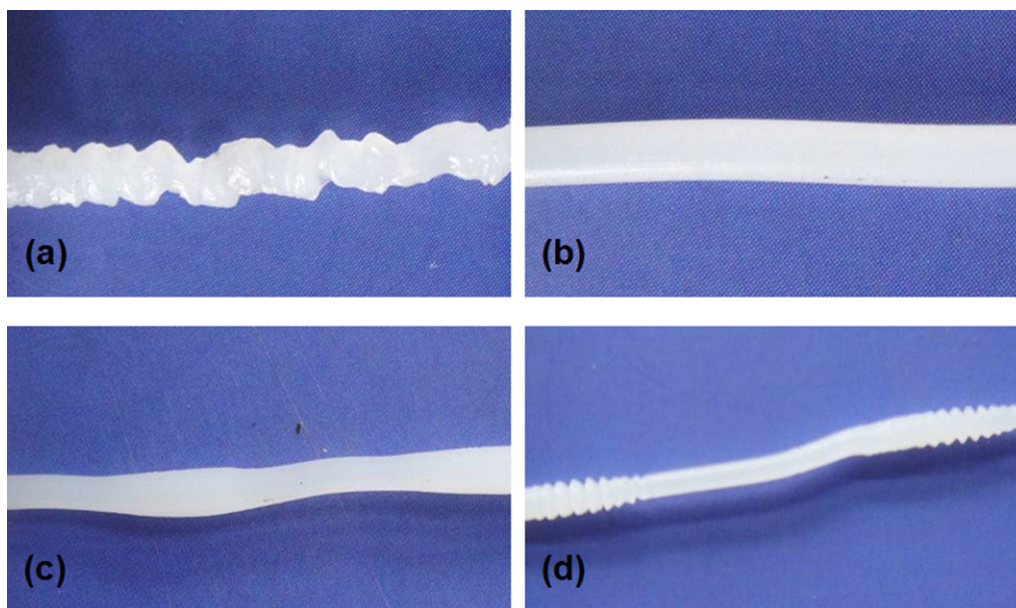
Figure 3. Photographs of extrudate obtained under different temperatures during the extrusion of TR-571 with $v = 1$ mm/min, (a) 148°C; (b) 151°C; (c) 153°C; (d) 157°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

steps; (7) finally, the sample was heated from 50°C to 200°C, and a multiple melting endotherm was obtained. In the whole process, both heating rate and cooling rate are 10°C/min.

Morphological Characterization

A scanning electron microscope (SEM) of JSM 5900 LV (Tokyo, Japan) was used to observe the morphologies of various polyethylenes. Before the SEM observation, specimens were prepared by fracture in liquid nitrogen. The fractured surfaces were immersed in a solution of 1.3 wt % $KMnO_4$ dissolved in a

$H_2SO_4/H_3PO_4/H_2O$ (10/4/1) mixture in order to etch out the amorphous phase.

Wide-Angle X-ray Diffraction

One-dimension WAXD (1D-WAXD) spectra were recorded with a Philip X'pert prd diffractometer (Japan). The X-ray beam was nickel-filtered Cu Kα ($\lambda = 1.5404$ Å) radiation operated at 40 kV and 100 mA. The scanning range was varied from $2\theta = 1°$ to $50°$ with a rate of $5°$/min. Two-dimension WAXD (2D-WAXD) experiments were performed using a Bruker D8
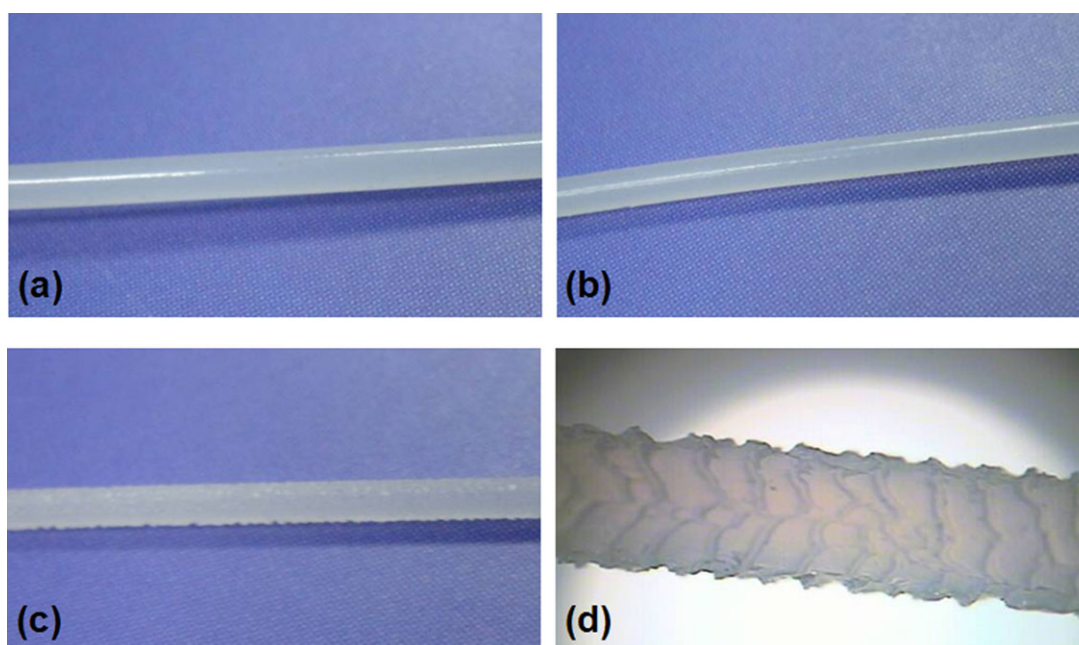
Figure 4. Photographs of extrudate obtained under different temperature during the extrusion of 5000s with $v = 8$ mm/min, (a) 140°C; (b) 148°C; (c) 157°C; (d) microphotograph of (c) ×5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
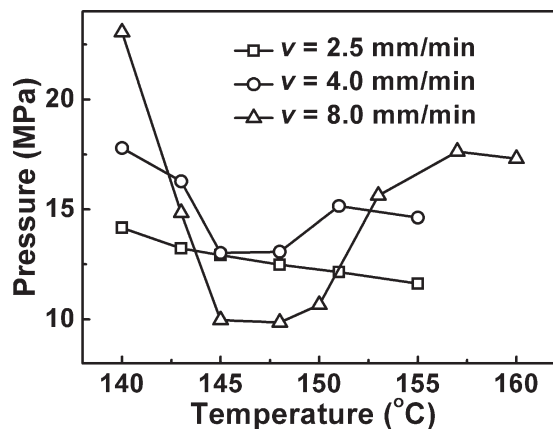
Figure 5. Pressure versus temperature traces recorded during the extrusion of 5000s with different piston velocities.
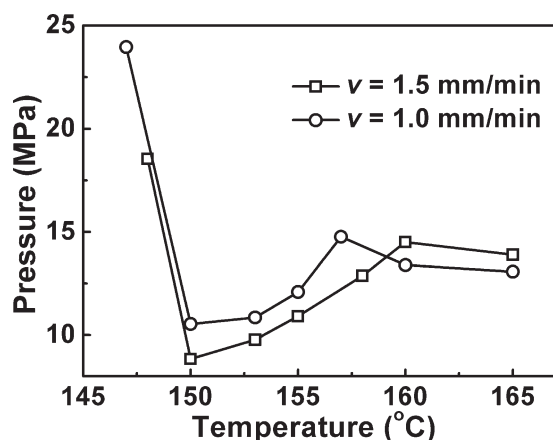

Figure 7. 1D-WAXD of extrudates obtained under different temperatures during the extrusion of TR-571. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Discover equipped with an Eulerian cradle. The diffraction patterns were obtained using a diffractometer equipped with a Cu Kα generator at 40 kV and 40 mA, in a 2θ range from 0.08° to 10°. The diffracted beam was detected by a position sensitive linear detector.
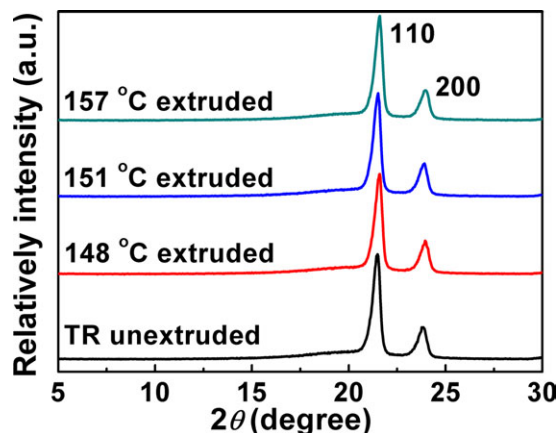
RESULTS AND DISCUSSION

Temperature Window of Various Polyethylenes

The Effect of Extrusion Temperature. The hexene copolymerized polyethylene of TR-571 and homopolymerized HDPE of 5000s were, respectively, melt at 200°C for 30 min, and then the melt was cooled to a given extrusion temperature and was kept constant for 15 min. At different temperatures, the pressure traces as functions of time were recorded in Figures 1 and 2 for TR-571 and 5000s, respectively. The corresponding photographs of extrudate surfaces were shown in Figures 3 and 4.

For TR-571 extruded at 148°C, the extrusion pressure monotonically increases with extrusion time within the primary 270 s. After that, the extrudate surface becomes severely distorted and the pressure fluctuation becomes violent [Figures 1 and 3(a)], as revealed by the pressure fluctuation amplitude and frequency. When the extrusion temperature reaches 157°C, the high temper-

Figure 6. Pressure versus temperature traces recorded during the extrusion of TR-571 with different piston velocities.

ature brings about more severe pressure fluctuation and melts fracture [Figures 1 and 3(d)]. At the extrusion temperature of 151°C, however, the pressure of 9.4 MPa is significantly lower than the average pressures (17.0 MPa) at 148°C and (11.8 MPa) at 157°C. Moreover, the pressure is very stable and the extrudate surface is extremely smooth (Figures 1 and 3). Both Figures 1 and 3 indicate that the temperature window effect appears during the extrusion of TR-571. For the homopolymerized HDPE of 5000s, a similar phenomenon occurs during the extrusion at different temperatures. However, the temperature window of about 148°C is notably lower than that of TR-571 (Figures 2 and 4).

Within these temperature windows of TR-571 or 5000s, the melt flows steadily and extrusion pressure decreases. The reason might be: (1) the molecule mobility is improved at temperatures 10°C higher than the theoretical equilibrium melting point of orthorhombic system of polyethylene[27]; (2) the molecules are extended at the orifice and aligned along the flow direction, resulting in elongational flow-induced crystallization[21] and forming a chain-extended structure similar to the hexagonal crystal phase with relatively higher flow ability.

The Effect of Piston Velocity. With determinations of the accurate temperature window for both TR571 and 5000s, the effect of piston velocity on extrusion pressure was also studied. The pressure traces were recorded as functions of temperature during the extrusion of 5000s with different piston velocities, as shown in Figure 5. For the lower piston velocity of 2.5 mm/min, p decreases steadily with T. However, with the value of v increasing to 4.0 mm/min, a sharp minimum of p in the range of 145–148°C appears. The threshold v value where the window effect set in at a given capillary geometry is defined as v_c. Thus, the value of 4.0 mm/min can be approximated as v_c for 5000s. On increasing v further (such as 8.0 mm/min), the p minimum deepens more dramatically, with its position along the temperature axis remaining unchanged essentially. For both $v = 4.0$ and 8.0 mm/min, p decreases sharply with increasing T in the temperature range of 140–145°C. On the other hand, p increases first and then decreases step-by-step with increasing T from about 148°C (Figure 5).
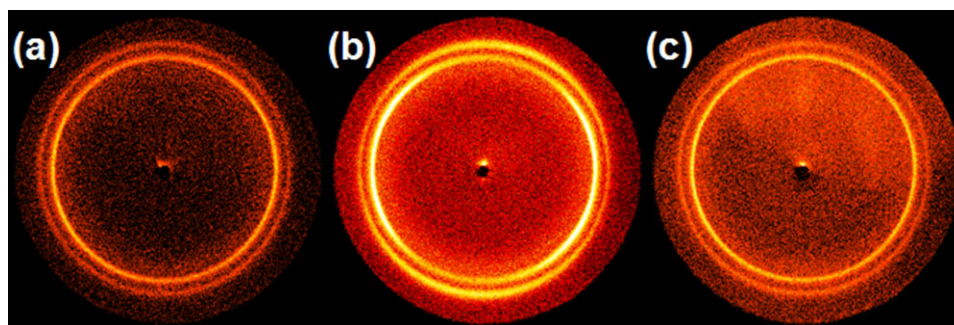
Figure 8. 2D-WAXD photographs of extrudates obtained under different temperatures during the extrusion of TR-571, (a) 148°C; (b) 151°C; (c) 157°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For TR-571, the traces of p versus T were recorded in Figure 6, which indicates that the p minimum also decreases with increasing v in the temperature window, but the v_c for TR-571 is manifestly higher than that of 5000s. Even v_c decrease to 1.0 mm/min, the window effect is still very evident. Besides, the temperature window for TR-571 is in the range of 150–155°C, which is remarkably higher than that of 5000s (Figure 6). Both lower v_c and higher temperature window for TR-571 can be attributed to the relatively higher molecular weight of TR-571 compared with 5000s.[6]
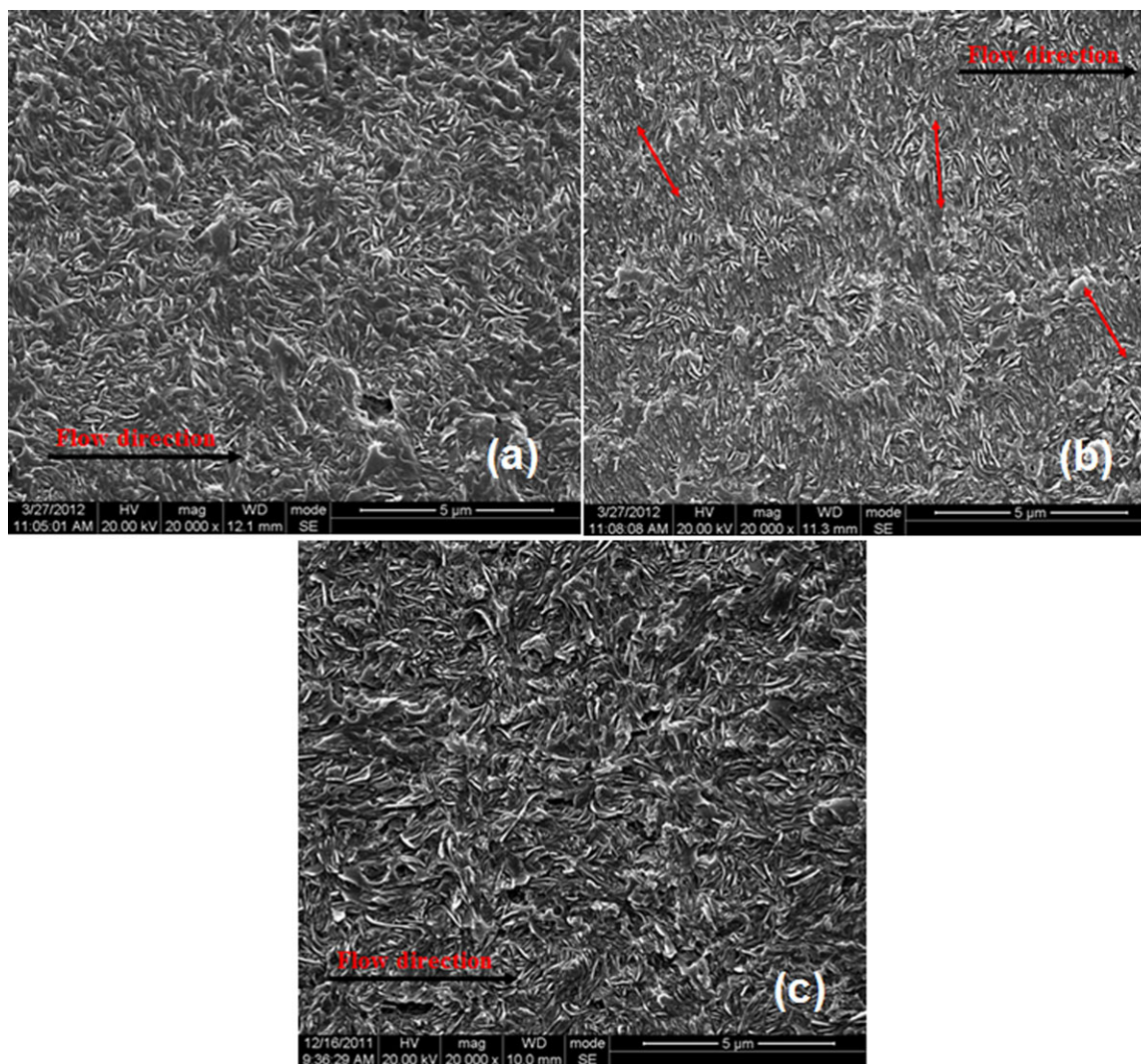
Figure 9. SEM photographs of etched extrudates obtained under different temperatures during the extrusion of TR-571 at a magnification of 20,000, (a) 148°C; (b) 151°C; (c) 157°C, → is flow direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. DSC Parameters of Extrudate Obtained Under Different Temperature During the Extrusion of 5000s

Samples	First heating		Cooling	Second heating		
	T_m^1 (°C)[a]	X_c (%)	T_c (°C)	T_m^2 (°C)	X_c (%)	$T_m^2 - T_c$ (°C)
Extruded at 143°C	134.09	77.42	114.69	133.63	79.02	18.94
Extruded at 148°C	134.46	73.44	114.84	133.83	77.90	18.99
Extruded at 157°C	133.84	73.26	114.84	133.36	77.32	18.52

[a]T_m^1 and T_m^2 are recorded during the first heating procedure and the second one, respectively.

Micro-Morphologies of Various Extrudates

The micro-morphologies of various polyethylene extrudates were studied using WAXD and SEM. Figures 7 and 8 show the 1D-WAXD and 2D-WAXD photographs, respectively, for the TR-571 extrudates obtained at various temperatures. The corresponding SEM observations are shown in Figure 9.

As can be seen from Figure 7, there are not any obvious difference between the diffraction traces of unextruded TR-571 and those of the extrudates obtained inside and outside the temperature window. In Figure 8(b), the two bright arcs indicate that there are chain axis orientations in the sample obtained in the temperature window. The 2D-WAXD results show bright arcs rather than bright points, which might attribute to the molecule chain relaxation after the extrusion. However, no crystal orientation is found for E148 and E157 [Figure 8(a,c)]. Besides, the SEM photographs indicates that the lamellas of E151 for TR-571 obtained at 151°C have remarkable crystal orientation

which is approximately perpendicular to the melt flow direction, and no crystal orientation for E148 and E157 of TR-571 (Figure 9). The crystal orientation in Figures 8 and 9 indicates that the chain alignment induced by elongational flow in the temperature window can at least be partially maintained and leave a structure memory in the melt state because the chain relaxation time of the TR-571 molecular chains is much longer.

Thermal Properties of Various Polyethylenes

Homopolymerized Polyethylene of 5000s. The thermal properties of E143, E148, and 151°C for 5000s were studied by DSC. These extrudates were prepared with the piston velocity of 8.0 mm/min. The results are listed in Table I which indicates: (i) the extrudates obtained both inside and outside the temperature window have similar crystallization and melting behaviors, (ii) for different heating runs, T_m, T_c, X_c, and subcooling ($T_m^2 - T_c$) of the a sample are basically invariable, respectively.

The SSA fractionation applies self-nucleation and annealing steps sequentially to a polymer sample to promote the potential molecular fractionation occurred during crystallization and to encourage the unmolten crystals to anneal at each stage of the process, so that small differences in molecular structure can be magnified. SSA was widely used in analyzing the microstructure
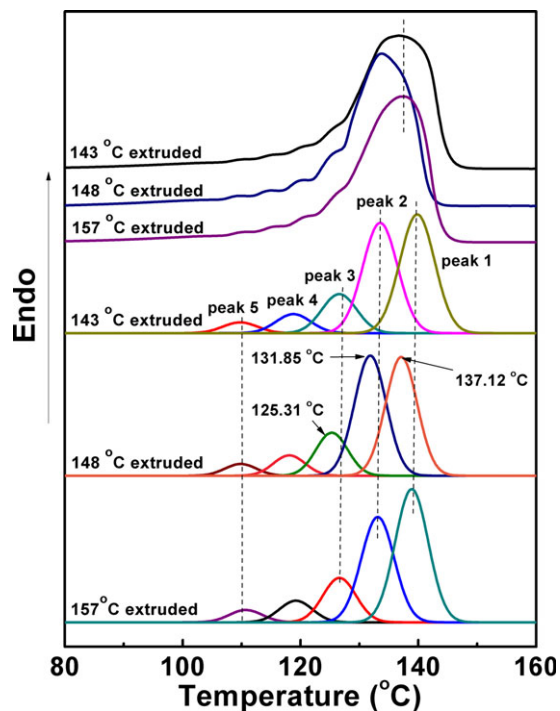
Figure 10. DSC melting curves in SSA thermal fractionation of 5000s extrudates obtained at 143°C, 148°C, and 157°C, the corresponding fitting parameters (r^2) are 99.7%, 99.8%, and 99.8%, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
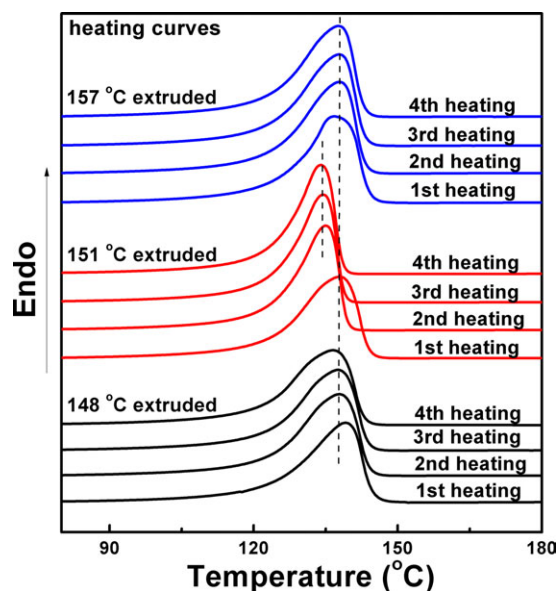
Figure 11. Heating DSC curves of extrudate obtained under different temperatures during the extrusion of TR-571. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
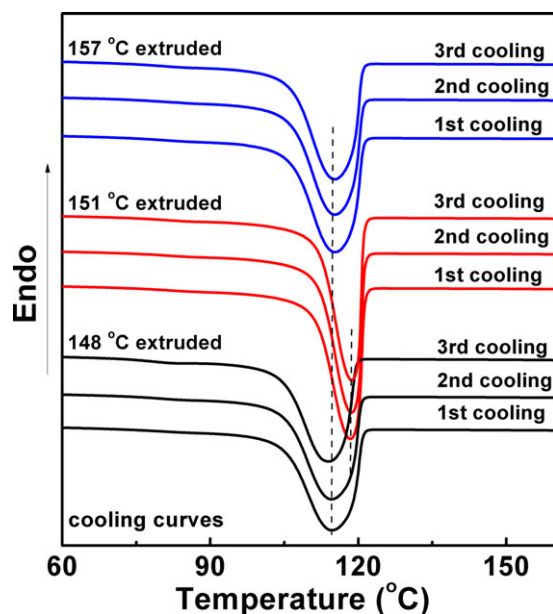
Figure 12. Cooling DSC curves of extrudate obtained under different temperatures during the extrusion of TR-571. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of polyolefin, due to their enhanced resolution, free of solvent, effective molecular segregation, relatively short measurement times, and additional molecular structural information. In this work, this method was used to revealing the effect of processing within temperature window on thermal properties of homopolymerized and copolymerized polyethylenes.

Figure 10 shows the SSA final melting curve of 5000s, which is fitted into five individual peaks using Peakfit 4.12 software. This figure indicates that the SSA curve comprises two main peaks in the high temperature region and three minor peaks in the low temperature region. For the convenience of discussion, the main peak located at the highest temperature region is denoted as peak 1, the other main peak at higher temperature region is denoted as peak 2, and the rest peaks are in turn denoted as peak 3, peak 4, and peak 5, as shown in Figure 10.

According to the literatures,[28,29] peak 1 corresponds to the melting of thick lamellae, which is crystallized by the molecules with high isotacticity. With the melting peak shifts to a lower temperature, the thickness of the corresponding lamellae decreases. Figure 10 shows that each melting peak on the SSA curves of E143 and E157 are almost the same, as well as the relative height of peak 1 for both E143 and E157 are slightly higher than those of their peak 2.

Figure 10 also shows that the SSA curves of the extrudates obtained inside and outside the window are quite different. Peak 1, peak 2, and peak 3 of E148 are remarkably lower than those of E143 and E157. Beside, for E148, the relative height of peak 2 is higher than peak 1, which is completely opposite to those of E143 and E157. The differences of peak temperatures and relative heights between E143, E157, and E148 indicated that the lamellae of the extrudates obtained in the window are thinner than those obtained outside the window. Figure 10 also shows that all the peaks 1 of E143, E157, and E148 differ slightly, which suggest that the 5000s molecules, with low isotacticity, display similar thermal behaviors in the process of extruding though capillary. In the second heating or cooling cycle, these well-aligned chains as a result of structure memory effect can act as nucleating agent, so the number of the lamellae increases and the thickness decreases.

Copolymerized Polyethylene of TR-571. Figures 11 and 12 show the heating and cooling curves of TR-571 extrudate, respectively, obtained under different extrusion temperatures. These extrudates were prepared with the piston velocity of 1.0 mm/min. Some thermal analysis results corresponding to the first and second heating, and the first cooling runs are listed in Table II.

Figure 11 and Table II show that all the first heating curves of E148, E151, and E157 are similar, and their corresponding melting points and crystallinities are much closed, respectively. After the first cooling run, however, the crystallization peak temperature of the E151 increases to 118.58°C which is, respectively, higher 4.56°C and 3.74°C than those of E148 and E157 (Figure 12 and Table II). With the second heating run, the T_m of E151 decreases to 134.56°C. However, the T_m^2 of E148 and E157 changed slightly compared with their corresponding T_m^1. Table II also shows that, under the same conditions, the subcooling ($T_m^2 - T_m^1$) for the extrudates obtained within the temperature window is lower about 7°C than those for the extrudates obtained outsides the temperature window. This phenomenon still exists when the third and forth heating and cooling runs were carried out, as well as T_m and T_c did not change any more compared with T_m^2 and T_c^1, as indicated in Figures 11 and 12.

The lamellar thickness and its distribution can be estimated from the SSA curves using the Gibbs-Thomson equation[30]

$$T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta H_0 L}\right) \qquad (1)$$

where $T_m^0 = 415$ K (equilibrium melting temperature),[31,32] $\Delta H_0 = 286 \times 10^6$ J/m³ (equilibrium melting enthalpy per unit

Table II. DSC Parameters of Extrudates Obtained Under Different Temperatures During the Extrusion of TR-571

Samples	First heating		Cooling	Second heating		
	T_m^1 (°C)	X_c (%)	T_c^1 (°C)	T_m^2 (°C)	X_c (%)	$T_m^2 - T_c^1$ (°C)
Extruded at 148°C	138.93	78.85	114.02	137.85	81.76	23.83
Extruded at 151°C	138.26	80.38	118.58	134.56	83.16	15.98
Extruded at 157°C	138.12	81.29	114.84	138.13	84.89	23.29

Table III. Lamellar Thickness of TR-571 Extrudates from DSC Parameters

Samples	l^1 (nm)[a]	l^2 (nm)
Extruded at 148°C	44.26	36.90
Extruded at 151°C	41.66	24.98
Extruded at 157°C	51.58	53.25

[a] l^1 and l^2 are the average lamellar thickness of TR-571 extrudates recorded during the first heating procedure and the second one, respectively.

volume), $\sigma = 90 \times 10^{-3}$ J/m^2 (surface energy), and L is the lamellar thickness.[33] The lamellar thicknesses of E148, E151, and E157 are calculated by Gibbs-Thomson equation, and the results are listed in Table III. This table shows that after the first heating and cooling run, the lamellar thicknesses of E151 are significantly thinner than those of E148 and E157. Thus, Table III also indicates that the structure memory effect formed in temperature window can effectively increase the lamellae number and decrease the thickness.

CONCLUSIONS

Both hexene copolymerized polyethylene of TR-571 and homopolymerized polyethylene of 5000s were ram extruded at low temperature and pressure using the temperature window effect. The effects of temperature window on rheological behaviors and micro-morphologies were studied, and the conclusions are summarized as follows:

The v_c of TR-571 is manifestly higher than that of 5000s, and the temperature window for TR-571 is in the range of 150–155°C, which is remarkably higher than that of 5000s. Both the higher temperature window and the lower v_c of TR-571 can be attributed to the relatively higher molecular weight of TR-571 compared with 5000s. The crystal orientation shown in 2D-WAXD and SEM photographs indicates that the chain alignment induced by elongational flow in the temperature window can at least be partially maintained and leave a structure memory in the melt state because the chain relaxation time of long molecular chains is much longer. SSA fractionation results suggest that these well-aligned chains as a result of structure memory effect can act as a nucleating agent. Thus, the number of the lamellae increases and the thickness decreases, which finally leading to higher T_c and lower T_m of extrudates obtained inside a temperature window.

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