Melt Flow Crystallization of Ultrahigh Molecular Weight Polyethylene under Curvilinear Flow Conditions

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Synopsis

Multiaxially oriented ultrahigh molecular weight polyethylene films were prepared recently under curvilinear flow conditions generated by the combined effects of compression and rotation. The films were prepared by melt flow crystallization in an optical apparatus specially designed for rheo-optical observations. Morphological studies indicate that the films were fibrillar with the fibrils oriented along the circular flow lines. The fibrils were lamellar, and their lamellar thickness (150–450 Å) and spacing (400–2000 Å) depended on the processing conditions. The film exhibited strong birefringence (1.4×10^{-2}) and had a Young modulus of 15–25 GPa along the flow lines and 3–5 GPa in the transverse direction.

INTRODUCTION

In a recent report[1] we discussed the development of a novel technique for producing multiaxially oriented polymers with ultrahigh planar mechanical and impact properties. According to this technique, the polymer is processed in a contained geometry under the combined effects of a compressive force and a rotational force perpendicular to the compressive force at a temperature near to but below the isotropic crystalline melting point of the polymer. In compression or injection molding experiments with high density polyethylene, the combination of compression and rotation—obtained by rotating one half of the mold cavity—generates curvilinear flow conditions which induce chain orientation in more than one direction. The morphology obtained is fibrillar and has a structure which can be controlled to resemble the cross-ply laminated structure of fiber-reinforced composites. As a result, the mechanical properties such as the tensile modulus and strength in the plane of rotation are dramatically increased in comparison to the properties of the conventionally molded specimens. Furthermore, the impact strength is greatly enhanced, and the lateral weakness ordinarily observed with uniaxially drawn filaments and films is minimized. Thus, the multiaxially oriented high density polyethylene circular films obtained by rotational injection molding under an appropriate combination of injection pressure, mold temperature, and mold rotation conditions had a tensile modulus and strength along the planar flow lines of 10 GPa and 0.15–0.2 GPa, respectively. The flexular modulus was 12 GPa, and the impact strength was at least eight times higher than the impact strength of the conventional injection molded polyethylene sample. Though the effectiveness of our process has been demonstrated in rotational compression and injection molding applications with other

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thermoplastic and thermotropic polymers, the preparation of multiaxially oriented morphologies with ultrahigh mechanical properties in more than one direction has not been explored as yet and requires an understanding of the orientation effects in the curvilinear flow fields. Rheo-optical studies with polymer melts have provided useful information for deciding the processing conditions in our molding experiments and achieving ultrahigh mechanical properties. In this report we discuss the results of such studies with the ultrahigh molecular weight polyethylene melt, particularly in view of its exhibited melt anisotropy[2] at elevated temperatures. The studies were carried out using the simple torsional flow field of a parallel circular plate system under compression and in a temperature range where the polymer melt crystallized under the combined effects of compression and rotation. The properties of the prepared multiaxially oriented morphologies are also discussed.

EXPERIMENTAL

Apparatus

A diagram of the apparatus used for the rheo-optical studies is depicted in Figure 1. This is a typical plate–plate rheometer equipped with optically clear quartz plates 3 cm in diameter for *in situ* observations. The top plate was fixed, whereas the bottom plate could rotate and/or travel along the optical axis for the gap adjustments between the two plates. The plate–plate arrangement was surrounded by a cylindrical wall which prevented the polymer melt from flowing past the two plates when compression or high shear rate was applied. The whole assembly was enclosed into a cavity which was heated by convection with ample amounts of nitrogen heated in a specially designed heating system. Temperatures up to 550–600°C could be reached and maintained readily to ±2°C. The optical observations were conducted on a Zeiss Photomicroscope III.

Methods and Materials

The ultrahigh molecular weight polyethylene (UHMWPE HiFax 1900 $M_w \geq 2 \times 10^6$) was kindly provided by Hercules Inc. The processing conditions were decided by the optical studies made with the UHMWPE melt. These, discussed in detail elsewhere,[2] indicated that the melt of UHMWPE was anisotropic above its melting point and that its anisotropy persisted at 345°C, i.e., the temperature

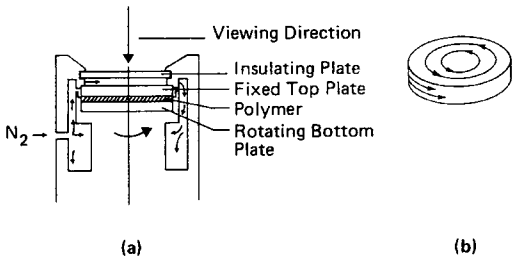


Fig. 1. Schematic diagram of (a) the optical apparatus for the rheo-optical and melt flow crystallization studies and (b) the flow lines generated under the torsional flow conditions.

at which degradation commences in a nitrogen atmosphere. Intrinsic viscosity measurements indicated also that the average molecular weight M_w decreased to ~160.000 by heating the polymer to 410°C, where melt anisotropy is lost completely. Therefore, we decided to prepare the films from melts which were heated to either above or below 345°C. Since the melt viscosity of the polymer was very high at temperatures <200°C, the lowest temperature that was chosen was 335°C and the highest 410°C. A small amount of the polymer powder was placed between the quartz plates, and it was melted by flushing the cavity with hot nitrogen to obtain the chosen temperature. The heating rate was 100°C/min. After temperature equilibration for 5 min, the melt was compressed gently ($\leq$5 atm) by closing the gap between the two plates. Quenching of the melt by flowing nitrogen chilled in a liquid nitrogen bath (−193°C) resulted in uniformly thin (~60 μ) unoriented films. The cooling rate was ~250°C/min. Oriented films were obtained by rotating the lower plate as the melt crystallized. When the polymer solidified completely, the rotation was stopped, and the film was retrieved after cooling to room temperature.

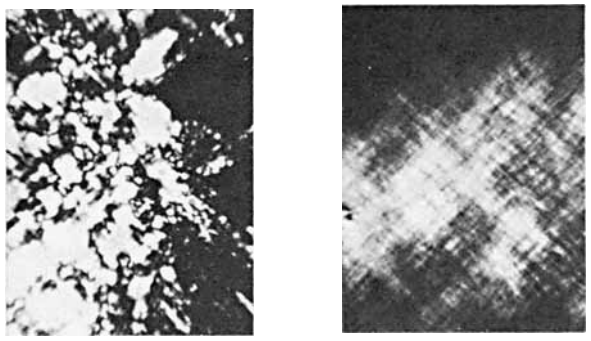
Physical Property Measurements

Thermal analysis data were obtained with a DuPont Thermal Analyzer (Model 990) calibrated with the melt transition of lead. The melt behavior of the samples (~4 mg) was followed at a heating rate of 10°C/min. The crystallinity was determined assuming that the heat of fusion of perfect polyethylene crystal is 69 cal/g.[3] The total birefringence was measured with an Ehringhaus compensator. The morphology of the films was studied by scanning (SEM) and transmission (TEM) electron microscopy. The surface morphology was studied using a Hitatsi S-500 SEM and the internal morphology with a Phillips 301 microscope equipped with a (S) TEM attachment using microtomed sections ~800 Å thick. These were coated with carbon for beam stability.

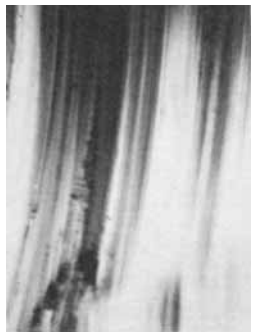
The tensile properties of the oriented films were measured, with ribbon specimens cut off along the flow direction, using a custom made microtensile testing instrument. The Young modulus was measured at a strain rate of $1.7 \times 10^{-3}\ s^{-1}$. The tensile strength value is the average of three measurements.

RESULTS

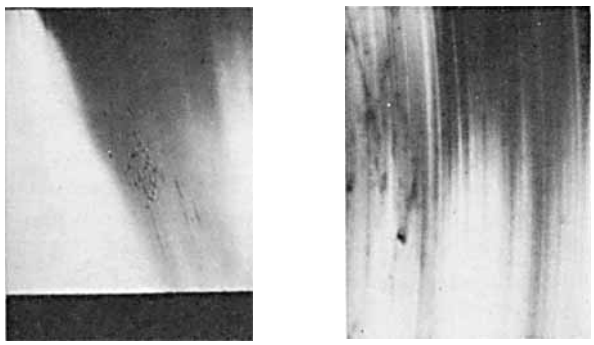
The initial melt flow crystallization studies were carried out with melts heated to temperatures below 345°C, i.e., the decomposition temperature of the polymer. At first the polymer when melted at 220°C formed the anisotropic melt shown in Figure 2(a). After further heating to 335°C and thermal equilibrium for 5 min, the melt was sheared. Upon shearing, the melt exhibited a fine ordered texture perpendicular to the flow direction [Fig. 2(b)], which was discernable on cooling until the first growth of fibrous crystals was observed at 140°C [Fig. 2(c)]. Fibrillar crystallization occurred on further cooling. Similar were the experiments with melts heated to temperatures above the decomposition temperature of the polymer. As the melt was heated to 410°C, the viscosity decreased perceptibly and the anisotropy disappeared, as shown in Figure 2(d). After thermal equilibrium for 2 min, the polymer was sheared. However, flow birefringence was not observed on cooling until the polymer began crystallizing



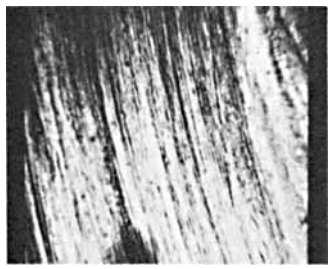
(a) (b)



(c)



(d) (e)



(f)

Fig. 2. Optical micrographs of the UHMWPE (a) anisotropic melt at 220°C; (b) anisotropic melt under shear at 335°C (fine ordered texture perpendicular to the flow direction; (c) growth of fibrillar crystals at 140°C; (d) melt at 410°C; (e) crystallizing polymer at ~130°C; (f) crystallized polymer under rotational-compression conditions at <130°C.

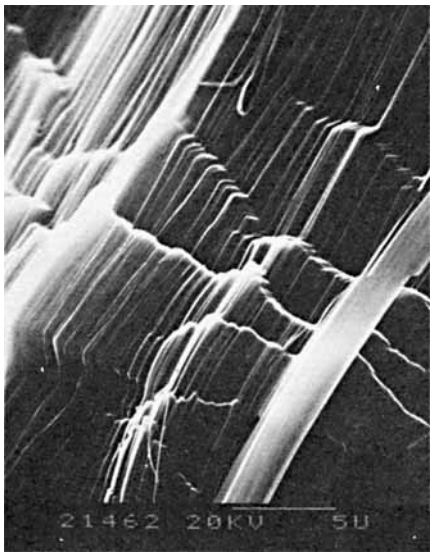
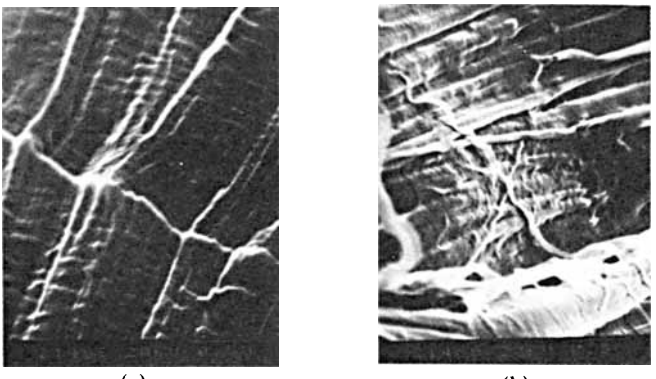


Fig. 3. Electron micrograph of fibrillar morphology obtained from a melt heated to 335°C (low magnification).

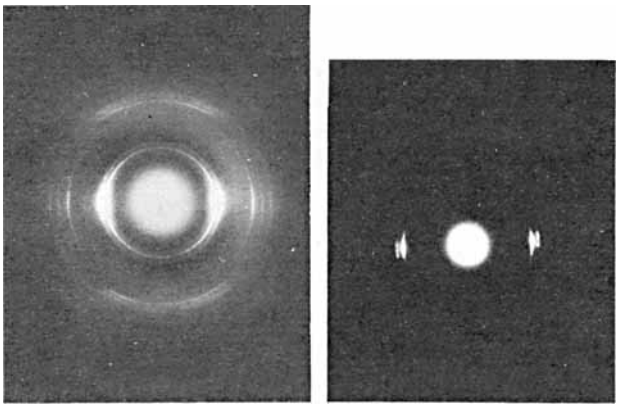
at ~130°C [Fig. 2(e)]. Fibrillar crystallization then followed as shown in Figure 2(f). It should be remarked that melt crystallization by cooling from temperatures ≥335°C without rotation resulted in a spherulitic morphology. As shown by the electron micrograph at low magnification in Figure 3, the fibrillar films were made of well-aligned fibers along the circular flow lines with kink bands perpendicular to the fiber direction. Electron micrographs at higher magnification indicate that the macrofibers are made of fibrils with lamellar structure. The lamellae had an average thickness of 450 Å and spacing of 2000 Å when the fibrillar morphologies were obtained from melts heated to 335°C [Fig. 4(a)] while a lamellar thickness of 150–300 Å and a spacing of ~400 Å were observed when the fibrillar morphologies were obtained from melts heated to 410°C [Fig. 4(b)].

Photographs of the electron diffraction patterns for well-oriented UHMWPE films prepared from melts heated to above or below 345°C are shown in Figure



(a) (b)

Fig. 4. Electron micrographs of fibrillar morphologies obtained from melts heated to (a) 335°C and (b) 410°C (high magnification).



(a) (b)

Fig. 5. Electron diffraction patterns of oriented UHMWPE films prepared from melts heated to (a) >345°C and (b) <345°C. (Electron beam perpendicular to the fiber direction.)

5. The diffraction patterns were obtained with the electron beams along the aligned fibers, i.e., the circular direction. The patterns illustrate the high degree of chain orientation along the circular direction. The results of our diffraction studies are discussed in a separate report. A photomicrograph of an oriented film as viewed between cross-polarizers is shown in Figure 6. A "gigantic maltese cross" with narrow extinction bands was observed which indicated a high degree of chain alignment along the circular flow lines. The birefringence of the oriented film was 1.4×10^{-2}; no birefringence difference was detectable in the oriented films which were prepared from melts heated to above or below 345°C. The calculated crystallinity data from thermal analysis showed that the fibrillar crystalline morphologies produced under the rotational-compression conditions from melts heated to 335°C or 410°C had a percent crystallinity ~35% higher from the crystallized morphologies obtained from melts heated to these temperatures without rotation. The melting points of the fibrillar crystallized morphologies produced under the rotational compression conditions were also

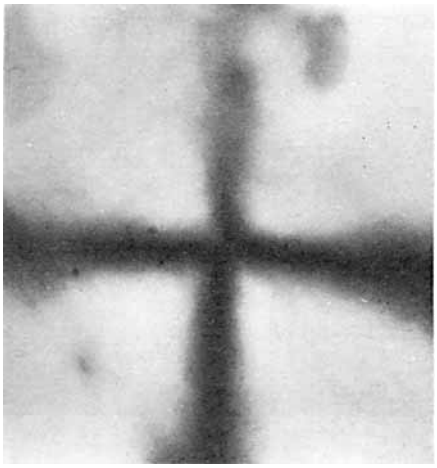


Fig. 6. Optical micrograph of an oriented UHMWPE film as viewed between cross polarizers.

TABLE I
Thermal Analysis Data of UHMWPE

Sample	T_m (°C)	Crystallinity (%)
As-received polymer powder	145	77.6
Melt-crystallized morphology obtained from melts heated to ≥335°C	110, 123	56.6
Fibrillar-crystallized morphologies obtained under rotational-compression conditions from melts heated to (a) 335°C and (b) 410°C	143 (a), 136 (b)	85.7 (a), 84 (b)

higher from the melting point temperature of the crystallized morphology obtained without rotation by cooling from temperatures ≥335°C. The thermal analysis data are summarized in Table I.

The Young modulus of sections cut off along the circular flow lines was in the range of 15–25 GPa and of specimens cut off across the flow lines was 4 GPa. The tensile strength of the specimens cut off along the flow lines was 0.2 GPa and the elongation at break 6%.

DISCUSSION

Studies on the growth of fibrillar crystals under flow conditions have been described previously. Pennings and co-workers[4,5] have studied the crystallization of fibers using Poiseulle and Couette flow conditions. The fibers were grown on crystal seeds, which were placed in the streaming polymer solution at a temperature slightly above the crystallization temperature, and they were drawn out of the solution. The fiber had a lamellar structure of the well-known shish-kebab type. Filaments of the same morphology were produced independently by Odell et al.[6] from the melt state in a capillary rheometer.

In our studies, the polymer melt is crystallized under curvilinear flow conditions. In the particular case of the plate–plate geometry, which is only one example of curvilinear shear flow, the flow is unidirectional[7] with the flow lines along the circumference of the sample as shown in Figure 1(b). The cylindrical wall around the plate–plate arrangement prohibits the melt from being thrown outwards and supports the development of compression during rotation. Although it is difficult at this stage to clarify the possible site at which the crystallization commences, i.e., surface of the rotating plate or within the polymer melt, it is observed that the fibrous crystals are grown by row nucleation. The crystallized lamellar fibers grow along the circular flow lines in the plane of the film with the lamellae perpendicular to the fiber direction, i.e., the growth front proceeds in the chain direction. Lamellar twisting of the type described by Keller and Machin[8] at low stress crystallization was not observed, although the preparation of the lamellar morphology was carried out at low pressure.

The different lamellar thickness and spacing in the fibrous crystals grown from melts heated to above or below 345°C is understood by considering the significant decrease in molecular weight and change in molecular structure by chain slip and rupture as a result of the degradation at 345°C. The shorter molecular chains of the melts heated to temperatures >345°C orient and crystallize under

the flow conditions only near the crystallization temperature into small aligned lamellae. Flow birefringence observations also indicate that chain slip in the melts at >345°C is very facile and the molecular relaxation very fast since no birefringence is observed upon rotation until the polymer begins crystallizing on cooling at ~130°C. On the contrary, the polymer melts heated to temperatures below 345°C are anisotropic and under rotational conditions exhibit a high degree of order, which apparently is associated with the long nature of the molecular chains and the slow molecular relaxation. Thus, upon crystallization at 140°C, the polymer crystallizes into large lamellae. Evidence for the different nature of the molecular chains in the melts heated to above and below 345°C is provided by the fact that the anisotropy disappears on heating above 345°C and it is not reversible on cooling. Furthermore, the electron diffraction patterns of the oriented fibrillar morphologies preparerd from the melts heated to temperatures <345°C show bright spots on the equitorial arcs, which indicate the existence of large crystals and are not observed in the diffraction patterns from the oriented fibrillar morphologies obtained from melts heated above 345°C. The total birefringence of the multiaxially oriented films is by a factor of 4 lower than the value for the perfect crystal and indicates the high degree of chain orientation in the circumferential direction.

Tensile testing measurements with fine ribbons cut along and across the circumference of the sample indicate that the curvilinear shear flow allows the development of planar mechanical performance, which is not possible to achieve by any known deformation process. The typical Young modulus values along the circumference were in the range of 15–25 GPa; the modulus across the circumference was 3–5 GPa. There were no differences in the measured modulus values of the films obtained from melts exposed above or below 345°C. It should be remarked that the aspect ratio of the tested samples was ~20. Since the tensile modulus of a highly anisotropic material increases significantly with the aspect ratio by up to a factor 3 and reaches a constant value at an aspect ratio ~80,[9] it is believed that the measured moduli were significantly lowered.

The increase in the crystallinity and the melting point values of the morphologies prepared under the rotational-compression conditions by comparison to those crystallized without the application of rotation and compression arises from the high degree of chain orientation and crystal perfection in the multiaxially oriented samples and it is well documented in the literature.[10] Finally, the formation of kink bands arises from the application of shear stresses and has been reported by many authors.[11,12]

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