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Ultradrawing at Room Temperature of High Molecular Weight Polyethylene

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ABSTRACT: Films of ultrahigh molecular weight (6×10^6) polyethylene were produced by gelation/crystallization from dilute solutions according to the method of Smith and Lemstra. Under ambient conditions the dried gel films could be readily stretched to the remarkably high draw ratio of 20. This interesting phenomenon is discussed in terms of the morphology of the dry gel film as studied by wide-angle X-ray diffraction, small-angle X-ray scattering, and small-angle light scattering techniques. The facile drawability is thought to be due to the extremely high molecular weight and the low concentration of the solutions; these ensure a suitable level of the entanglement mesh that effectively transmits the drawing force.

Introduction

There is currently considerable interest in the deformation behavior of polyethylene, with the ultimate goal of the production of ultrahigh-modulus films and fibers.[1] The deformation of the polymer molecules has been achieved both in the liquid phase, for example, in hydrodynamically or stress-induced crystallization,[2,3] and in the solid state, such as in solid-state extrusion[4,5] or in drawing processes.[6–11] Invariably, the most pronounced molecular extension was attained for polyethylene at elevated temperatures, generally above about 60 °C.[1–11]

In the present paper we report the remarkably high drawability at room temperature, with maximum draw ratios up to 20, of ultrahigh molecular weight polyethylene films ($\bar{M}_w = 6 \times 10^6$) that were produced by gelation/crystallization from semidilute solutions according to the method of Smith and Lemstra.[8–11] This interesting phenomenon was investigated by small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), small-angle light scattering, and optical microscopy.

Experimental Section

A linear polyethylene with the very high molecular weight of 6×10^6 (Hercules 1900/90209) was used. Solutions containing 0.5% by weight of the polymer in decalin were prepared by heating well-blended polymer/solvent mixtures at 165 °C for 5 min and subsequently at 158 °C for 55 min. The homogenized solution was poured into an aluminum tray that was surrounded by ice water to form a gel. The decalin was allowed to evaporate from the gels at ambient conditions for 14 days. The nearly dried film, which had a thickness of about 150 μm, was immersed in an excess of ethanol for 1 day and subsequently dried for 6 days to remove residual traces of decalin.

The dried polyethylene films were cut into strips of length 50 mm and width 12 mm. These specimens were elongated at room temperature with an Instron tensile tester at a crosshead speed of 10 mm/min, which appeared by trial and error to be the most suitable rate. Draw ratios were determined in the usual way by measuring the displacement of ink marks placed on the specimen prior to drawing.

The various films were analyzed by optical microscopy, wide- and small-angle X-ray scattering, and light scattering. X-ray patterns were obtained with Ni-filtered Cu Kα radiation produced by a Philips generator that was operated at 40 mA and 40 kV. Light scattering patterns were recorded using a 15-mW He–Ne gas laser as a light source. Diffuse scattering was avoided by sandwiching the specimen between cover glasses, with silicone oil (refractive index 1.533) as an immersion fluid.

Results and Discussion

Figure 1 presents a typical nominal stress/strain curve that was recorded at room temperature for the dried polyethylene gel film. This figure evidently shows that under ambient conditions the remarkably high draw ratio of ~20 was attained for this ultrahigh molecular weight polyethylene. This value should be compared with the so-called "natural draw ratio" at room temperature of melt-crystallized polyethylene, which ranges from 4 to 10, depending on the molecular weight of the sample.[13] The

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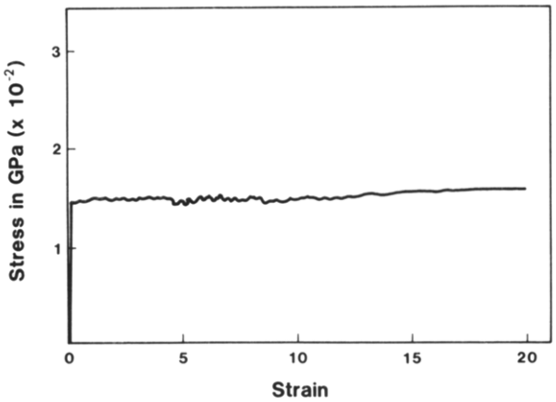

Figure 1. Nominal stress/strain curve recorded at room temperature of dry gel film of ultrahigh molecular weight polyethylene ($\bar{M}_w = 6 \times 10^6$).

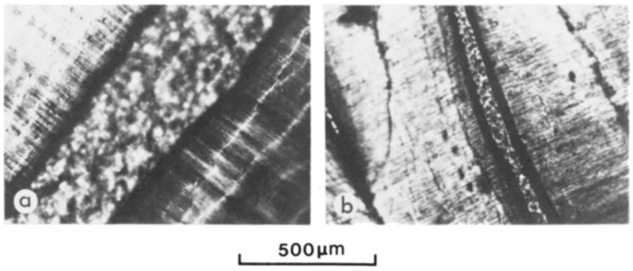

Figure 2. Optical micrographs of drawn polyethylene gel film: (a) at low draw ratios the sample is composed of alternating unoriented and highly drawn areas; (b) at higher draw ratios the oriented areas increase at the expense of the unoriented domains.

nominal drawing stress amounted to about 14 MPa and it remained nearly constant throughout the drawing experiment.

As illustrated in Figure 2, observations in the optical microscope revealed that the drawn film consists of two alternating zones: unoriented areas with a structure corresponding to that of the original undrawn specimens and highly drawn domains oriented parallel to the drawing direction. As the draw ratio increases, the oriented regions are enlarged at the expense of the unoriented zones. Thus the drawing process is nonuniform. When fracture occurs after extensive stretching, it is invariably at the boundary between the two zones. It is noteworthy that the decrease in transverse specimen dimensions with increasing length occurred mainly in the direction of the film thickness and much less in the film width. For example, the final thickness of the 20× drawn film amounted to about 10 μm (original thickness 150 μm), whereas the film width decreased only by about 20%. This observation can readily be explained by the particular microstructure of the dried gel films as will be shown below.

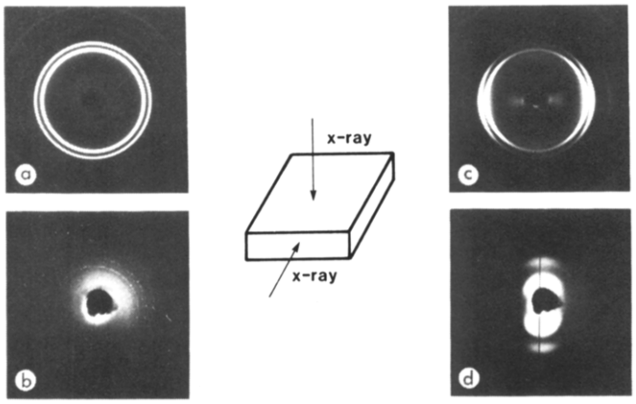

Figure 3. X-ray patterns of undrawn polyethylene film: WAXD (a) and SAXS (b) patterns perpendicular to the film surface; WAXD (c) and SAXS (d) patterns parallel to the film surface. The sharp diffraction lines seen in (b) and (d) are artifacts caused by scattering from the edge of the beam stop.

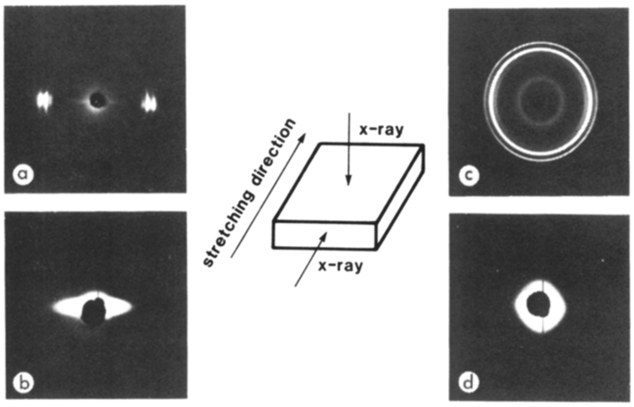

Figure 4. X-ray pattern of 20× drawn polyethylene film: WAXD (a) and SAXS (b) patterns perpendicular to the film surface; WAXD (c) and SAXS (d) patterns parallel to the film surface. The strong arc in (a) and ring in (c) close to the typical (110) and (200) reflections is due to the presence of the triclinic modification (see text).

Figure 3 shows WAXD and SAXS patterns for the original film. The WAXD pattern in part c indicates the preferential orientation of the crystal *c* axes perpendicular to the film surface. The SAXS pattern in part b shows circular-type diffuse scattering and that in part d shows the meridional scattering having scattering maxima corresponding to a long period of about 10 nm. The two SAXS patterns indicate that the dried gel film is composed of crystal lamellae that are highly oriented with their large flat faces parallel to the film surface but randomly oriented with respect to the direction normal to the film surface.[12] The four patterns together indicate that within the lamellar crystals constituting the gel, the crystal *c* axes are oriented perpendicular to the large flat faces. Thus when the as-cast polyethylene gel films are dried by slow evaporation of the solvent, the constituent lamellar crystals become oriented parallel to the film surface in a manner similar to mats of single crystals.[14,15] This concept of the morphology of the dried gel film is supported by the observed changes in the dimensions of the film during drawing as described above. Because of the anisotropic structure of the film, the unfolding and elongation of the polyethylene molecules during drawing occur primarily in the plane perpendicular to the film surface, causing a strong reduction in the film thickness.

The various WAXD and SAXS patterns presented in Figure 4 were obtained for the film that was drawn at room temperature to a draw ratio of 20. The through WAXD pattern a displayed a high orientation of the polyethylene molecules into the direction of draw, as opposed to pattern c, taken parallel to the draw direction. In addition to the strong equatorial (110) and (200) reflections, weak rings, corresponding to the same reflections, were observed in pattern a; these rings derive from unoriented crystallites corresponding to the undrawn areas shown in Figure 2. Apart from the typical (110) and (200) reflections of the orthorhombic polyethylene unit cell, the WAXD patterns displayed a rather strong diffraction arc at an angle of 19.6° (twice the Bragg angle), which is due to the presence of the triclinic unit cell.[16] This triclinic phase is the unstable crystal modification of polyethylene that frequently has been observed in strained crystals.[17] The SAXS pattern taken perpendicular to the direction of draw (Figure 4b)

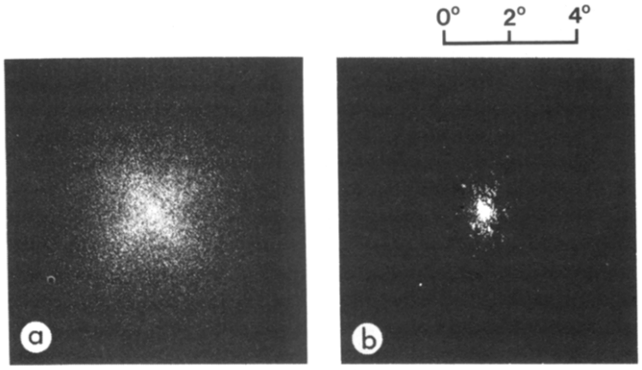

Figure 5. Light scattering patterns (H_v polarization conditions) of (a) undrawn film and (b) 20× drawn film.

showed an equatorial streak that originates in scattering from elongated voids. The SAXS pattern d in the direction of elongation displayed the disappearance of lamellae due to the transformation from a folded to a fibrous structure.

Small-angle light scattering (SALS) studies were carried out both on the undeformed and the 20× drawn film, as shown in Figure 5. Pattern a of the undrawn film displays lobes of a diffuse X type. The intensity had a maximum in the center and it decreased monotonically with increasing scattering angle. These observations are indicative of scattering from rodlike textures.[18-20] The existence of rodlike textures in films prepared without stress as in this experiment is very interesting because it is well-known that polyethylene crystallized from stressed polymer melts and solutions has rodlike textures[21,22] whereas that crystallized without stress has spherulitic textures. The scattering pattern appears at a very low scattering angle in comparison with the ones that had been reported previously for collagen and poly(tetrafluoroethylene)[19,20] and, in addition, the notch of the four lobes is less clearly defined. Such a pattern presumably indicates the existence of large-size rods with finite length and width,[23] the optical axes being oriented normal to the film surface but showing orientation disorder with respect to the rod axis.[24] This confirms the conclusion arrived at in the SAXS and WAXD investigations that the structure of the dried gel films comprised lamellar crystals. Upon drawing up to a draw ratio of 20, the disappearance of the rodlike texture due to the transformation into a fibrous structure may be discerned from the disappearance of light scattering patterns shown in Figure 5b.

The results in the present study show that lamellar polyethylene crystals can readily be destroyed by elongation, even at room temperature. At this temperature the polymer crystals do not seem to act as rigid bodies and the macromolecules exhibit a surprising mobility when subjected to strain. Obviously, the chain mobility at room temperature is much less than at elevated temperatures, where drawing is usually performed. Accordingly, the perfection and crystallinity of the drawn samples were relatively low (about 60%, determined by differential scanning calorimetry). The films contained numerous voids, giving rise to scattering of X-rays at small angles (Figure 4b) and to an opaque appearance.

The question can be raised as to whether or not drawing may have caused a significant local rise of the specimen temperature,[25] thus facilitating plastic flow. In view, however, of the very low rate of elongation (10 mm/min) and the relatively low drawing stress, this seems highly unlikely.[25]

It is well-known that melt-crystallized ultrahigh molecular weight polyethylene exhibits a very poor drawability. Even at temperatures as high as 130 °C the maximum draw ratio observed for such samples is well below 10.[8-11] Recent work of Smith, Lemstra, and co-workers[8-11] showed that the drawability of high molecular weight polyethylene can be drastically improved by gelation/crystallization from semidilute solutions. These authors reported, however, that drawing of dried gel films was unsuccessful at room temperature, unlike the results in the present work. In our opinion, the high draw ratio of 20 achieved under ambient conditions in the present study is due to the extremely high molecular weight ($\bar{M}_w = 6 \times 10^6$) of the polyethylene used, which exceeds by 4 times the $\bar{M}_w$ of the sample employed by Smith and Lemstra.[8-11] As a result there are fewer chain interruptions that may cause premature fracture of the tenuous macromolecular network. It is thought that the high molecular weight of the sample and the low concentration of the solutions ensure the existence of a suitable level of the entanglement mesh that acts as interlamellar crosslinks and effectively transmits the drawing force. However, this problem remains for further investigation.

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