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Mechanical Relaxations of Oriented Gelation-Crystallized Polyethylene Films

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ABSTRACT: The mechanical relaxations of oriented gelation-crystallized films of ultrahigh molecular weight polyethylene ($M_w \simeq 6 \times 10^6$) have been studied by dynamic mechanical measurements, in comparison with the behavior of undrawn melt-crystallized specimens. Four-centimeter gauge-length samples of the gelation-crystallized films were uniaxially drawn in air at 130 °C in an Instron tensile testing machine at a crosshead speed of 20 mm/min. The draw ratios ranged from 12 to 220. The orientation and crystallinity of the specimens were characterized by a variety of methods. The melt-crystallized sample, which has a crystallinity of approximately 55%, shows pronounced α, β, and γ peaks. In contrast the undrawn gelation-crystallized sample (crystallinity >80%) exhibits less pronounced α and γ peaks and the β peak is not discernible. It is thus evident that the β relaxation in the melt-crystallized sample must be associated with the amorphous regions. Both the α and γ relaxations of the gelation-crystallized sample disappear completely when the sample is stretched to draw ratios in excess of 150. The absence of the γ relaxation in highly drawn gelation-crystallized samples indirectly suggests that the γ process may be related to the local motions of the chain segments located in the amorphous or crystal defective regions. The α relaxation in the gelation-crystallized samples is sharper as compared with that in the melt-crystallized sample. The strength of the α relaxation decreases with stretching while shifting to higher temperature; this indicates that the α_2 process is the dominant mechanism in the highly drawn gelation-crystallized material. This may be associated with the inability of crystal grain boundary relaxation or crystal orientation relaxations to occur in such highly crystalline (in excess of 96%) and highly oriented ($f_c = 1$) materials.

Introduction

The mechanical relaxations of polyethylene have attracted considerable interest. The interpretation of these relaxation mechanisms is hindered by the complex morphology of the polymer. In general, three relaxation processes labeled α, β, and γ have been observed at temperatures of 70, −20, and −110 °C, respectively. The classical interpretation of the α relaxation is that it consists of two overlapping mechanisms known as the α_1 and α_2 relaxations. Nakayasu et al.[1] were the first to separate the two contributions and apparent activation energies of 25 and 45 kcal/mol were reported for the α_1 and α_2 processes, respectively. Takayanagi et al.[2,3] observed a composite of the two processes in melt-crystallized polyethylene, but only the α_2 relaxation was seen in single crystal mats.

The lower temperature α_1 relaxation has been explained in terms of so called grain boundary relaxation phenomenon by Takayanagi.[4] However, the existence of such a grain boundary structure has not been confirmed by electron microscopy or other independent methods and thus is subject to considerable debate. Stein,[5] Iwayanagi et al.,[6] Hideshima et al.,[7] and McCrum et al.[8] have attributed the α_1 process to interlamellar grain boundary slip. This has been contradicted by recent dynamic X-ray diffraction studies of Kawai et al.[9] who found that the α_1 relaxation takes place at the crystal grain boundaries within the lamellae.

While disagreement exists in the interpretation of the α_1 mechanisms, the assignment of the α_2 process is relatively straightforward. It has been attributed to rotational and translational motions of chain molecules within the crystal lattice. This mechanism has been theoretically treated by Okano[10] based on the smearing out effect of lattice potential. With use of a kinetic approach, a similar mechanism has been proposed by Hoffman et al.[11] This process has been experimentally confirmed by the rheo-optical method of Kyu et al.[12] In the vicinity of the α_2 region, crystal lattice dispersion has been observed by dynamic X-ray diffraction; this supports the proposal that the α_2 process takes place within the crystal lattice. This type of molecular motion does not give rise to birefringence changes; consequently it is not observed in dynamic birefringence studies.

The assignment of the β relaxation is controversial. The classical interpretation is that it is due to branch points. Kline et al.[13] showed that the magnitude of the β relaxation increased markedly as the number of chain branches increased. Since the degree of crystallinity decreases with increasing chain branching, the β peak has been attributed to the amorphous regions of the polymer. This is in good accord with observations of the β-relaxation in various ethylene containing copolymers[14–16] and chlorinated polyethylenes.[17]

The β peak is not unique to branched polyethylene. Matsuoka et al.[18] observed this peak in medium density polyethylene, but it disappeared upon annealing. Kyu and co-workers[19] observed a pronounced β peak in linear low density polyethylene. Recently, Popli et al.[20] found that the β relaxation in polyethylene copolymers is present only in the composition range for which the copolymers are crystalline and the transition temperature is invariant over a rather large range in copolymer composition. The authors concluded that the β transition results from the relaxation of chain units that are located in the interfacial regions. Recent dynamic X-ray diffraction studies[21] showed that lamellar reorientation (crystal b axis orientation) takes place in the β region; accordingly this process was attributed to an interlamellar shear process associated with interlamellar amorphous material. This interpretation is consistent with that proposed by Starchurski and Ward[22] for high density polyethylene and also with the results of Popli et al.[20]

There are numerous suggestions for the origin of γ relaxation in polyethylene. Bohn[23] and Boyer[24] considered this relaxation to be associated with the motion of a small number of methylene units in the amorphous domains of

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semicrystalline polymers. Schatzki[25] proposed a crank shaft motion of methylene units for this process, while Fischer et al.[26] and Wada et al.[27] attributed the γ relaxation to localized chain rotation or translation.

Pechold,[28] Sinnott,[29] Takayanagi,[4] and Illers[14] considered that the γ relaxation arises at least in part from motion of defects in the crystalline regions. In an examination of dielectric relaxation of poly(chlorotrifluoroethylene) (PCTFE), Hoffman et al.[11] found that the γ relaxation exists both in completely amorphous and in highly crystalline (approximately 85% crystallinity) PCTFE. They concluded that the γ relaxation is a composite of γ_a and γ_c attributed to amorphous and crystalline regions, respectively. Crissman[30] found that the γ peak was not observed in *n*-paraffin crystals which are completely crystalline, implying that the γ relaxation originates in the amorphous regions. This is also suggested in a recent review paper by Boyd.[31] Other workers[13,29] have argued that the γ relaxation strength increases with increasing crystallinity. Furthermore, the reverse trend, that is, a decrease in the γ peak intensity with increasing crystallinity has also been observed by many groups.[32,33] Yet others[11] claim that the γ relaxation peak intensity is invariant with crystallinity.

It is obvious from the foregoing discussion that there is at present no generally accepted interpretation of the mechanical relaxations in polyethylene. In this connection, it is important to recognize that in most of the experiments discussed above measurements were made on melt-crystallized samples with a spherulitic texture. Difficulty in arriving at an unequivocal interpretation of the relaxations probably derives from the morphological complexity of the spherulitic specimens. New approaches, using samples of well-defined morphology, are required to further elucidate the origin of the relaxations. Accordingly, the purpose of this paper is to examine the origins of the various relaxations in polyethylene with a well-defined morphology that is simpler than that found in melt-crystallized samples. As a model for such a system we have chosen to use specimens of ultrahigh molecular weight polyethylene (UHMWPE) prepared by gelation/crystallization from dilute solution. The films obtained by this method have a stacked lamellar single-crystal texture with crystallinity in excess of 80%.[34] Under appropriate conditions these films can be stretched up to 300 times the original length. In this process there is a transformation from a folded to an extended chain structure and a substantial increase in crystallinity. The pattern of the paper is as follows. First we compare the dynamic mechanical properties of melt and solution crystallized UHMWPE in order to ascertain whether differences in the relaxation spectra can be associated with the morphological differences of the samples. The next stage in the paper involves the examination of the effect of drawing on the mechanical relaxations of solution-crystallized material. Finally, the origin of the observed relaxation mechanisms is discussed in comparison with the earlier proposals.

Experimental Section

Materials and Sample Preparation.
The sample used was ultrahigh molecular weight polyethylene (Hercules 1900 resin; $\bar{M}_w \simeq 6 \times 10^6$).

Melt-pressed samples were prepared in the following manner. Molds of flat aluminum plates with suitable spacers containing the sample were heated at 210 °C for 10 min. A pressure of 3000 psi (2×10^7 Pa) was then applied for the subsequent 10 min. While under pressure the mold temperature was brought down to 110 °C by cold water circulation. At this stage the pressure was released and the sample was further quenched by immersing the mold in cold water.

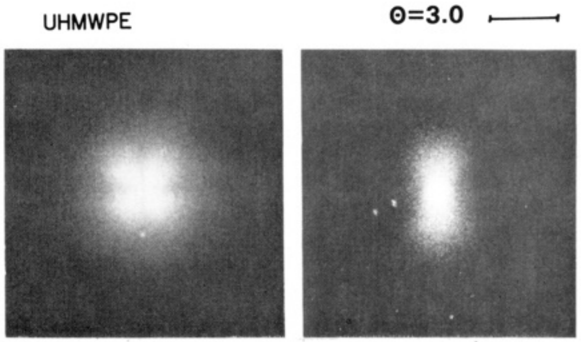

Figure 1. Small-angle light scattering (SALS) patterns of melt-crystallized UHMWPE. Both H_v (left) and V_v (right) patterns are shown.

Gelation-crystallized samples were prepared following the procedure described by Matsuo and Manley,[34] with minor modifications. The modification includes the use of a different antioxidant (IRGONOX 1076; Ciba-Geigy) and a dissolution temperature of about 165–175 °C instead of 150 °C as mentioned in ref 34. The polymer was dissolved in decalin, with vigorous mechanical stirring, at 165–175 °C for 30–40 min under nitrogen. The hot solution (0.4% w/v) was then transferred to an aluminum tray held at 0 °C in an ice water bath. The initially clear solution turned turbid and formed a gel on standing, indicating the onset of gelation. Decalin expelled through syneresis was pipetted off, and the remaining decalin was allowed to evaporate under an air current in a laboratory fumehood for several weeks. The now dry gel film was then placed in an ethanol bath to remove the last traces of decalin and antioxidant. These dry films are typically 300–500 μm in thickness.

Hotdrawing of the Gel Films. Strips with typical dimensions of 1 cm × 4 cm were cut from the dry gel films and drawn on a table model Instron tester, equipped with a hot air oven, at 130 °C and 20 mm/min crosshead speed. The draw ratios (λ) were calculated in the usual manner by noting the displacement of ink marks placed at 1-mm intervals on the sample prior to drawing.

Characterization of Orientation and Crystallinity. The orientation and crystallinity of the samples were assessed by DSC, birefringence, density, and infrared dichroism measurements. Complete experimental details are given in the companion paper.[42]

Small-Angle Light Scattering (SALS). SALS patterns were recorded by using a 15-mW He–Ne gas laser as a light source. Both cross (H_v) and parallel (V_v) polarized scattering patterns were recorded.

Wide-Angle X-ray Diffraction (WAXD) and Small-Angle X-ray Scattering (SAXS) Measurements. WAXD patterns were recorded with a flat film camera by using nickel-filtered Cu Kα radiation (Philips X-ray generator operated at 40 kV and 20 mA). The X-ray beam was perpendicular to the film surface.

SAXS patterns were obtained with the 10-m camera at Oak Ridge National Research Laboratory, through the kindness of Dr. J. S. Lin. A Rigaku rotating anode X-ray generator was used, and the X-ray patterns were recorded with a two dimensional detector. Both through view (beam perpendicular to film surface) and edge view (beam parallel to the film surface) scattering patterns were recorded.

Dynamic Mechanical Properties. Dynamic mechanical properties were measured using a Rheovibron DDV-IIc mechanical spectrometer (Toyo Baldwin Company, Japan) at 3.5, 11, and 110 Hz. The experiments were performed in the temperature ranges of −160 °C to the softenting point of the samples at a heating rate of less than 1 °C/min. The softening point is reached when a constant tension on the sample cannot be maintained for the dynamic measurements. The onset of softening occurs usually a few degrees below the melting temperature.

Results

Characterization of Orientation and Crystallinity. Figure 1 shows the polarized small-angle light scattering patterns of the melt-crystallized UHMWPE sample. The four-leaf-clover pattern under the H_v condition is characteristic of the typical spherulitic structure of poly-

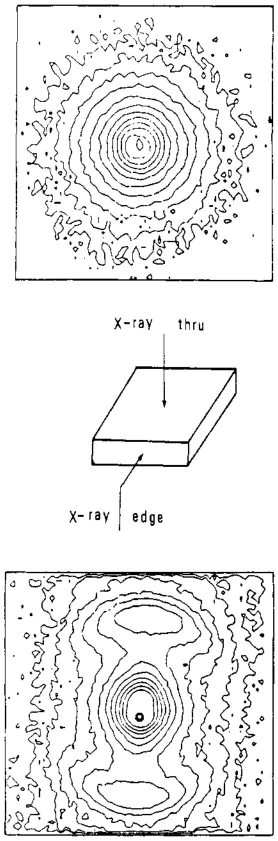

Figure 2. Small-angle X-ray scattering (SAXS) from UHMWPE gel film (both through and edge views are shown).

ethylene. From the H_v pattern, the average radius of the spherulites is estimated to be 3.5 μm. From the two-lobe V_v pattern it was deduced that these are so-called negative spherulites within which the refractive index in the radial direction is smaller than that in the tangential direction.[9] The degree of crystallinity as determined by a density gradient column and differential scanning calorimetry was approximately 55%.

The WAXD pattern of the undrawn gelation-crystallized film showed that the molecular chain axis is oriented perpendicular to the plane of the film. Figure 2 shows the small-angle X-ray scattering (SAXS) profiles of such a film. Both the through and edge views are recorded. The edge view shows a long period estimated to be 117 Å. The WAXD and SAXS patterns taken together indicate that these gel films exhibit a stacked lamellar single-crystal texture. This is in accordance with the previous study of Matsuo et al.[34] and Smith et al.[35] The density of the undrawn gel films is very high ($\simeq$0.97 g/cm^3) corresponding to a crystallinity of about 80%. The percent crystallinity, as calculated from density measurements, increases with increasing draw ratio and attains a limiting value of about 96% at $\lambda \approx 100$. A similar result was obtained from heat of fusion measurements as a function of λ. The gradual disappearance of the amorphous regions may in part be associated with the transformation from a folded chain to an extended chain structure in the process of ultradrawing.

For the gelation-crystallized samples, the birefringence increases with increasing draw ratio up to $\lambda = 100$ and then levels off. The limiting birefringence value (61×10^{-3}) is close to the theoretical value of the n-paraffin ($C_{36}H_{74}$) crystal calculated by Bunn and Daubeny.[36] This behavior is in good agreement with the results of Cannon.[37]

For the gelation-crystallized samples the crystalline and amorphous orientation functions were evaluated as a function of draw ratio. The crystalline orientation function initially increases rapidly with stretching and reaches a limiting value close to unity at a draw ratio of about $\lambda = 10$. In contrast, the increase of the amorphous orientation function is almost linear at the early stages of drawing up to $\lambda \sim 100$ where it reaches a limiting value close to unity. This kind of gradual increase of amorphous orientation is consistent with that reported by Read and Stein.[38] The delayed response of the amorphous orientation was also reported by Kyu et al.[12] and Cembrola et al.[39] in their dynamic birefringence and X-ray diffraction studies.

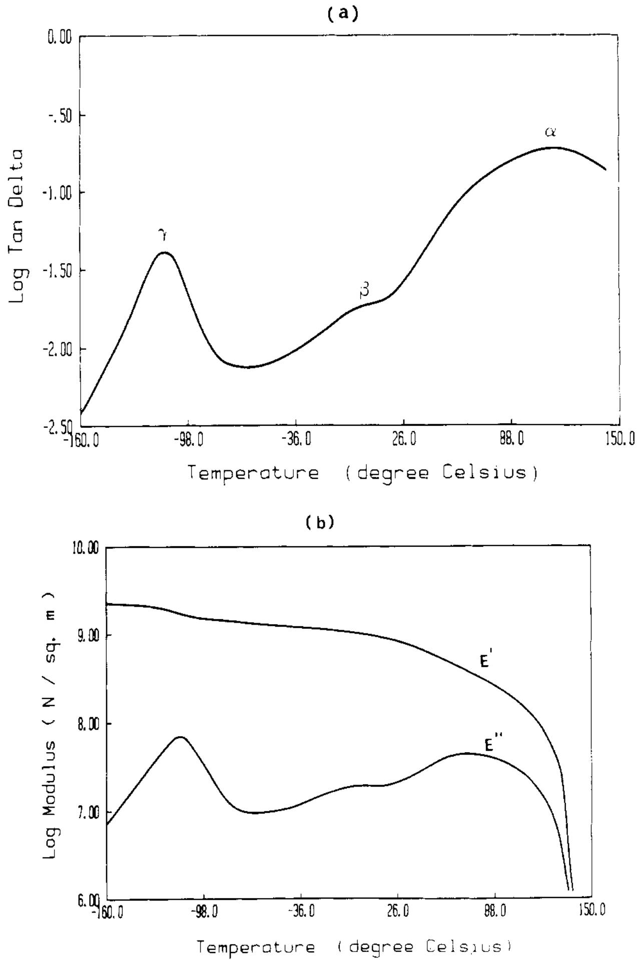

Figure 3. Dynamic mechanical properties at 3.5 Hz as a function of temperature for a melt-crystallized UHMWPE film. Legends: (a) loss tangent (tan δ); (b) storage (E′) and loss (E″) modulus.

The increased orientation of the crystal c axes in the draw direction was also evident from the WAXD patterns for the gel films drawn to various draw ratios.[40] As the draw ratio increased, the initially isotropic Debye rings transformed into arcs and finally to points at even higher λ, indicating fiber diffraction patterns with almost perfect c-axis orientation. This is similar to the results previously obtained by Smith et al.[41] Details of the density, heat of fusion, birefringence and infrared measurements as a function of draw ratio will be given elsewhere.[42]

Dynamic Mechanical Properties. The results of dynamic mechanical measurements of the melt-crystallized UHMWPE are shown in Figure 3 where the storage (E') and loss (E'') moduli and the loss tangent are plotted against temperature. These results were obtained at 3.5 Hz at a heating rate of less than 1 °C/min. Three relaxations labeled α, β, and γ in descending order of temperature are evident in both the E'' and tan δ curves. The α peak is rather broad as typical of conventional polyethylenes. The β peak appears as a clearly discernible

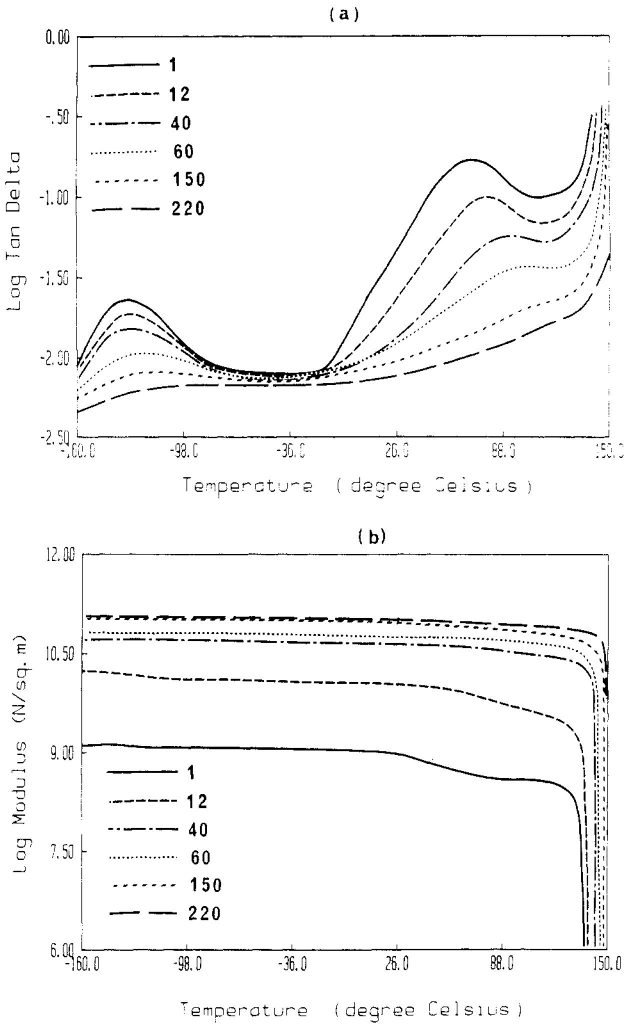

Figure 4. Dynamic loss tangent ($\tan\delta$; (a)) and storage modulus (E'; (b)), measured at 3.5 Hz, as a function of temperature for UHMWPE films of various draw ratios (λ). (Draw ratios are shown on the figure.)

shoulder on the α peak. This β peak is normally seen in the branched polyethylene (low density PE) and linear low density polyethylene. It is often less clearly discernible in the case of conventional high density polyethylenes. The γ peak is very pronounced in both the E'' and $\tan\delta$ curves.

In Figure 4 are shown the plots of E' and $\tan\delta$ as a function of temperature, obtained at 3.5 Hz for gelation-crystallized samples of various draw ratios. The undrawn sample ($\lambda = 1$) shows only the α and γ peaks. The α peak in the $\tan\delta$ curve is much sharper and distinct as compared to that of the melt-crystallized sample. This suggests that the α peak in the gelation-crystallized sample may derive from a single relaxation process. The β peak is completely undetectable. The low-temperature γ peak can be clearly seen; however, its magnitude is significantly lower than that in the melt-crystallized material. The E' curve shows an inflection corresponding to the α peak. The value of E' reduces drastically above 136 °C as the temperature approaches the crystal-melting temperature.

When the sample is drawn beyond 60 times its original length, the temperature at which E' drops sharply shifts at least 10 °C, reflecting an increase in crystal-melting temperature. The strength of the α peak decreases dramatically with ultradrawing while the position of the maximum moves to higher temperatures; the peak virtually disappears when the draw ratio $\lambda > 150$. The β peak is also undetectable in the drawn samples. It is also striking that the γ peak completely disappears for the ultradrawn samples with $\lambda > 150$.

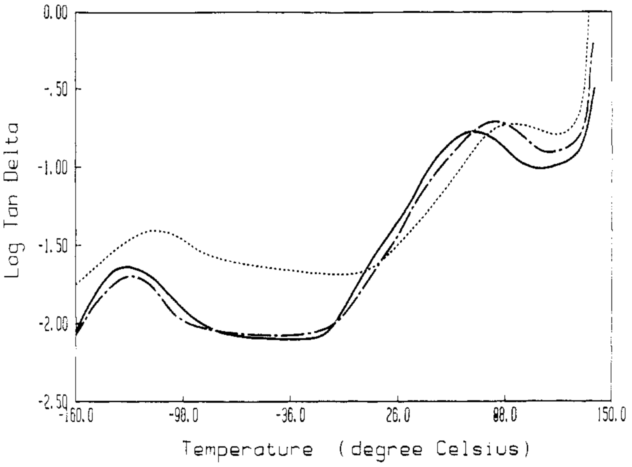

Figure 5. Loss tangent ($\tan\delta$) as a function of temperature for undrawn UHMWPE gel film at various frequencies (legends: —, 3.5 Hz; ·–·, 11 Hz; ···, 110 Hz).

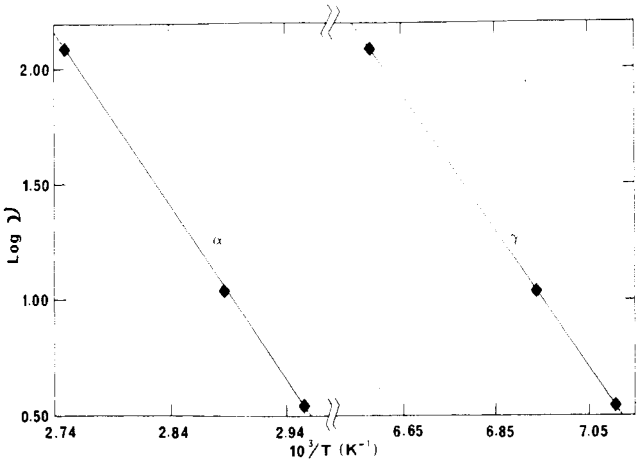

Figure 6. Arrhenius plots of α and γ relaxations for undrawn UHMWPE gel films: plots of log frequency versus inverse absolute temperature.

Figure 5 shows the plots of $\tan\delta$ versus tempeature for frequencies of 3.5, 11, and 110 Hz for unstretched gelation-crystallized material. The α and γ peaks move to higher temperature with increasing frequency. Plots of frequency versus reciprocal absolute temperature of the α and γ peak maxima are shown in Figure 6. The corresponding apparent Arrhenius activation energies are estimated to be 36.2 and 6.7 kcal/mol, respectively.

The activation energy for the α process of the undrawn gelation-crystallized UHMPE differs significantly from the literature values for both α_1 (25 kcal/mol)[1,11] and α_2 (45 kcal/mol).[1,3] Thus the activation energy by itself cannot be used as a basis for deciding whether the observed α peak corresponds to the α_1 or α_2 process. However, we note that the α peak moves to higher temperatures with stretching, and in the highly drawn specimens (i.e., for $\lambda > 40$) it is located in the vicinity of 90 °C, which is normally associated with the α_2 process of conventional polyethylene. Thus the α_2 mechanism appears to be dominant in the gelation-crystallized samples. This conclusion is in good accord with the work of Takayanagi, who observed a single α_2 process in polyethylene single-crystal mats.[44]

Discussion

Consider first the α relaxation of the gelation-crystallized sample and its melt-crystallized counterpart. The melt-crystallized material shows a very broad α peak, characteristic of typical polyethylenes. It is well-known that the α process in conventional polyethylenes is a composite process of the α_1 and α_2 mechanisms.[1-3] The former is attributed to crystal orientation relaxation occurring at the crystal grain boundary within the lamellar structure. The latter is assigned to the rotational and translational chain motions within the crystal lattice. The relative contributions of the α_1 and α_2 processes lead to a broad α peak.

Kyu[45] predicted that the α_1 process, associated with crystal orientation relaxation, may be absent if the crystal chain orientation is very high and the concentration of crystal defects is very low, as in the case of a highly oriented fibrous structure. In such a case, the α_2 process is expected to be dominant. This appears to be the situation in the present oriented gelation-crystallized specimens.

The reduction of the α relaxation strength coupled with its shift to higher temperature with increasing draw ratio suggests that the intracrystalline chain motions experience increased difficulty in occurring due to the enormous constraint forces imposed by the ultradrawing. Ultradrawing results in an extended-chain crystalline structure with concomitant increase in the size of the crystalline continuum. This minimizes the possibility of incoherent chain motions (origin of viscoelastic loss), and hence the relaxation strength diminishes.

The β relaxation process is very obvious in the melt-crystallized sample but is not detectable in the gelation-crystallized material. The crystallinity of the undrawn melt- and gelation-crystallized UHMWPE are approximately 55 and 82%, respectively. Since the crystallinity of the melt-crystallized sample is significantly lower than that of the gelation-crystallized material, the β peak can be simply attributed to the amorphous regions, in line with the classical concept of the origin of this peak. Recently Popli et al.[20] have proposed that the β-relaxation in polyethylene arises from the interfacial zones of the crystalline and amorphous regions, while Kawai et al.[9] have attributed this mechanism to an interlamellar shear process. It is clear, however, that the present work does not provide any basis for such a specific assignment.

Another interesting observation in the present study concerns the γ relaxation that is quite pronounced in the unstretched gelation-crystallized UHMWPE but completely disappears when the sample is stretched beyond 150 times its original length. This may be associated at least in part with the disappearance of the amorphous regions accompanying the transformation of a folded-chain structure to extended-chain crystals.

The absence of the γ relaxation in the ultradrawn highly crystalline (in excess of 98%) UHMWPE samples strongly suggests that the γ process originates in the amorphous regions or defective crystalline regions of melt-crystallized UHMWPE or of conventional polyethylenes. This is consistent with the results of Crissman[30] who showed that the γ peak completely disappeared in the 100% crystalline extended-chain structure of *n*-paraffins. According to Hoffmann et al.[11] the γ peak exists in 100% amorphous PCTFE and is also present in 85% crystalline PCTFE material. Consequently, the existence of γ_c and γ_a was proposed. It should be noted that in the present work the γ relaxation does exist in the undrawn UHMWPE gel film whose crystallinity exceeds 80%; it only disappears when the crystallinity increases further upon ultradrawing. Thus, unlike PCTFE, γ_c does not exist in these highly crystalline ultradrawn polyethylenes.

Conclusions

In the present investigation it has been clearly demonstrated that the crystalline morphology exerts profound effects on the mechanical relaxations of UHMWPE. The β relaxation is evident in melt-crystallized UHMWPE (55% crystallinity) but is totally absent in the gelation-crystallized material (over 80% crystallinity). It is therefore evident that this relaxation process must be associated with the amorphous material in the melt-crystallized sample. Both the γ and α relaxations of the gelation-crystallized film disappear completely when the sample is stretched to draw ratios in excess of 150; this implies that the ultradrawn UHMWPE responds like a rigid crystalline continuum up to the crystal melting temperature.

The α relaxation in the gelation-crystallized material is similar to the α_2 process of conventional polyethylene which is generally considered to arise from intracrystalline chain motions. Finally, the present experiments suggest that both the β and γ relaxations originate in the amorphous regions. It is, however, difficult to make an explicit assignment of T_g to either β or γ, because the amorphous regions in such a highly crystalline ultradrawn material are practically indistinguishable from the defects trapped in the crystalline continuum.

Registry No. Polyethylene, 9002-88-4.

References and Notes

(1) Nakayasu, H.; Markovitz, H.; Plazek, D. J. *Trans. Soc. Rheol.* **1961**, *5*, 261.
(2) Takayanagi, M. *J. Macromol. Sci., Phys.* **1974**, *B9*(3), 391.
(3) Manabe, S.; Sakado, A.; Katada, A.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1970**, *B4*(1), 161.
(4) Takayanagi, M. In *Molecular Basis of Transition and Relaxations*; Meier, D. J., Ed.; Gordon and Breach: New York, 1978.
(5) Tanaka, A.; Chang, E. P.; Delf, B.; Kimura, I.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1891.
(6) Iwayanagi, S.; Miura, I. *Jpn. J. Appl. Phys.* **1965**, *4*, 94.
(7) Saito, N.; Okano, K.; Iwayanagi, S.; Hideshima, T. In *Solid State Physics*; Seitz, F., Turnbull, D., Eds.; Academic: New York 1963; Vol. 4.
(8) McCrum, N. G.; Morris, E. L. *Proc. R. Soc. London A* **1966**, *292*, 506.
(9) Kawai, H.; Hashimoto, T.; Suehiro, S.; Fujita, K. *Polym. Eng. Sci.* **1984**, *24*(5), 361.
(10) Okano, K. *J. Polym. Sci., Part C* **1966**, *15*, 95.
(11) Hoffmann, J. D.; Williams, G.; Passaglia, E. *J. Polym. Sci., Part C* **1966**, *14*, 173.
(12) Kawai, H.; Suehiro, S.; Kyu, T.; Shimomura, A. *Polym. Eng. Rev.* **1983**, *3*, 109.
(13) Kline, D. E.; Sauer, J. A.; Woodward, A. E. *J. Polym. Sci.* **1956**, *22*, 455.
(14) Illers, V. K. H. *Rheol. Acta* **1964**, *3*(4), 194.
(15) Nielsen, L. E. *J. Polym. Sci.* **1960**, *42*, 357.
(16) Reding, F. P.; Faucher, J. A.; Whitman, R. D. *J. Polym. Sci.* **1962**, *57*, 483.
(17) Schmieder, V. K.; Wolf, K. *Kolloid Z. Z. Polym.* **1953**, *134*, 149.
(18) Moore, R. S.; Matsuoka, S. *J. Polym. Sci., Part C* **1963**, *5*, 163.
(19) Stein, R. S.; Hu, S. R.; Masaoka, T.; Kyu, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(1), 117.
(20) Popli, R.; Glotin, M.; Mandelkern, L.; Benson, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 407.
(21) Kyu, T.; Yamada, M.; Suehiro, S.; Kawai, H. *Polymn. J. (Tokyo)* **1980**, *11*, 809.
(22) (a) Starchurski, Z. H.; Ward, I. M. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1083. (b) Ibid. **1968**, *6*, 1817.
(23) Bohn, V. L. *Kolloid Z. Z. Polym.* **1964**, *194*, 10.
(24) Boyer, R. F. *J. Macromol. Sci., Phys.* **1974**, *B8*, 503.
(25) Schatzki, T. F. *J. Polym. Sci.* **1962**, *57*, 496.
(26) Fischer, E. W.; Schmidt, G. F. *Agnew Chem., Intl. Ed. Engl.* **1962**, *1*, 488.
(27) Wada, Y.; Tsuge, K. *Jpn. J. Appl. Phys.* **1962**, *1*, 64.
(28) Pechhold, W. *Kolloid Z. Z. Polym.* **1968**, *228*, 1.
(29) Sinnot, K. M. *J. Appl. Phys.* **1966**, *37*, 3385.
(30) Crissmann, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1407.
(31) Boyd, R. H. *Macromolecules* **1984**, *17*, 903.
(32) Stehling, F. C.; Mandelkern, L. *Macromolecules* **1970**, *3*, 242.
(33) Matsuoka, S. In *Macromolecules: An Introduction to Polymer Science*; Bovey, F. A., Winslow, F. A., Eds.; Academic: New York, 1979.

(34) Matsuo, M.; Manley, R. S. J. *Macromolecules* **1982**, *15*, 985.
(35) Smith, P.; Lemstra, P. J.; Pijpers, J. P. L.; Kiel, A. M. *Colloid Polym. Sci.* **1981**, *259*, 1070.
(36) Bunn, C. W.; de Daubeny, R. *Trans. Faraday Soc.* **1954**, *50*, 1173.
(37) Cannon, C. G. *Polymer* **1982**, *23*(8), 1123.
(38) Read, B. E.; Stein, R. S. *Macromolecules* **1968**, *1*, 116.
(39) Cembrola, R. J.; Kyu, T.; Stein, R. S.; Suehiro, S.; Kawai, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 881.
(40) Roy, S. K. Ph.D. Thesis, McGill University, Montreal, Canada, 1986.
(41) Smith, P.; Lemstra, P. J. *J. Mater. Sci.* **1980**, *15*, 505.
(42) Anandakumaran, K.; Roy, S. K.; Manley, R. S. J. *Macromolecules*, following paper in this issue.
(43) Takayanagi, M.; Matsuo, T. *J. Macromol. Sci. Phys.* **1967**, *B1*, 407.
(44) Takayanagi, M. *Mem. Fac. Eng., Kyushu Univ.* **1963**, *23*(1), 1.
(45) Kyu, T. Ph.D. Thesis, Kyoto University, Kyoto, Japan, 1980.

Drawing-Induced Changes in the Properties of Polyethylene Fibers Prepared by Gelation/Crystallization

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ABSTRACT: Fibers of ultrahigh molecular weight polyethylene were prepared by drawing dry specimens obtained by gelation/crystallization from solution. The maximum draw ratio (λ) attained was 250. The properties of the fibers were assessed by measurements of density, birefringence, differential scanning calorimetry, infrared dichroism, sonic velocity, and dynamic modulus. The results have been analyzed in terms of a two-phase model of crystalline and amorphous regions. All properties approach a limiting value at a draw ratio of about 100. The degree of crystallinity and melting point decrease initially (for $\lambda < 12$) and then increase rapidly with λ up to their limiting values. The crystalline orientation function, as determined from measurements of infrared dichroism, increases rapidly with λ and reaches its maximum value at $\lambda \simeq 10$. In contrast, the amorphous orientation function, as estimated from sonic velocity and birefringence measurements, increases almost linearly and reaches its maximum value at $\lambda \simeq 100$. The increase in modulus with draw ratio correlates with the amorphous orientation function but not with the orientation of the crystalline phase. On the basis of the various observations, the sequence of events during drawing is discussed.

Introduction

In recent years the processing of high molecular weight polyethylene to give fibers with high stiffness and strength has attracted considerable interest. The basic prerequisite for achieving this objective is that the chain molecules should be fully extended and aligned in the draw direction. For this purpose Smith and Lemstra[1,2] have introduced the technique of gelation/crystallization. In this process a thermoreversible gel is formed by rapidly quenching a hot dilute solution of the polymer. In the three-dimensional network thus formed the crystalline regions act as junction points.[3] The gels exhibit very high extensibility, even after removal of the solvent, and this is attributed to the significantly reduced chain entanglement density in comparison with melt-crystallized material.[1]

The structure and properties of drawn gelation-crystallized specimens have been extensively studied, especially for the range of draw ratios below 100, but the details of the deformation process are not fully understood. In particular there is the question as to whether the properties increase linearly up to the highest attainable draw ratios or approach a limiting value. Secondly since, as will be seen later, gelation-crystallized specimens are essentially a two-phase system, it is of interest to ascertain the effect of draw ratio on the molecular orientation of the crystalline and amorphous phases. The present work attempts to address these issues by a quantitative study of the uniaxial deformation process in dry ultrahigh molecular weight polyethylene gelation/crystallized samples. Toward this end changes in the properties of the uniaxially deformed films with increasing draw ratio have been assessed by measurements of birefringence, density, differential scanning calorimetry, infrared dichroism, sonic velocity, and dynamic modulus. The results allow characterization of the deformation mechanism that is involved.

Experimental Section

Specimen Preparation. The sample used was linear polyethylene (Hercules 1900/90189) with a nominal intrinsic viscosity of 30 dL/g, corresponding to a molecular weight of 6×10^6. The solvent was decalin.

Gel films were prepared by crystallization from solution. The decalin solution at a concentration of 0.4 g/dL, containing 0.1% w/w of the antioxidant di-*tert*-butyl-*p*-cresol, was prepared by heating the polymer/solvent mixture at 150 °C for about 1 h under nitrogen. The hot solution was quenched by pouring into an aluminum tray surrounded by ice water, thus generating a gel. The decalin was allowed to evaporate from the gel in a current of air under ambient conditions. Residual solvent in the film thus obtained was removed by extraction with ethanol, and after air-drying the thickness of the film was about 300 μm.

Rectangular shaped samples with dimensions of 50 × 10 mm were cut from the film and drawn on an Instron tensile testing machine fitted with a temperature-regulated oven. The samples were drawn at a cross head speed of 10 mm/min at a temperature of 130–135 °C. The draw ratio (λ) was determined in the usual way by measuring the displacement of ink marks placed on the sample surface prior to drawing at intervals of 2 mm.

Density. Densities (ρ) of the various samples were measured in an 2-propanol–water density gradient column calibrated with glass beads of known density. From the measured densities (ρ), the weight fraction of crystalline material W_c was calculated from eq 1 where ρ_c is the density of the crystalline material, taken as

$$W_c = \frac{\rho_c\,(\rho - \rho_a)}{\rho\,(\rho_c - \rho_a)} \qquad (1)$$

0.997 g/cm^3, and ρ_a, the density of the amorphous phase, was assumed to be 0.854 g/cm^3.[4]

For oriented samples it was necessary to remove air bubbles, by pressing at 3000 psi (2×10^7 Pa) at room temperature, prior to the flotation measurements.