Cross-Linking of Ultrahigh Molecular Weight Polyethylene Films Produced by Gelation/Crystallization from Solution under Elongation Process

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ABSTRACT: Dicumyl peroxide (DCP) was used to cross-link ultrahigh molecular weight polyethylene gels that were prepared by gelation/crystallization from a dilute solution. The cross-linking was carried out under elongation of gel films containing DCP. The storage modulus for cross-linked polyethylene drawn up to 50 times was 46 GPa at room temperature and 0.5 GPa at 230 °C. The deformation mechanism was investigated in morphological terms by using wide-angle X-ray diffraction, small-angle X-ray scattering, small-angle light scattering, and scanning electron microscopy.

Introduction

It is well-known that cross-linking of polyethylene can be performed with γ- and electron-beam irradiation, and that this is desirable since the range of application of polyethyelne is limited by its low melting point.[1-7] Both methods have played an important role in cross-linking the polymer chains in the amorphous regions. The effect of irradiation on mechanical properties is initially to increase the modulus as well as the yield stress and to reduce ductility. This effect is rather small in conventional high-density polyethylene (HDPE) but quite pronounced in ultrahigh molecular weight polyethylene (UHMWPE).[7] This phenomenon is attributed to the fact that since the crystallinity of UHMWPE melt film is lower than that of HDPE because of a large number of molecular entanglements within the melt, radiation-induced increase in crystallinity occurs because of scission of tie chain molecules followed by crystalline reorganization.

Most irradiation studies, however, have dealt with undrawn films. Recently, the application of cross-linking to an oriented system has been carried out by Pennings et al.[8,9] in order to produce polyethylene fibers with improved mechanical and thermal properties. According to their report, cross-linked UHMWPE fibers could be prepared by γ-irradiation without destroying the specific fiber structure. They pointed out that apart from cross-linking, γ-irradiation also unfortunately causes main-chain scission, thus reducing the tenacity of the filaments. A similar study was carried out by Sawatari and Matsuo[10] using electron beam irradiation. They exposed ultradrawn films whose draw ratio was greater than 50 to an electron beam under nitrogen flow. The mechanical properties of the resultant specimens were found to become much weaker with increasing dose, and the specimens with a dose of 200 Mrad were easily torn by hand. This result was attributed to the considerable radiation-induced scission of extended chains forming the crystals. Consequently it turned out that the irradiation is not appropriate for producing a net cross-linking effect occurring preferentially in the amorphous regions. This unfavorable finding is due to the high crystallinity of ultradrawn polyethyelene films.

In order to avoid rupture of chains, Pennings et al.[11] used dicumyl peroxide (DCP) to cross-link UHMWPE fibers. They pointed out that the DCP should be introduced into the filaments before they attain a high degree of crystallinity, i.e., prior to hot drawing. Therefore, as-spun polyethylene fibers, which are highly porous, were swollen in solutions of DCP in *n*-hexane. After swelling and drying, DCP-containing as-spun porous fibers were hot-drawn under nitrogen at 150 °C. Through a series of experimental procedures it was observed that cross-linking prevents the fiber from fibrillation upon fracture at room temperature and that cross-linked filaments can be kept at 195 °C for prolonged time without significantly influencing the tenacity of the fiber at 20 °C.

Based on the approach of Pennings et al.,[11] this paper is concerned with the mechanical and morphological properties of cross-linked ultradrawn polyethylene by DCP. The method for producing specimens is different from that of Pennings et al. and is related to the ultradrawing of gel films produced by gelation/crystallization from solution.[12,13] It will be shown that in this way dry gels containing DCP can be elongated up to a draw ratio of 50 under nitrogen at 150 °C. The real part E' of the complex dynamic tensile modulus E^* for the resultant specimen was 46 GPa at 20 °C and 0.5 GPa at 230 °C. Such excellent mechanical behavior is due to completely gelled fiber networks. The extent of improvement of the high-temperature resistance of the drawn films upon cross-linking is particularly striking if one realizes that non-cross-linked high-strength polyethylene fibers cannot exist at temperatures beyond 200 °C.

Experimental Section

The sample used was linear polyethylene (Hercules 1900/90189) with an intrinsic viscosity of 30 dL/g, corresponding to a moleclar weight of 6×10^6. The solvent was decalin. Three experimental methods to introduce DCP into gels were adopted as follows:

Method I. Decalin solutions (1500 mL) containing 0.5 (w/w) polyethylene were prepared by heating the well-blended polymer/solvent mixture at 135 °C for 30 min under nitrogen. The hot solution was quenched by pouring into an aluminum tray at room temperature, thus generating a gel. The decalin was allowed to evaporate from the gel under ambient conditions. When the volume of the gel approached a 70% decrease, 300 mL of a decalin solution of DCP at 50 °C containing twice as much DCP as polyethylene was poured into the aluminum tray. The decalin was again evaporated at 50 °C. The nearly dry gel film was vacuum-dried for 1 day to remove residual traces of decalin.

Method II. Hot decalin solutions of polyethylene (1500 mL) at 135 °C and a decalin–DCP solution (300 mL) prepared by Method I were poured into an aluminum tray at the same time. The decalin was evaporated at 50 °C and the nearly dry gel film was vacuum-dried.

Method III. Decalin solutions (1500 mL) containing 0.5% (w/w) of polyethylene and 1.0% (w/w) of DCP were prepared by heating the well-blended polymer/solvent mixture at 135 °C for 30 min under nitrogen. The hot homogenized solution was quenched by pouring into an aluminum tray, thus generating a gel, and the decalin was evaporated at 50 °C. The nearly dry gel film was vacuum-dried.

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The above three methods were adopted because they allow all the DCP to be introduced into a dry gel film. The weight percentage of the DCP in the dry gel film is 200%.

The dry gel film was cut into strips 24 mm long and 15 mm wide. The strips were clamped in a manual stretching device in such a way that the length to be drawn was 4 mm. The specimen was placed in an oven at 150 °C under nitrogen and immediately elongated manually to the desired draw ratio. The manual stretching device was warmed prior to clamping the specimen in order to avoid as much as possible a decrease of temperature when placing the device in the oven. The temperature 150 °C was chosen to be similar to the preliminary experiment of Pennings et al.[11] Actually, the vulcanization reaction at 150 °C is almost completed during elongation, and the maximum draw ratio of 50 is attained. In contrast, the cross-linking at 135 °C was insufficient to prepare films with high temperature resistance, although the maximum draw ratio was close to 100. When the film was stretched beyond a draw ratio of 25 at 135 °C, oriented crystallization was found to be predominant at the expense of the amorphous regions. This was discerned by small-angle light scattering and by pycnometer.[14,15] This phenomenon hampered cross-linking since the crystal regions were too densely packed to facilitate easy DCP penetration; in addition, there was a higher rate of cross-linking at temperatures higher than 150 °C. As discussed by Pennings et al.,[11] too many cross-links are introduced into the gel in a rather short period of time, resulting in a random connectedness of the polyethylene chains and thus inhibiting chain alignment in the direction of stretching during hot drawing.

The drawn films were annealed for 90 min in an oven at 150 °C under nitrogen in order to promote cross-linking in the amorphous regions. Subsequently the annealed films were immersed in an excess of ethanol at 50 °C for 6 h.

The temperature dependence of the complex dynamic tensile modulus function was measured by a viscoelastic spectrometer (VES-F) of the Iwamoto Machine Co., Ltd. The specimens used in this experiment were cut to a length of 60 mm and width of 1.5 mm and were clamped over a length of 10 mm at the ends. The measurement was carried out over a temperature range of −50 to +232 °C at a fixed frequency of 10 Hz. In actual measurement, the film was subjected to static tensile strain due to the stress 0.018 GPa in order to apply a dynamic displacement of 0.01 mm smoothly.

The thermal behavior was estimated from the melting endotherm in differential calorimetry (DSC) curves. Dried gels, weighing 5 mg, were placed in a standard aluminum sample pan. Films were heated at a constant rate of 10 °C/min.

The X-ray measurement was carried out with a 12-kW rotating anode X-ray generator (Rigaku RAD-rA). Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera with Cu K_α radiation at 200 mA and 40 kV. The X-ray beam was monochromatized by a curved graphite monochrometer. The exposure time for all specimens was 30 min with the incident beam directed parallel to film surface (end view). It was 1 h when the beam was normal to the film (through view). Small-angle X-ray scattering (SAXS) patterns were obtained with a flat-film camera. The exposure time was 100 h in both cases.

Scanning electron micrographs and polarized micrographs were obtained with a JSM-T300 and a Nikon Optiphot Pol. (XTP-11), respectively.

Small-angle light scattering (SAXS) patterns were obtained with a 3-mW He–Ne gas laser as a light source. Diffuse scattering was avoided by sandwiching the specimen between cover glasses with silicon oil as an immersion fluid.

Results and Discussion

Figure 1 shows SAXS and WAXD patterns (end view) from dry gel films prior to annealing. The patterns on line A show the scattering from an original film without DCP. The patterns on line B, C, and D show scattering from the films prepared by methods I, II, and III, respectively. As can be seen in the patterns, the WAXD pattern from the specimen prepared by method I exhibits diffraction rings from the DCP crystallites in addition to the equatorial (110) and (200) reflections of polyethylene crystallites, and the corresponding SAXS pattern shows distinct scattering

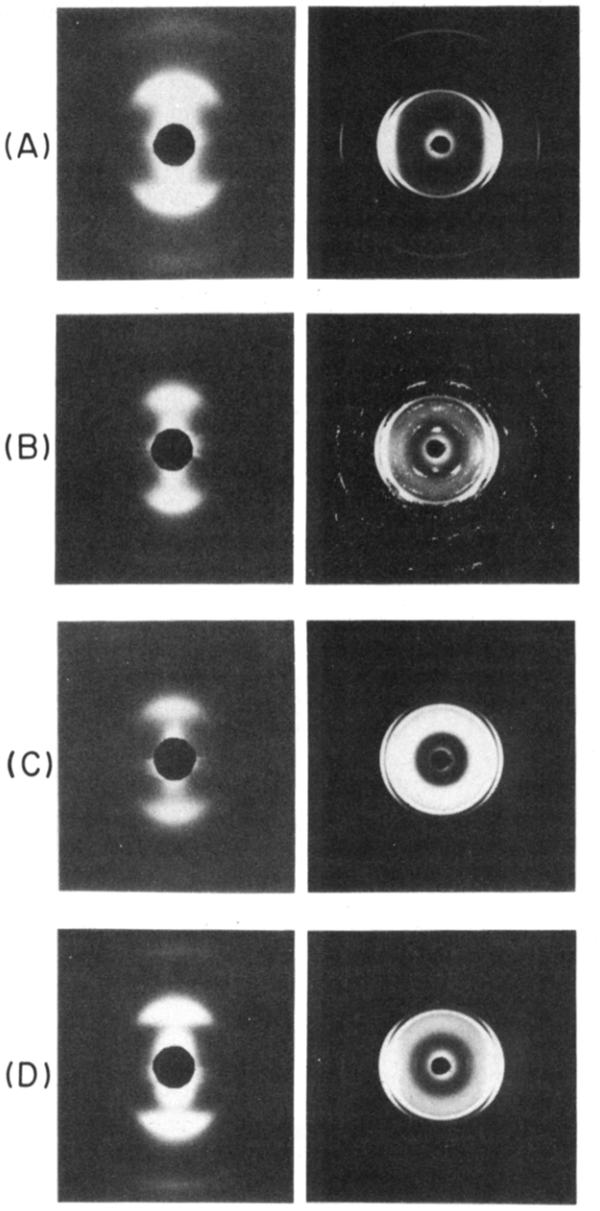

Figure 1. SAXS and WAXD patterns from dry gel films prior to annealing (end view): line A, original film; line B, film prepared by method I; line C, film prepared by method II; line D, film prepared by method III.

maxima, as can be seen in the pattern from the original film. The two patterns indicate that the dry gel film prepared by method I is composed of crystal lamellae that are highly oriented with their large flat faces parallel to the film surface, and, within the lamellar crystals, the crystal *c* axes are oriented perpendicular to the large flat faces. Furthermore the scattering maxima move to the scattering center in comparison with those of the original film. This indicates that the DCP crystallites exist in many gaps between crystal lamellae. However, the WAXD and SAXS patterns in lines A and B show that the introduction of DCP into the gel film hardly affects either the orientational mode of the crystal lamellae or their formation.

When dry gel films are prepared by methods II and III, there are no diffraction rings from the DCP crystallites. Especially, the WAXD and SAXS patterns from the specimen prepared by method III are almost the same as those from the original film, resulting from the reaction of most of the DCP with decalin under the sample preparation. The WAXD pattern from the specimen prepared by method II shows an indistinct amorphous ring. This

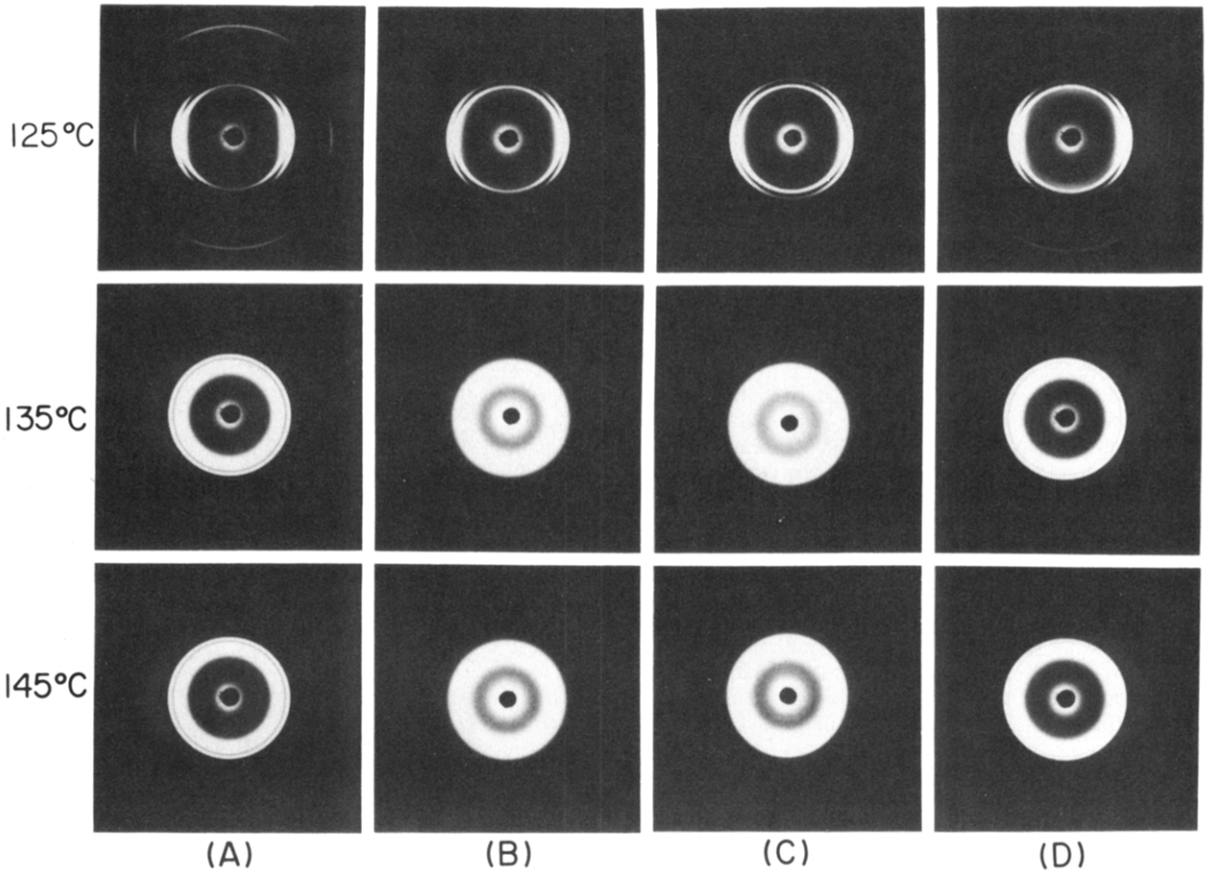

Figure 2. WAXD patterns (end view) from undrawn films annealed for 90 min at the indicated temperature: line A, original film; line B, film prepared by method I; line C, film prepared by method II; line D, film prepared by method III.

indicates the reaction of DCP with the polymer chains as well as with decalin on pouring the hot decalin–polyethylene solution (1500 mL at 135 °C) and decalin–DCP solution (300 mL at 50 °C) into an aluminum tray simultaneously. Vulcanization diminishes the high drawability of a dry gel film since cross-linking hampers chain movement during hot drawing.

Figure 2 shows WAXD patterns (end view) from undrawn films annealed under nitrogen for 90 min at the indicated temperatures. The WAXD patterns on line A show the diffraction from an original gel film and those on lines B, C, and D from the specimens prepared by methods I, II, and III, respectively. When the films are annealed at 125 °C, the patterns show no significant change in crystallinity and crystal orientation. When the annealing temperature is increased, however, the WAXD patterns are strongly affected by the method of sample preparation. The patterns from the specimens prepared by methods I and II show an amorphous ring and it is evident that peroxide decomposition and concomitant cross-linking are enhanced with increasing annealing temperature. This tendency is particularly noticeable for the specimen prepared by method I, since most of the DCP contributes to the occurrence of vulcanization. The patterns of the specimens prepared by method III are almost same as those of the original film, indicating that most of the DCP was already reacted with decalin in the sample preparation process, as discussed before. Accordingly, the following sample preparations in this paper were carried out by method I.

Figure 3 shows the change in the profile of the DSC curves of specimens with 200% DCP with increasing annealing temperature. The annealing condition is the same as for the sample preparation discussed in Figure 2. The profiles for unannealed and annealed specimens (at 125 °C) show a single peak. The peak of the annealed specimen is sharper than that of the unannealed one and the peak position shifts to higher temperature. This behavior implies an increase in crystallinity due to annealing. The annealing at 125 °C seems to be almost independent of the chemical reaction associated with cross-linking. In contrast, there exists no peak in the profile of specimens annealed at 135 and 145 °C, indicating the disappearance of crystal phases owing to the chemical reaction. Such profiles are in good agreement with the patterns shown in Figure 2B. The profile of DSC curves of both the annealed specimens implies that the possibility of chain fracture during cross-linking is excluded even at 300 °C. Actually, when the sample was picked up from a standard sample pan after the DSC measurement, the specimen became like

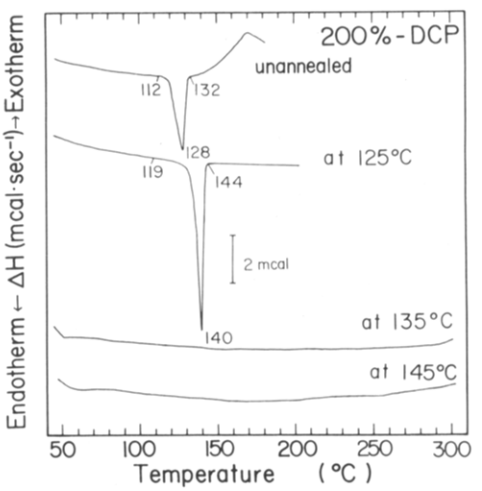

Figure 3. DSC curves of specimens prepared by method I with increasing temperature.

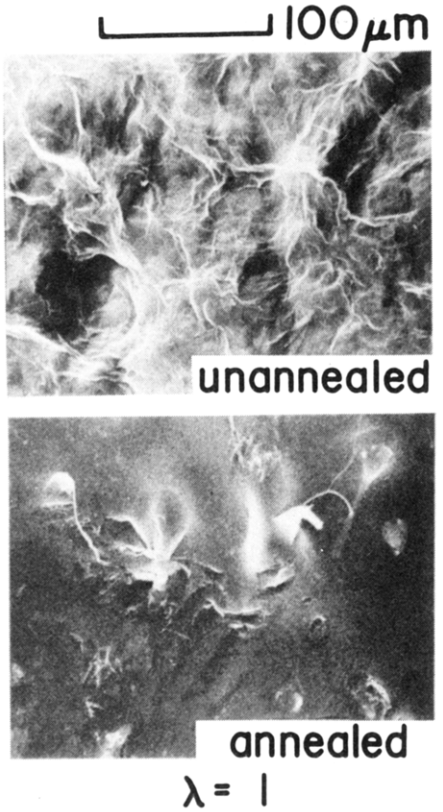

Figure 4. Scanning electron micrographs of dry gel films in an undeformed state unannealed and annealed.

charcoal without any indication of melting.

Figure 4 shows morphological changes between unannealed and annealed dry gel films (200% DCP) under scanning electron microscopy. The texture of the unannealed specimen is fibrillar like spongy tissue while that of the annealed specimen has a smooth surface like a melt film. As mentioned before, the annealing was carried out at 145 °C for 90 min under nitrogen. Thus, the drastic change in the appearance is obviously due to a partial melting of the film surface. Considering that the half-life of the DCP at 150 °C is about 20 min, it is evident that the chemical reaction associated with cross-linking occurred smoothly in the melt regions because of the easy penetration of DCP.

Figure 5 shows the change in the appearance of cross-linked dry gel films with increasing draw ratio λ under scanning electron microscopy. The elongation was carried out at 150 °C under nitrogen and the drawn films were annealed at 150 °C for 90 min under nitrogen. As λ increases, the width of fibrillar texture is decreased and finally the fibrillar texture seems to be disruptively deformed into fine filaments. The filaments are also highly oriented parallel to the drawing direction. As illustrated in a series of the photographs, this tendency becomes clear beyond λ = 25. In the polarizing microscope the development of the fibrous texture could be readily followed. As can be seen in Figure 6, observations revealed the uniform deformation process of the fibrous textures. At λ = 12, the elongated birefringent regions are predominantly oriented in the direction of stretching. With further increases in the draw ratio, the elongated birefringent regions seem to be disruptively deformed into fine filaments, which are also highly oriented parallel to the drawing direction. This deformation mode is very similar to that of the original films (0% DCP) at 150 °C, although the photographs of the original films are not shown in this paper.

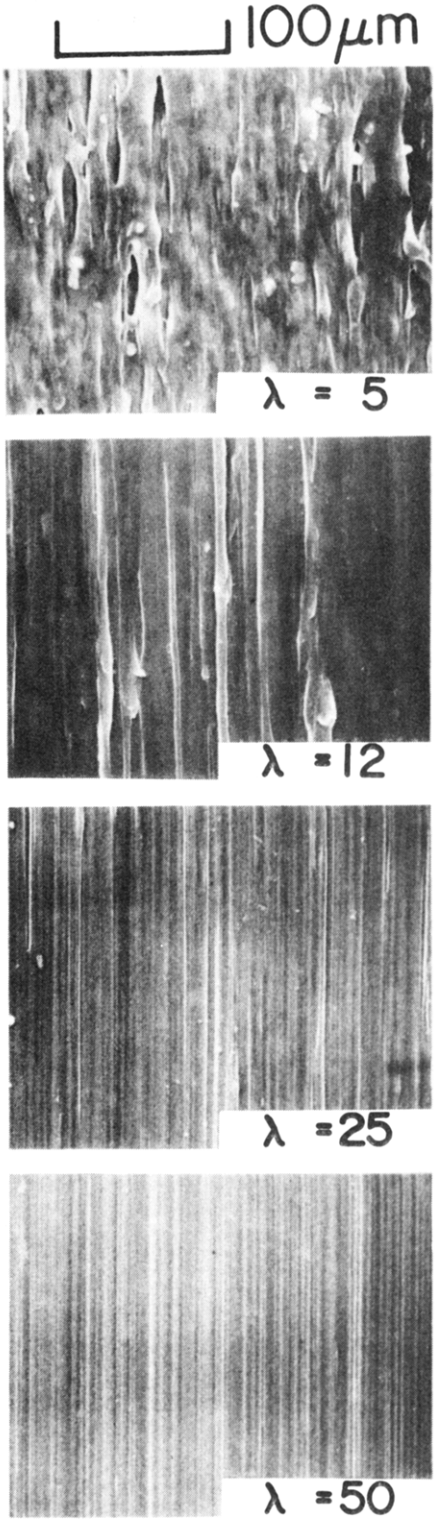

Figure 5. Scanning electron micrographs of cross-linked polyethylene films with varied draw ratio λ.

Figure 7 shows the corresponding Hv light scattering patterns from the drawn films observed under the polarizing microscope in Figure 6. The pattern from the undrawn film shows no significant profile, indicating that the superstructure remains essentially a random aggregation, although the pattern from the original film (0% DCP) shows an X-type pattern, indicating the existence of a rodlike texture that mainly consists of crystallites, as discussed in previous work.[14] This difference is probably due to the melting of most of the crystallites under the annealing process at 150 °C, higher than the normal

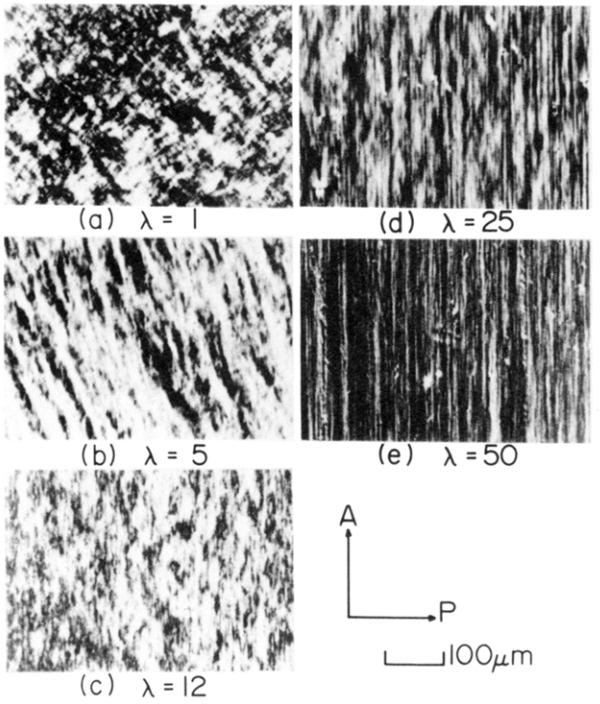

Figure 6. Polarized micrographs of cross-linked polyethylene films with varied draw ratio λ.

melting point of undrawn polyethylene. Also, annealing enhanced the cross-linking in the amorphous (melt) regions, since the amorphous regions are too porous to facilitate easy peroxide penetration.

Patterns b, c, d, and e show scattering from the drawn films prepared by the same method as in the case of Figures 5 and 6. As illustrated in these patterns, the scattering lobes are extended in the horizontal direction and this tendency becomes considerable with increasing draw ratio. Beyond λ = 25, the lobes become like sharp streaks. These streaks correspond to scattering from fine filaments oriented in the scattering direction, observed in the polarized micrographs in Figure 6. The profiles at λ = 12 and 15 exhibit the scattering from rodlike textures oriented in the scattering direction. The appearance of the rods is probably related to the aggregation of crystallites surrounded by the cross-linked amorphous regions. Interestingly, such profiles in Figure 7 were also observed for scattering from the original gel films stretched beyond λ = 12 at 150 °C, although they are not shown in this paper. This indicates that the orientational mode of the rods is independent of the chemical reaction in the amorphous regions.

According to our previous work,[14] the patterns shown in Figure 7 were quite different from those from the gel films stretched at 135 °C, especially in the range of draw ratios from λ = 5 to 20. In this region of λ, the scattering showed the indistinct pattern whose lobes are extended in the vertical direction, and, especially in the range from λ = 15 to 20, the scattering shows the four-leaf pattern with an azimuthal angle dependence of the scattered intensity distribution. Such patterns have been observed under the oriented crystallization process for poly(ethylene terephthalate)[16] and poly(tetramethylene terephthalate).[17,18] The patterns from specimens drawn at 150 °C were independent of the oriented crystallization, which hampers cross-linking. Accordingly, it may be concluded that 150 °C is a suitable temperature for cross-linking under elongation. This result is in good agreement with that reported by Pennings et al.[11]

Figure 8 shows WAXD patterns (through view) with an increasing draw ratio λ. All drawn films were annealed at

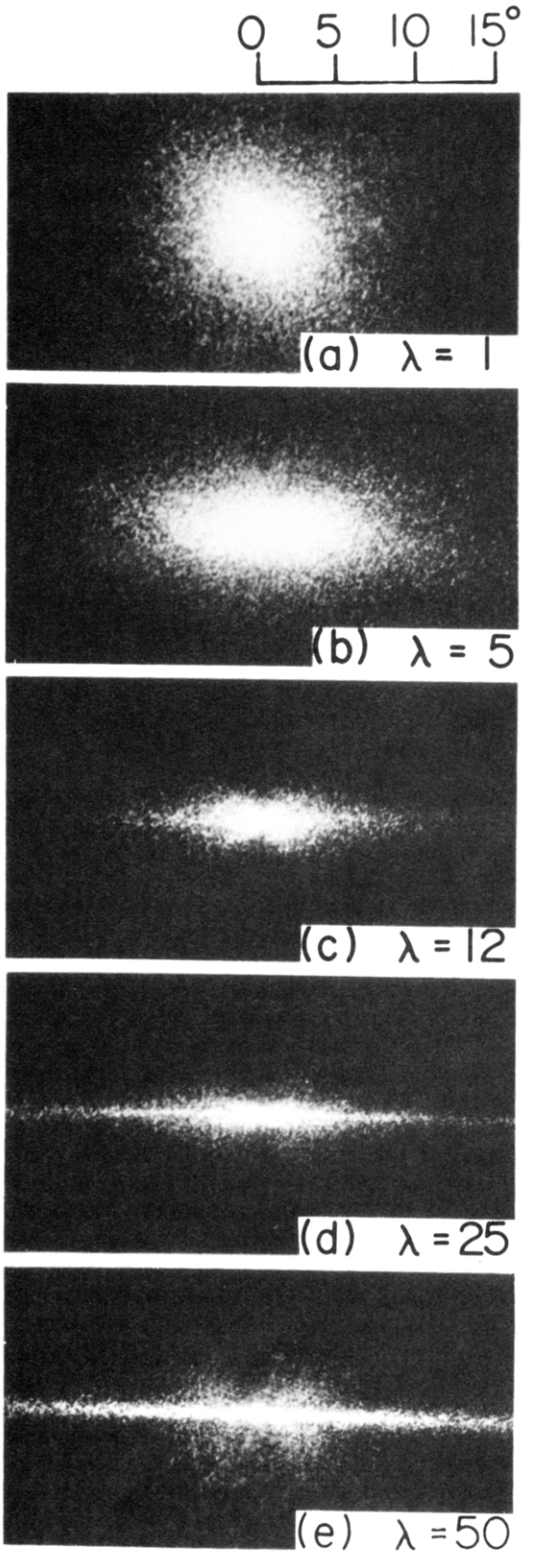

Figure 7. Hv light scattering patterns from cross-linked polyethylene films with varied draw ratio λ.

145 °C for 90 min under nitrogen, as mentioned before. The patterns on the right and left sides show diffraction spots from the films containing 0 and 200% DCP, respectively. When the specimen containing 200% DCP was stretched to λ = 5, the pattern exhibits an amorphous ring, indicating the effect of cross-linking on most of the molecular chains by the vulcanization reaction under the elongation and annealing processes in addition to very weak diffraction arcs from oriented crystallites. The annealing, especially, plays an important role in cross-linking

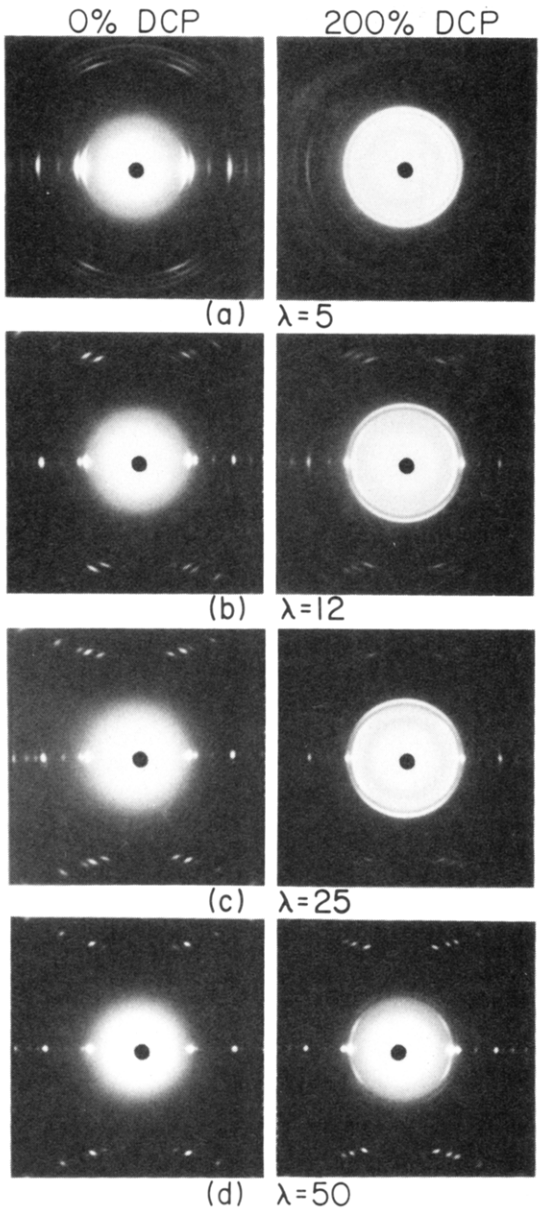

Figure 8. WAXD patterns (through view) with increasing λ: (a) un-cross-linked polyethylene films, and (b) cross-linked polyethylene films.

amorphous regions in the melted state. As λ increases to 12, the left pattern from the gel film (200% DCP) exhibits clear diffraction spots characterizing a very high orientation of crystallites, and this tendency becomes considerable at a maximum draw ratio of 50. This implies that the annealing does not improve cross-linking of the amorphous phase associated with the melting of crystallites, since most of crystallites still remain at 145 °C. This will be discussed later (see Figure 13). Incidentally, in order to avoid misunderstanding, we emphasize that the crystal diffraction spots exhibit only the orientation of crystallites formed in the undrawn film as shown in Figure 1B, since the elongation at 150 °C is independent of oriented crystallization, as discussed on the basis of the SALS patterns in Figure 7.

Figure 9 shows DSC curves of un-cross-linked (0% DCP) and cross-linked (200% DCP) polyethylene films drawn up to λ = 50. The profile of the un-cross-linked film shows a large main peak with a small shoulder, while that of the cross-linked film shows three peaks that appear around 130, 140, and 150 °C. The appearance of the three peaks is believed to be due to a solid–solid transformation from

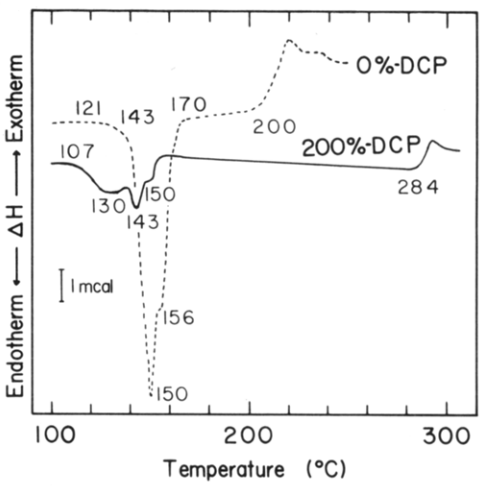

Figure 9. DSC curves for un-cross-linked and cross-linked polyethylene films drawn to λ = 50.

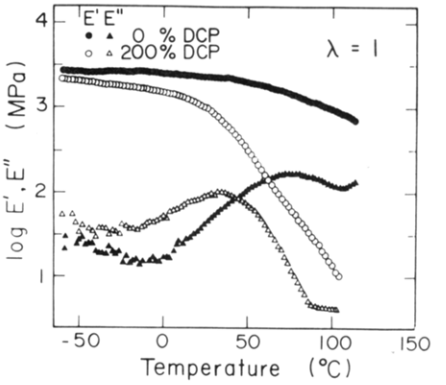

Figure 10. Temperature dependence of the complex dynamic tensile modulus of cross-linked and un-cross-linked polyethylene films (λ = 1).

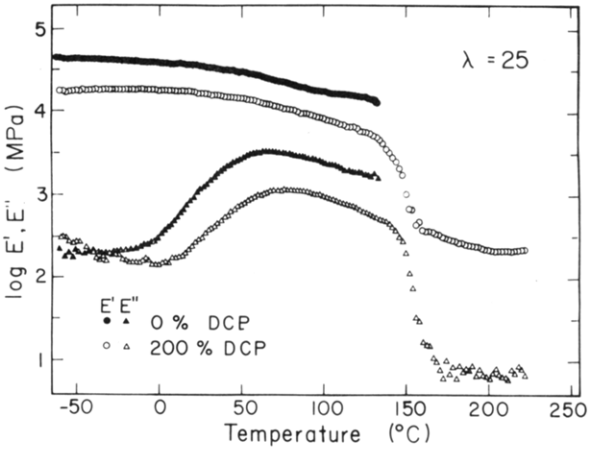

Figure 11. Temperature dependence of the complex dynamic tensile modulus of cross-linked and un-cross-linked polyethylene films (λ = 25).

an orthorhombic to a hexagonal crystal phase. The cross-linking causes decreases in crystallinity and melting point, but it excludes chain fracture even at 284 °C. The brown film heated to 285 °C in a standard aluminum sample pan shows a WAXD pattern exhibiting the refraction rings of the crystal (110) and (200) planes in addition to an amorphous ring.

Figures 10–12 show the temperature dependence of the complex dynamic tensile modulus function for un-cross-linked and cross-linked polyethylene films with draw ratios of λ = 1, 25, and 50. As can be seen in Figure 10, the

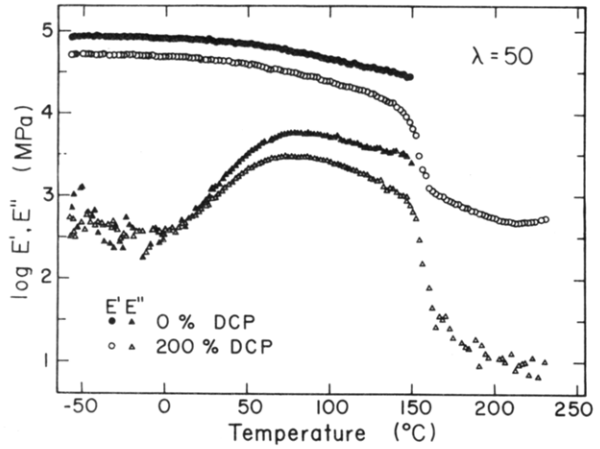

Figure 12. Temperature dependence of the complex dynamic tensile modulus of cross-linked and un-cross-linked polyethylene films (λ = 50).

un-cross-linked film at λ = 1 melted around 120 °C while the cross-linked film was too soft to measure the modulus at 100 °C. The storage modulus E' of both films decreased with increasing temperature. The value for the un-cross-linked film is higher than that of the cross-linked film over the whole temperature range. This implies that cross-linking is unfavorable for undrawn gel films. However, cross-linking causes a significant effect on drawn films in terms of thermal properties, as shown in Figures 11 and 12. The cross-linked film drawn to λ = 25 was maintained at 220 °C although the corresponding un-cross-linked film melted around 150 °C. Furthermore, the cross-linked film drawn to λ = 50 was maintained at 230 °C. The storage moduli E' of the cross-linked films at λ = 25 and 50 decrease considerably around 150 °C and decrease gradually beyond 160 °C. The values at λ = 25 and 50 are about 18 and 46 GPa, respectively, at 20 °C and are about 0.2 and 0.5 GPa, respectively, at 220 °C. Thus, we conclude that the draw ratio of cross-linked films is a very important factor in promoting the improvement of high temperature resistance.

The loss modulus E'' of un-cross-linked and cross-linked films at λ = 1 shows maxima around 80 and 40 °C, as shown in Figure 10. In contrast, the peaks for the other two films drawn to λ = 25 and 50 appeared around 80 °C, as shown in Figures 11 and 12, and the peak position is hardly affected by the draw ratio or by cross-linking. This peak has been reported to correspond to the α-dispersion associated with grain boundary phenomena of deformation and/or of crystallites within an amorphous medium as well as associated with the crystal disordering transition due to the onset of the torsional oscillation of polymer chains within the crystal lattice.

Here it is of interest to consider whether crystallites are melted beyond the normal melting point (145 °C) of polyethylene. In order to study this problem, WAXD patterns were observed in the horizontal direction with increasing temperature. Figure 13 shows the result for cross-linked polyethylene films with λ = 50, when the sample was fixed at a constant stress of 0.018 GPa to avoid shrinkage of the films. The specimen was annealed for 20 min at the indicated temperatures prior to taking a picture. As can be seen in the series of patterns, the strong equatorial reflections from the (110) and (200) crystal planes shift to the scattering center and their intensities become weaker as the temperature increases to 160 °C. This tendency becomes considerable for the crystal (200) plane associated with the thermal expansion of the crystal a axis. Beyond 180 °C, the patterns show the crystal (100) reflection from the hexagonal phase, indicating a transformation to the hexagonal rotator phase, and the reflection spots also shift to the scattering center with increasing temperature. Here it should be noted that there exist hexagonal crystalline phases up to 230 °C. This observed abnormally high apparent melting temperature may be explained by the fact that the polymer chains within crystallites in the cross-linked amorphous medium were obliged to retain the extended chain arrangement, and therefore the entropy of fusion would obviously be smaller than the value calculated for a random coil in the melt.[19] It is evident that such melting behavior of crystallites is due to the strong superheating behavior of cross-linked polyethylene.

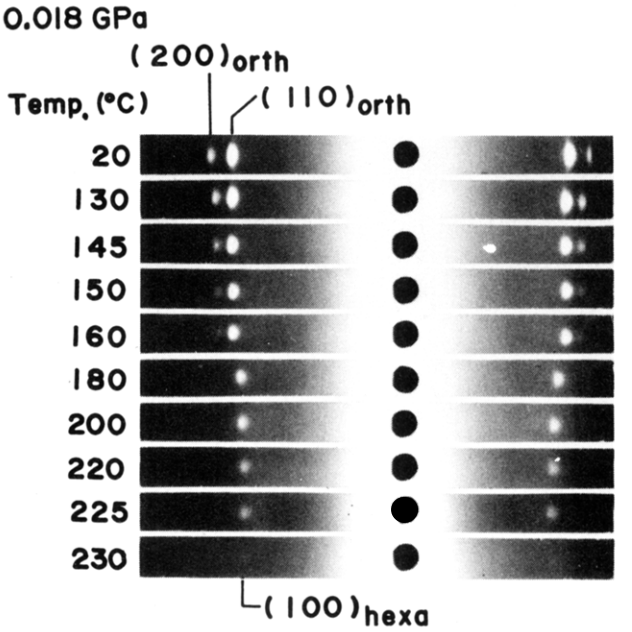

Figure 13. Change in WAXD patterns (through view) in the horizontal direction from cross-linked polyethylene films (λ = 50) annealed at the indicated temperature.

In order to check the transformation of crystallites, intensity distributions for the (002) crystal plane were observed by the step-scanning method. The measurement was carried out with point focusing with a system in which an incident beam was collimated by a collimater 2 mm in diameter, and the diffraction beam was measured by a square slit of 0.9 mm × 0.9 mm. The intensity distribution was measured with a step-scanning device with a step interval of 0.1°, with time intervals of 10 s, in the range from 71° to 79° (twice the Bragg angles). Figure 14 shows the results corresponding to Figure 13. This diagram shows that the intensity becomes weaker with increasing temperature and disappears around 180 °C, resulting in the transformation from an orthorhombic to a hexagonal phase. This is in good agreement with the results in Figure 13.

Figure 15 shows the temperature dependence of the stress corresponding to a constant strain of 10% for a drawn specimen with λ = 50. With increasing temperature from 40 to 130 °C, the stress decreases, as has been generally observed for crystalline polymers. On the other hand, when the temperature is beyond 130 °C, the stress increases with increasing temperature. This is characteristic of rubbery elasticity arising from the cross-linked amorphous regions. In the temperature range from 160 to 170 °C, a discontinuity of increasing stress curve can be observed. This is probably related to the relaxation of extended chains during the transformation from an orthorhombic to a hexagonal phase. The descrepancy be-

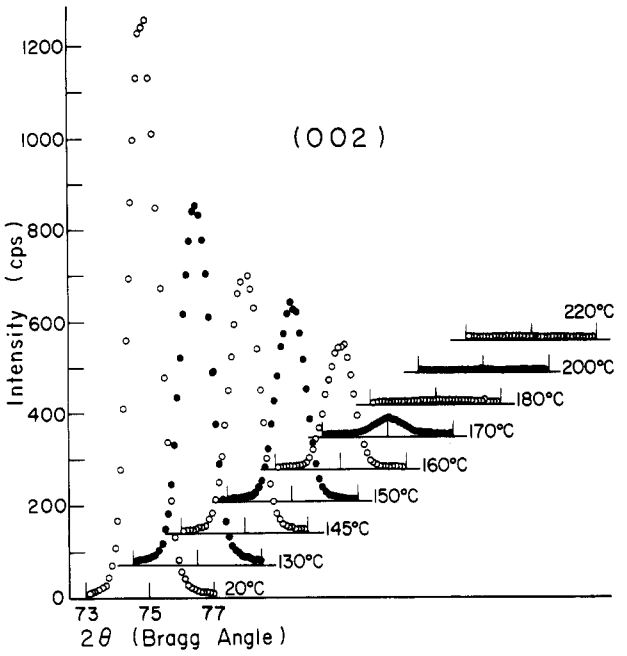

Figure 14. Change in intensity distributions for the crystal (002) plane measured for cross-linked polyethylene films (λ = 50).

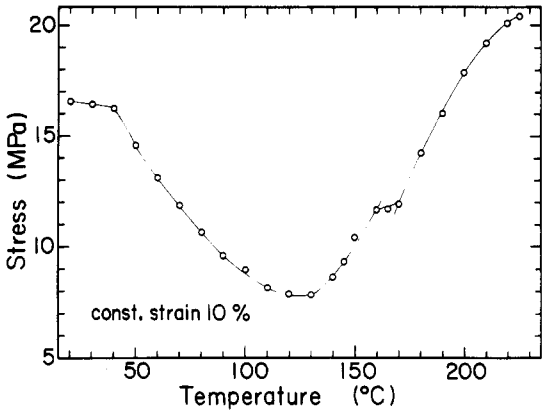

Figure 15. Temperature dependence of the stress relaxation mechanism of cross-linked polyethylene films (λ = 50) at the fixed strain of 10%.

tween the transformation temperature in Figures 13 and 14 and that in Figure 15 is probably due to the difference of each experimental stress of 0.018 GPa while the stress at 160 °C in the latter is 0.012 GPa. Therefore it would be expected that the crystal regions in the latter system have mobile polymer chains, in comparison to those in the former system; the transformation shifts to lower temperature as stress decreases. It should be further noted that the sample length at which the sample was removed from the clamps was almost equal to the initial length of the sample prior to heating, as pointed out by Pennings et al.[11] This indicates a marked fixation of the chains in the fiber network and supports the concept that fiber drawability during hot drawing is limited by the introduction of the cross-links.

Conclusion

Dicumyl peroxide has been introduced into ultrahigh molecular weight polyethylene gel films prepared by gelation/crystallization from a dilute solution in decalin according to method I. After evaporating the solvent, dry gel films can be readily elongated to the desired draw ratios at 150 °C under nitrogen. The maximum draw ratio was 50. In order to promote cross-linking in the amorphous regions, 150 °C was a suitable temperature of elongation to avoid oriented crystallization. As for films drawn up to 50-fold, the storage modulus was 46 GPa at 20 °C and decreased with increasing temperature. Surprisingly, the drawn film was maintained at 230 °C, and the storage modulus was about 0.5 GPa at 220–230 °C. The observed abnormally high apparent melting temperature may be explained by assuming that the polymer chains in the melt retain the extended chain arrangement, and therefore the entropy of fusion would obviously be smaller than the value calculated from random coils in the melt. In any event, the dramatic improvement in the high temperature resistance is due to the cross-linking, since un-cross-linked ultrahigh strength polyethylene films cannot even exist at temperatures beyond 150 °C.

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