Development of High-Modulus Polyethylene with Heat-Resistant Properties

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ABSTRACT: Dicumyl peroxide was used to cross-link ultrahigh molecular weight polyethylene gels that were prepared by gelation/crystallization from dilute solution. The cross-linking was carried out under elongation of gel films containing dicumyl peroxide in an oven at a temperature between 140 and 150 °C under nitrogen and H_2SO_4 vapor. The specimen drawn up to 100-fold and cross-linked with 40% dicumyl peroxide showed a storage modulus greater than 110 GPa at 20 °C and still showed a value of 2.0 GPa even at 200 °C, but the specimen could not be maintained beyond 200 °C, because it broke. The value of the storage modulus at 20 °C is comparable to Young's modulus of copper (120 GPa) and is much higher than the moduli of aluminum (70 GPa), cast iron (90 GPa), and tin (40 GPa). Furthermore, the value at 200 °C is higher than Young's modulus of commercial high-density polyethylene (1.3 GPa) at room temperature.

Since 1974 the preparation of polymeric fibers and films with high modulus has been extensively investigated and results of interest have been obtained for polyethylene.[1-9] Recently, Matsuo et al.[9] produced ultradrawn polyethylene film whose Young's modulus at 20 °C was 216 GPa, which is nearly equal to the crystal lattice modulus of polyethylene. However, although the theoretical Young's modulus of polyethylene is one of the highest among crystalline polymers, the range of application is limited by its low melting point. Attempts have been made to remove this defect by cross-linking with dicumyl peroxide (DCP).[10,11] In a recent paper, it was shown that the introduction of cross-links into polyethylene gel films drawn to $\lambda = 50$ increases the heat resistance, but the room temperature modulus was relatively low (about 46 GPa).[10] The purpose of the present paper is to describe similar studies with samples drawn to $\lambda = 100$ in order to further improve the mechanical properties at room temperature.

Decalin solutions (1500 mL) containing 0.5% (w/w) polyethylene with molecular weight of 6×10^6 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.[6,7] 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 the appropriate amount of DCP, 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. A strip cut from the dry gel film was clamped in a manual stretching device. The specimen was placed in an oven at a temperature between 140 and 150 °C under nitrogen and H_2SO_4 vapor and immediately elongated manually to the desired draw ratio in excess of 50. The optimum elongation condition for each specimen was determined by trial and error. Based on the preliminary experiments, it is important to emphasize that for samples drawn to $\lambda = 50$ the cross-linking reaction occurs readily in the absence of H_2SO_4 vapor. However, for samples drawn to $\lambda = 100$ the presence of the H_2SO_4 vapor was essential for successful cross-linking. The mechanism of this effect is not understood at present. The temperature dependence of the complex dynamic modulus was measured with a viscoelastic spectrometer (VES-F) of Iwamoto Machine Co. Ltd. The measurements were carried out over a temperature range from −50 to 232 °C at a fixed frequency of 10 Hz. All the specimens were annealed for 30 min at 150 °C and cooled down to room temperature, prior to the measurement of the complex dynamic modulus. Through the annealing, any change of the specimens was not observed in a macroscopic sense. Accordingly, it may be expected that the initial properties of the specimens retained, at least, at 150 °C.

Figure 1 shows the temperature dependence of the complex dynamic tensile moduli, E' and E'', for uncross-linked and cross-linked polyethylene films drawn to $\lambda = 50$ at 150° C. The storage modulus E' decreases with increasing temperature. The value of E' for the uncross-linked film (0% DCP) is higher than that of the cross-linked films over the whole temperature range. However, cross-linking has a significant effect on thermal properties. The thermal stability of the cross-linked specimens was maintained up to 230 °C, while the corresponding un-cross-linked film melted at 150 °C. The magnitude of E' for the film cross-linked with 200% DCP is higher than that with 40% DCP. This indicates that the mechanical properties improve as the DCP content increases.

The loss modulus E'' of un-cross-linked and cross-linked films shows a broad dispersion peak centered around 80 °C and the peak position is hardly affected by cross-linking. This peak has been reported to correspond to the α dispersion associated with grain boundary phenomenon, such as intralamellar crystal reorientation, and with a crystal disordering transition due to the onset of the torsional oscillation of polymer chains within the crystal lattice.[12,13]

Figure 2 shows the temperature dependence of the complex dynamic tensile moduli, E' and E'', for uncross-linked and cross-linked films drawn to $\lambda = 100$. The specimens containing 40% DCP and 200% DCP were elongated at temperatures of 150 and 140 °C, respectively. These temperatures were found to give the maximum elongation for the specimens in question. Actually the specimens containing 200% DCP could not be elongated beyond $\lambda = 50$ at 150 °C because of the rapidity of the cross-linking reaction. In contrast, at a temperature of 140 °C, where the rate of cross-linking is lower, the specimens could readily be stretched at $\lambda = 100$. At a temperature of 135 °C the level of cross-linking achieved was insufficient to prepare heat-resistant polyethylene, since oriented crystallization is predominant at the expense of the amorphous regions.

As can be seen in Figure 2, the storage modulus E' for the specimen cross-linked with 40% DCP is 114 GPa at

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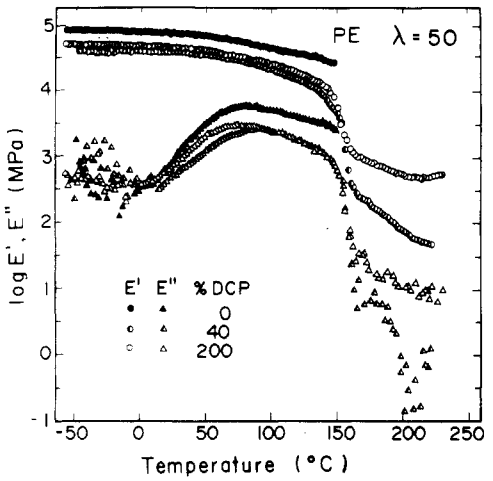

Figure 1. Temperature dependence of the complex dynamic tensile modulus function for un-cross-linked (0% DCP) and cross-linked (40% and 200% DCP) polyethylene films drawn to 50 times (λ = 50) at 150 °C.

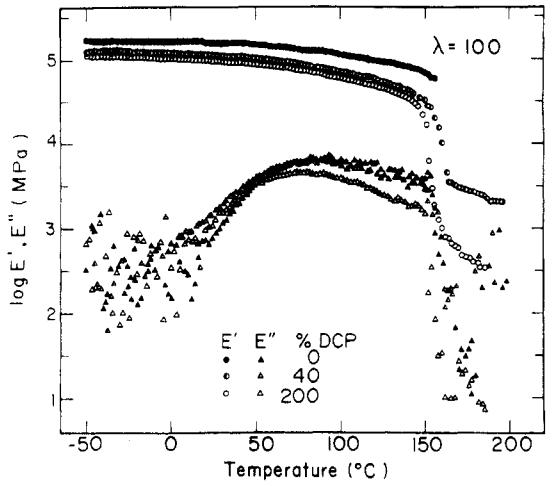

Figure 2. Temperature dependence of the complex dynamic tensile modulus function for un-cross-linked (0% DCP) and cross-linked (40% and 200% DCP) polyethylene films drawn to 100 times (λ = 100) at each suitable temperature.

20 °C and 2.0 GPa at 200 °C, while it is 101 GPa at 20 °C and 0.4 GPa at 188 °C for the specimen cross-linked with 200% DCP. This tendency is in contradiction with the result in Figure 1. Namely, in the case when the draw ratio is 50, E' for the specimen cross-linked with 200% DCP is higher than that cross-linked with 40% DCP. This result leads to the important conclusion that for preparing specimens with improved mechanical and thermal properties by cross-linking, the optimum content of DCP depends upon the draw ratio. Accordingly, efforts must be made to determine the optimum cross-linking condition for samples with different draw ratios. The question arises as to why E' for the specimen containing 200% DCP is lower than for that containing 40% DCP. This is probably due to chain scission in the cross-linked parts of the specimen during further elongation beyond 50 times.

Here it should be noted that the value of E' of the cross-linked specimen drawn to 100 times is 114 GPa at 20 °C which is comparable to the Young's modulus of copper (120 GPa) and is much higher than the moduli of aluminum (70 GPa), cast iron (90 GPa), and tin (40 GPa); furthermore this sample maintained a value of 2.0 GPa at 200 °Cwhich is higher than the Young's modulus of commercial high-density polyethylene (1.3 GPa) at room temperature.

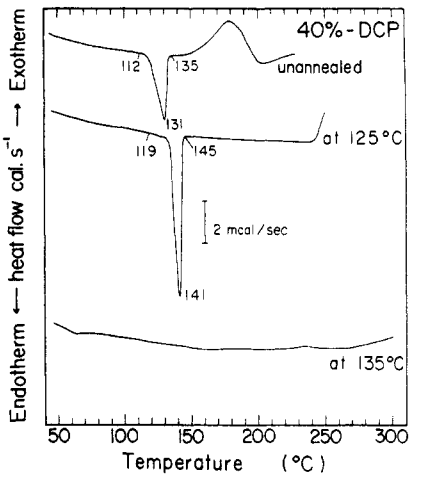

Figure 3. DSC curves of specimens with 40% DCP with increasing annelaing temperatures.

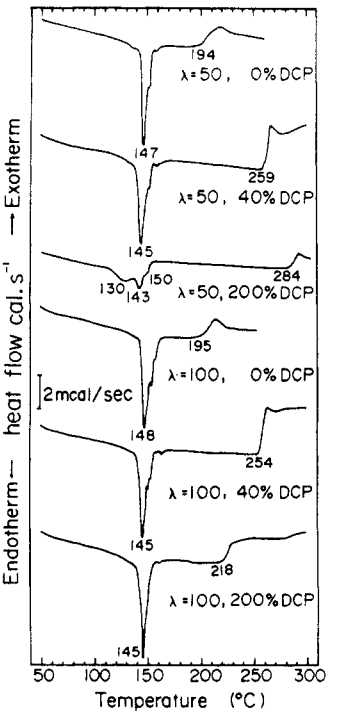

Figure 4. DSC curves for un-cross-linked (0% DCP) and cross-linked (40 and 200% DCP) polyethylene films drawn to the indicated draw ratios.

Figure 3 shows the change in the profile of the DSC curves of specimens with 40% DCP with increasing annealing temperature. The annealing was carried out under nitrogen for 600 min at the indicated temperatures. The profiles for the original unannealed sample and that for the sample annealed at 125 °C show a melting peak. The peak of the annealed specimen is sharter and more intense than that of the unannealed one and the peak position shifts to higher temperature. This behavior suggests that there is an increase in crystallinity due to annealing. In the specimens annealed at 125 °C the level of cross-linking must be very small because a high level of cross-linking would have caused a reduction of the peak intensity. In contrast, there is no peak in the profile of specimens annealed at 135 °C, indicating the disappearance of the crystalline phase owing to the cross-linking. Furthermore this inhibitation of crystallization is probably due to a high cross-linking density. This assumption is supported by the observation that after heating in the DSC experiment to

300 °C, the sample showed no indication of melting.

Figure 4 shows DSC curves of un-cross-linked (0% DCP) and cross-linked (40% and 200% DCP) polyethylene films drawn to $\lambda = 50$ and 100. The profile of the un-cross-linked films shows a large main peak around 148 °C in addition to smaller shoulders. In contrast, the peak position of all cross-linked films, except the film (200% DCP) drawn to $\lambda = 50$, shifts to 145 °C. In addition to the endotherms arising from melting of the crystalline regions, the profiles also show exotherms in the range from 194 to 284 °C. Examination of the specimen after the DSC experiments leads to the conclusion that these exotherms arise from oxidation and decomposition processes. It can be seen from the profiles that these effects occur at higher temperatures for the cross-linked than for un-cross-linked films. The specimen (200% DCP) drawn to $\lambda = 50$ shows three small peaks around 130, 140, and 150 °C. This indicates that considerable cross-linking causes a decrease in crystallinity owing to an increase in cross-linking in the amorphous phase.

In summary, measurements of the complex dynamic moduli have shown that for samples drawn to $\lambda = 50$ and extensively cross-linked (for example 200% DCP), there is a considerable improvement in high-temperature resistance, with maintenance of tensile properties up to 230 °C, but the storage modulus at 230 °C is only about 0.5 GPa. In contrast, samples drawn up to $\lambda = 100$ and cross-linked with a suitable amount of DCP (for example, 40% DCP) show a storage modulus greater than 110 GPa at 20 °C and it is still 2.0 GPa even at 200 °C, but the specimen cannot be maintained beyong 200 °C, because it breaks However, the latter specimen can be certainly termed "high-modulus polyethylene with heat-resistant properties", since un-cross-linked ultra-high-modulus polyethylene cannot exist at temperatures beyond 150 °C.

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Registry No. (DCP)(E) (copolymer), 106705-26-4.

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Template Effect on the Copolymerization of L-Alanine NCA and Sarcosine NCA

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ABSTRACT: Copolymerization of L-Ala NCA and Sar NCA catalyzed by poly(2-vinylpyridine) template was carried out. The effect of concentration and degree of polymerization of the template on the sequence of the resulting copolypeptide was determined by ^{13}C NMR. It was found that only the higher of the two molecular weight templates used had an effect on the sequence of the copolypeptide. Molecular weights of the copolypeptides were determined by gel permeation chromatography.

Introduction

Template polymerization, also termed replica or matrix polymerization, was first suggested by Szwarc.[1] In such systems the monomers are complexed or adsorbed on a macromolecular template and polymerized for at least the greater part of their growth. The mechanism of propagation of the growing chain may affect not only the reaction rate but also the molecular weight and the microstructure of the polymer formed. In most cases the presence of a template leads to rate enhancement. This phenomenon has been referred to as "chain effect" by Ballard and Bamford,[2] who first extensively studied this field. Since then many template systems have been investigated in various laboratories around the world,[3] involving free radical vinyl polymerizations.

Imanishi et al.[3a,4] found that poly(2-vinylpyridine) (P(2VPy)) catalyzes the polymerization of D,L-β-phenylalanine *N*-carboxy anhydride (NCA) faster than α-picoline. They showed that P(2VPy) adsorbs the NCA monomer by hydrogen bonding, which increases the local concentration of NCA. Since the polymer chain is flexible, the intramolecular reaction of the "activated" NCA[5] along the chain takes place frequently, resulting in a faster polymerization.

In the present study the effect of P(2VPy) on the copolymerization of L-Ala NCA and Sar NCA was determined. Since only L-Ala NCA is able to hydrogen bond to a P(2VPy) template (see Figure 1) its local concentration along the polymer catalyst should be higher than in solution, resulting in a copolypeptide with a block nature in L-Ala.

Procedure

NCA polymerizations were carried out in a nitrobenzene solution at 25 °C, at a constant monomer concentration of 0.50 M. The polymerization was started by mixing a catalyst solution with

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