Effect of Irradiation on Crystallinity and Mechanical Properties of Ultrahigh Molecular Weight Polyethylene

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SYNOPSIS

Ultrahigh molecular weight polyethylene (UHMWPE) has been irradiated (0–40 Mrad) with a Co^{60} source at room temperature under vacuum. The crystallinity has been investigated by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). The mechanical properties have been determined at room temperature. A significant increase of heat of fusion can be seen at low irradiation doses, which is attributed to crystallization, caused by chain scission during the process of irradiation. It is also observed that the thickness of the lamellae changes with irradiation dose. The Young's modulus has been improved significantly after irradiation at low doses. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since the irradiation-induced crosslinking phenomenon of polymer was discovered by Charlesby[1] and Dole[2] in the early 1950s, the effect of high energy irradiation on the structure and properties of polymers has arosed considerable attention. As it can significantly improve physical properties (memory effects, creep and thermal resistance), irradiation has been employed in commercial applications, such as in the manufacture of cable insulation (shrink tubes) and polymer foams. However, thus far, the mechanism of irradiation damage of crystallites and the crosslinks' location in semicrystalline polymers is still unclear. Generally, there are two different points of view. One, by Keller et al.,[3-5] suggests that crosslinking takes place primarily outside crystals. The other, by Hosemann et al.,[6,7] suggests that crosslinking occurs primarily inside the crystals. It is now well established that crosslinks, induced by irradiation, are highly dependent on the morphology of polymer. To date, research has been primarily focused on conventional polyethylene (HDPE or LDPE), hence, the crosslinks models were primarily based on such experimental data. Recently, for UHMWPE has been found a variety of applications, due to its excellent mechanical properties and abrasion resistance. It is well known that there exist serious chain entanglements within UHMWPE, which causes the morphology of UHMWPE to be different from that of conventional linear polyethylene. Thus, investigation of the effects irradiation on UHMWPE is important in order to improve its commercial application and to understand the mechanism of irradiation's effect on polymers.

The purpose of the present work is to investigate the changes of structure and mechanical properties of UHMWPE, irradiated at a dose of up to 40 Mrad. We hope that this can provide additional information about understanding the mechanism of irradiation-induced crosslinking at a low radiation dose.

EXPERIMENTAL

Samples

The UHMWPE, utilized in this work, was produced by Beijing additive agent factory, $M_w = 1.5 \times 10^6$. The raw polymer was in powder form. Selected samples were prepared by compression-molding the powder into plates that were about 1 mm thick.

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Irradiation

The compression-molded plates were evacuated in glass ampules at ambient temperature for 3 h under 10^{-3} Torr, and were sealed under vacuum. Samples were irradiated with γ rays from a Co^{60} source. The dose rate was 0.67 Mrad/h. Having been irradiated, the samples were stored at least 3 weeks before the tubes were opened.

Gel Fraction Measurement

Gel fraction was determined by the extraction method.[8] Samples were extracted with boiling xylene, under nitrogen atmosphere, for 72 h, then were washed with ethyl alcohol and were dried under vacuum at 80°C to a constant weight.

Thermal Analysis

Samples (5–10 mg) were melted at a heating rate of 10°C/min in a Perkin–Elmer DSC-2C. The heat of fusion and the melting temperatures were calibrated using indium. Analog data were digitized by an attached computer.

X-ray Analysis

Small angle X-ray scattering (SAXS) of the sample was measured with Kratky camera accessories from Anton Paar, Austria, connected with a Philips Automated Powder Diffractometery PW1700. A Cu anode tube was operational, with 40 mA and 40 KV. The incident beam was monochromatized with an Ni foil filter. The scattering data of the sample were subtracted by air scattering and were desmeared with Strobl's procedure.[9] The electron density correlation function was evaluated with Strobl's method.[10] from the slit-desmeared SAXS data, after substracting liquid scattering with Porod's procedure.[11]

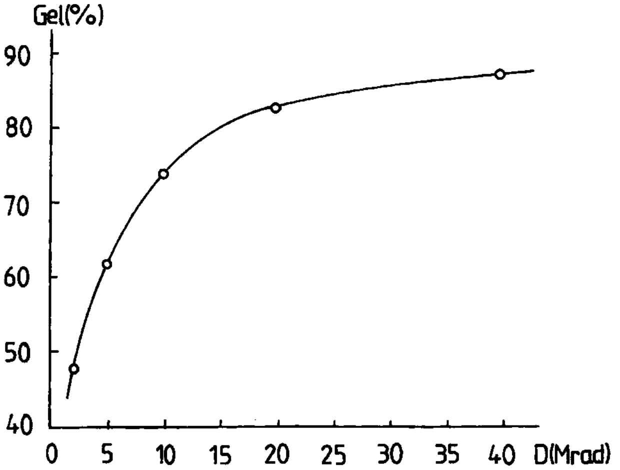

Figure 1 Gel content as a function of irradiation dose.

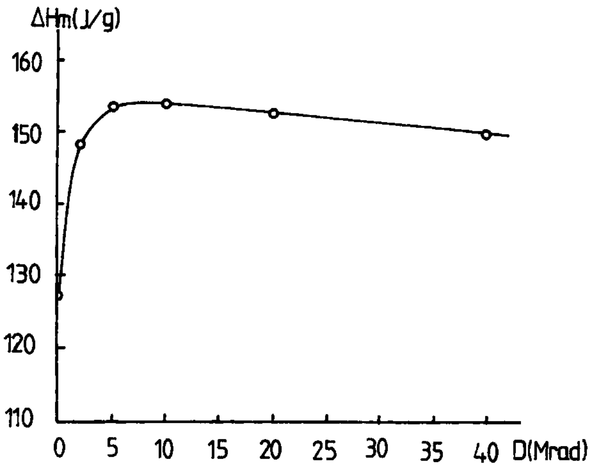

Figure 2 Apparent heat of fusion as a function of irradiation dose.

Tensile Test

Young's modulus and draw ratio were measured on an Instron instrument at ambient temperature, with a sample length of 10.0 mm and a crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Figure 1 shows the gel fraction of samples for various irradiation doses. As is known, the gel content increases with increasing irradiation dose.

Figure 2 shows changes of apparent heat of fusion with irradiation doses. Apparent heat of fusion increases significantly as UHMWPE was irradiated at low doses (up to 10 Mrad); it then begins to decrease slowly as the irradiation dose further increases.

Figure 3 shows that the melting points of samples remain almost constant with varied irradiation doses. Generally, the increase in fusion heat of irradiated polymers is explained in that molecular chains in noncrystalline surfaces of the crystals can recrystallize into lamellae that leads to an increase in the thickness of lamellae.[12-14] According to this explanation, the melting points would also increase. This, however, does not conform with the result of the work. It is suggested that crosslinking and chain scission take place simultaneously in the process of

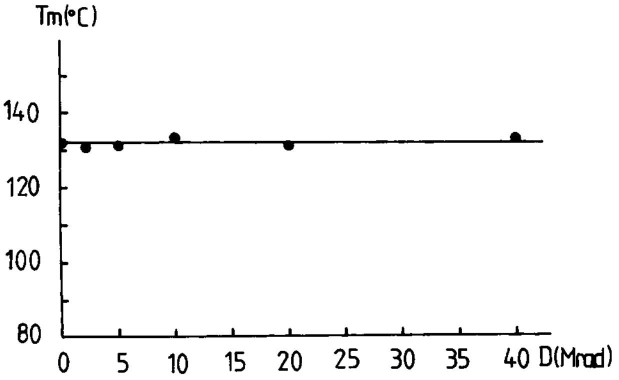

Figure 3 Melting temperature as a function of irradiation dose.

irradiation. As a result of the scission processes, the chain entanglements are reduced and new crystallites are formed by the rearranging of chain segments. This occurs, not only in the noncrystalline surfaces of crystals, but also in the amorphous region. For the apparent heat of fusion, we can write:

$$\Delta Hm = \alpha \Delta Hm^c + (1 - \alpha) \Delta Hm^a \qquad (1)$$

where α is the crystallinity, ΔHm^c is the change in the enthalpy of crystal, and ΔHm^c is the change in the enthalpy in the amorphous regions. Here, the value of ΔHm^a is lower than the value of ΔHm^c, so that the apparent heat of fusion is mainly determined by the value of $\alpha \Delta Hm^c$.

The melting points and the value of ΔHm^c remain constant because the crystalline regions are unaffected by the irradiation within the interval of dose up to 10 Mrad. The total crystallinity, α, increases significantly, due to new crystallites formed in noncrystalline surfaces of crystals and amorphous regions. According to eq. (1), the value of ΔHm increases markedly. As the irradiation dose further increases, the degree of crystallinity can no longer increase, because the formation of new crystals is hindered by the formation of crosslinks in the amorphous region. Meanwhile, ΔHm^c is slightly reduced, because the crystals can be affected by irradiation in such doses. This leads to the decrease of ΔHm. On the other hand, the melting points remain unchanged. This can be explained by the following equation:

$$Tm = \frac{\Delta Hm^c}{\Delta S} \qquad (2)$$

Where ΔS is the entropy difference between the molten and the crystalline states. At higher doses, the value of ΔS is reduced, due to the formation of crosslinks. Although the value of ΔHm^c decreases, the $\Delta Hm^c / \Delta S$ changes little, hence the melting points remain almost unchanged.

Figure 4 shows the slit-desmeared SAXS curves for samples irradiated with various doses. A long period of time does not change the dose remarkably. The scattering intensity of irradiated samples increases with an increase in irradiation dose at first, and then drops with a further increase in irradiation dose. The increase of the intensity at low doses corroborates the supposition that scission induces crystallization in amorphous regions, while the decrease of intensity indicates that crystallites were affected by irradiation at higher doses.

Figure 5 shows the correlation function, derived from Figure 4. The thickness of lamellae is obtained from the correlation function,[10,15] as shown in Figure 6. This shows that the thickness of lamellae increases slightly at first, and subsequently decreases with an increase in irradiation dose. This indicates that molecular chains in noncrystalline surfaces of lamellae undergo crystallization, due to chain scission at low doses, and crosslinking can occur in surfaces of crystals as the irradiation dose increases up to a higher value.

Figure 7 shows the dependence of the Young's modulus of UHMWPE films on irradiation dose. After irradiation, the Young's modulus of samples increases markedly. This can be explained in that irradiation-induced crosslinking forms a network and improves the number of tie molecules that are interconnecting with interfaces of lamella. Mean-

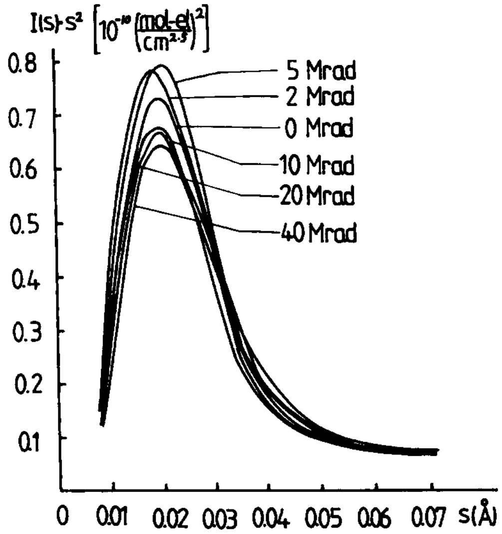

Figure 4 Slit-desmeared SAXS curves of UHMWPE, irradiated with various doses.

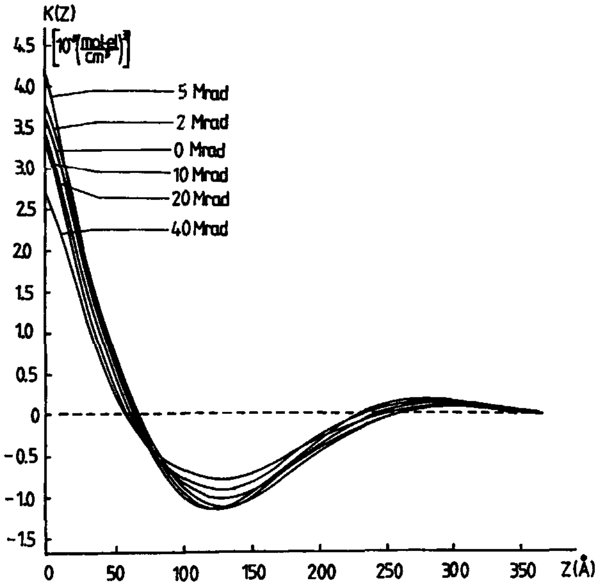

Figure 5 Correlation function of UHMWPE, irradiated with various doses.

while, irradiation enhances the crystallinity of the samples at such low doses. Figure 8 shows that the maximum draw ratio of UHMWPE films changes with dose. The maximum draw ratio decreases with an increase in irradiation dose. This is a result of the fact that a network, formed by irradiation-induced crosslinking in amorphous regions, restricts the molecular chains' stretching at the drawing process.

CONCLUSIONS

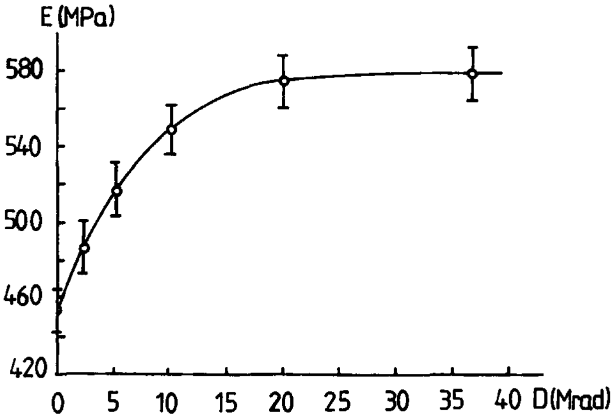

Figure 7 Young's modulus as a function of irradiation dose.

Compression-molded samples of UHMWPE are irradiated at doses ranging from 0 to 40 Mrad. It has been observed that the apparent heat of fusion increases markedly at low irradiation doses, while melting points remain almost unchanged. It can be concluded that scission and crosslinking take place simultaneously and that the scission of polymer chains, often of tie-molecule form, facilitates further folding and crystallization, which occurs not only in noncrystalline surfaces of crystals, but also in amorphous regions. The former leads to the increase of thickness of lamellae. As the irradiation dose further increases, the thickness of lamellae is gradually reduced, since the lamellae is affected by irradiation. It is suggested that crosslinking primarily occurs at the noncrystalline surfaces of lamellae, because the degree of defect at the noncrystalline surface is much higher than that inside the lamellae. After irradiation at low doses, the Young's modulus of UHMWPE films improved significantly, which will be helpful for the application of the material.

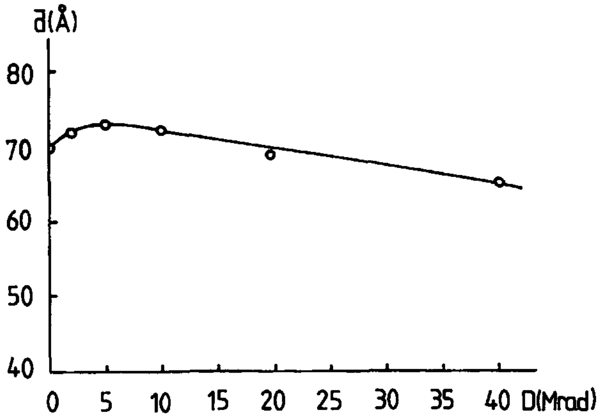

Figure 6 Thickness of lamellae as a function of irradiation dose.

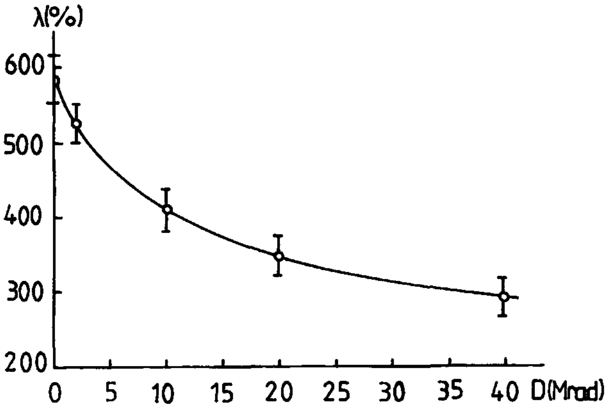

Figure 8 Maximum draw ratio as a function of irradiation dose.

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