Macromolecular Research, Vol. 12, No. 1, pp 141-143 (2004)

Notes

Dynamic Mechanical Behavior of Ultra-High Molecular Weight Polyethylene Irradiated with Gamma Rays

Choon Soo Lee and Jae Young Jho*

Hyperstructured Organic Materials Research Center and School of Chemical Engineering, Seoul National University, Seoul 151-744, Korea

Kuiwon Choi

Biomedical Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

Tae-Won Hwang

Research and Development Division for Hyundai Motor Company and Kia Motors Corporation, Kyunggi 445-850, Korea

Received Oct. 7, 2003; Revised Dec. 5, 2003

Abstract: We have investigated the dynamic mechanical behavior of ultra-high molecular weight polyethylene (UHMWPE) irradiated with varying doses of gamma rays. A relaxation peak in the loss factor curve, which has not been reported previously in the literature, is observed at a temperature above the crystal melting temperature. The peak is unique to UHMWPE and appears to be related to the high degree of entanglement. Because the temperature and intensity of the peak are reduced by irradiation-induced chain scission and crosslinking, respectively, we believe that the peak is associated with disentanglement relaxation. The behavior of the storage modulus in the melt state agrees with the classical theory of rubber elasticity.

Keywords: polyethylene, ultra-high molecular weight, dynamic mechanical analysis, irradiation, crosslinking.

Introduction

Ultra-high molecular weight polyethylene (UHMWPE), in virtue of its superb wear resistance, good mechanical property, and biocompatibility, has been used as a cartilage substitute in total joint prosthesis for many years.[1] On purpose to further enhance the wear resistance and to sterilize the UHMWPE prosthesis, irradiation with gamma rays has been performed. Upon gamma irradiation, following the formation of free radicals, crosslinking and chain scission occur.[2] In the course of studying the effect of irradiation and heat-treatment conditions on the properties of UHMWPE, we observed a peculiar phenomenon in dynamic mechanical spectra (DMS) of some samples. The phenomenon we report is the emergence of an additional relaxation peak at a temperature higher than melting point of UHMWPE. Although some supposedly-related phenomena have been remarked,[3-5] a direct observation of the relaxation in the melt state of polyethylene or UHMWPE was not reported. The present study reports the dynamic mechanical behavior of UHMWPE irradiated with varying dose of gamma rays.

Experimental

UHMWPE used was GUR 4120 from Ticona with the reported weight average molecular weight of 5×10^6 g/mol. The powder UHMWPE was compression molded at 200 °C for 15 min and then slowly cooled to ambient temperature. Gamma ray irradiation was performed at room temperature in a nitrogen atmosphere using a cobalt-60 source at a rate of 7.5 kGy/h. The irradiated samples were annealed at 100 °C for 72 h in a vacuum oven in order to stabilize the residual radicals.[1] Swell ratio of the irradiated samples was determined by comparing the weights of swollen gel to dried gel after extraction.[6] DMS was obtained using a TA Instruments DMA 2980 in the tensile mode. The tests were conducted for the sheet samples of dimensions 3 mm × 10 mm × 1 mm at a frequency of 1 Hz in the temperature range from -150 to 350 °C at a heating rate of 3 °C/min under a nitrogen atmosphere.

*e-mail: jyjho@snu.ac.kr

1598-5032/02/141-03

Results and Discussion

The results of the measurements for the samples are listed in Table I. Swell ratio, which inversely reflects the extent of crosslinking, decreases with increasing dose of gamma ray. The chain mobility in the sample should be affected by the induced crosslinks.[7]

Figure 1 is the DMS of UHMWPE, showing the storage modulus (E') and loss factor (tan δ) curves. Each tan δ curve shows five peaks. The three peaks at lower temperatures are γ, β, and α relaxation peaks reported in the literature.[8,9] The γrelaxation peak at -110 °C (T_γ) has been assigned in previous studies to the local chain motion in the amorphous region.[9] The peak temperature is not changed by irradiation, indicating that the type of motion is the same for all the samples. The intensity (I_γ) decreases with increasing irradiation dose, as the crosslinks prevent some of the chain segments from relaxing. The β relaxation peaks in the range of -30 to 10 °C

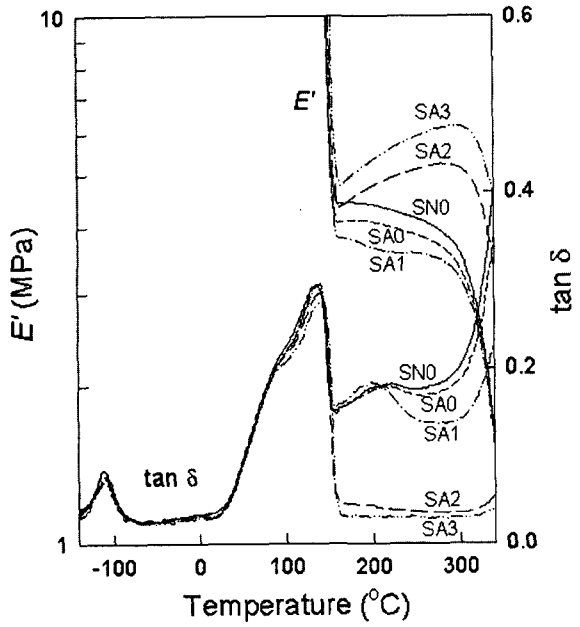

Figure 1. Dynamic mechanical spectra of UHMWPE.

are rather flat and small, and are not discussed here. The α relaxation peaks, which are located at around 80 °C, are not well separated from the melting peaks. Deconvolution of the peaks was not attempted, since the difference in intensity and peak temperature between the samples would not be significant. It has been characterized in the previous works that β and α relaxation of polyethylene is originated from the motion of chains in the interfacial region and the crystallites, respectively.[8,9] The peak at around 130 °C is the melting transition peak. The increase in melting temperature (T_m) from SN0 to SA0 is associated with the lamellar thickening by annealing. The higher temperature and lower intensity (I_m) of melting peak for the sample irradiated with higher dose is attributed to the higher concentration of crosslinks introduced, which kinetically arrest the melting process.[2] The SAXS result of the samples indicates that the gamma irradiation does not result in the lamellar thickening; the result is shown elsewhere.[10]

At temperatures above T_m, there exist broad humps in the tan δ plots of some samples, which have not been reported before. As the behavior appears unique to UHMWPE, it should be related to the structure of UHMWPE. It is known that, due to its high molecular weight and consequent high degree of entanglement, UHMWPE crystallizes to form randomly arranged lamellae, not well-stacked lamellae.[1] We propose that the peak observed at around 210 °C is originated from the chain motion enabled by disentanglement. It is thought that entanglement of UHMWPE is of high enough degree not to be all loosened up to a temperature above T_m. In fact the retained entanglement of UHMWPE at a temperature above T_m has been recognized in the literature; anisotropy of the melt,[3] grain boundaries in the molded samples,[4] miscibility with high density PE only at high temperatures.[5] The disentanglement proceeds over a temperature range, as other relaxation processes do, due to the inhomogeneity of the environment, in which the relaxation takes place. At temperatures above 300 °C thermal degradation and excessive flow result in the steep rise in the tan δ curves.

The disentanglement relaxation appears to be affected by irradiation-induced chain scission and crosslinking. For SA1, the relaxation peak is located at a lower temperature,

Table I. Characteristics of the UHMWPE Studied

Sample[a]	Irrad. Dose (kGy)	Swell Ratio	T_γ (°C)	I_γ	T_m (°C)	I_m	E' at -110 °C (GPa)	M_c (g/mol)	Slope (MPa/°C)[b]
SN0	0	-	-110	0.084	136	0.30	3.48	2,200	-0.003
SA0	0	-	-110	0.083	137	0.30	3.45	2,400	-0.002
SA1	10	18.1	-110	0.077	139	0.30	2.87	2,600	-0.005
SA2	50	5.2	-110	0.074	140	0.29	3.13	2,100	0.010
SA3	100	3.9	-110	0.070	141	0.28	3.43	1,900	0.014

[a] All the samples except SN0 were annealed at 100 °C for 72 h after irradiation.
[b] Slope of E' determined in the temperature range from 170 to 220 °C.

in comparison to that of SA0. This is the result of reduced relaxation time for disentanglement, which is again the result of reduced molecular weight by chain scission. In the samples irradiated with higher doses, SA2 and SA3, disentanglement appears largely prevented by high degree of crosslinking. It is thought that the crosslinks lower the population of entanglements that can be loosened, suppressing the relaxation intensity.

In the solid state, E' of the irradiated samples increases with increasing dose, as shown in Table I. In the melt state, E' slowly decreases with temperature for the unirradiated samples, resulting from continuous slip and disentanglement. The lower E' of SA0 than that of SN0 is thought to be due to disentanglement during the annealing process. For the irradiated samples, except for SA1, the modulus increases as a function of temperature. Modulus and its slope is higher for the samples with higher irradiation dose and higher degree of crosslinking, consistent with rubber elasticity theory.[11] The low and decreasing E' of SA1 is thought to be due to the chain scission overweighing the effect of crosslinking. Average molecular weight between entanglements or crosslinks (M_c) was determined from the value of E' at 180 °C according to the rubber elasticity equation, $E' = 3\rho \cdot R \cdot T \cdot M_c^{-1}$, where R is the gas constant and T is the temperature.[11] The density ρ was assumed equal to that of amorphous polyethylene (0.8621 g/cm^3) for all the samples. M_c is well correlated with swell ratio, and decreases with irradiation dose as shown in Table I. It is concluded that, in uncrosslinked UHMWPE, the entanglements or physical crosslinks act like the chemical crosslinks, holding the chains at temperatures higher than crystal melting temperature. Disentanglement proceeds gradually with increasing temperature until chain degradation occurs. Upon irradiation the crosslinks substitute for the entanglements in holding the chains, and remain up to the degradation temperature.

Acknowledgements. This work was supported partly by Korean Ministry of Health and Welfare (98-PJ7-PG4-2-0054) and partly by Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center.

References

(1) S. M. Kurtz, O. K. Muratoglu, M. Evans, and A. A. Edidin, *Biomaterials*, **20**, 1659 (1999).
(2) V. Premnath, A. Bellare, E. W. Merrill, M. Jasty, and W. H. Harris, *Polymer*, **40**, 2215 (1999).
(3) A. E. Zachariades and J. A. Logan, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 821 (1983).
(4) F.-W. Shen, H. A. McKellop, and R. Salovey, *J. Biomed. Mater. Res.*, **41**, 71 (1998).
(5) L. Minkova and M. Mihailov, *Colloid Polym. Sci.*, **265**, 1 (1987).
(6) A. P. de Boer and A. J. Pennings, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 187 (1976).
(7) P. H. Kang, J. S. Park, and Y. C. Nho, *Macromol. Res.*, **10**, 332 (2002).
(8) R. Popli, M. Glotin, L. Mandelkern, and R. S. Benson, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 407 (1984).
(9) Y. P. Khanna, E. A. Turi, T. J. Taylor, V. V. Vickroy, and R. F. Abbott, *Macromolecules*, **18**, 1302 (1985).
(10) C. S. Lee, S. H. Yoo, J. Y. Jho, K. Choi, and T.-W. Hwang, *Macromol. Res.*, submitted.
(11) A. J. Peacock, *Handbook of Polyethylene*, Marcel Dekker, New York, 2000, pp 399-401.