

Radiation-Induced Crosslinking of Ultra High Molecular Weight Polyethylene Fibers by Means of Electron Beams

Chunling Gao,^{1,2} Shujun Li,³ Hongbing Song,¹ Liqing Xie¹

¹The Key Laboratory of Beam Technology and Materials Modification of Ministry of Education, Beijing Normal University; Institute of Low Energy Nuclear Physics (Beijing Radiation Center); Beijing Normal University, Beijing 100875, China

²The 174th Hospital of People's Liberation Army, Xiamen, Fujian Province, 361003, China

³Institute 53, Jinan 250031, China

Received 12 March 2004; accepted 16 December 2004

DOI 10.1002/app.22360

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Crosslinking of ultra high molecular weight polyethylene fibers (UHMW-PE fibers) is investigated by means of electron beam irradiation. The structure and mechanical properties of the fibers in different irradiation atmospheres are discussed. The results show that the gel fraction and crosslinking density increase with the increase of absorbed dose. The swelling ratio and average molecular weight of crosslinked net decrease with the increase of absorbed dose. The relation between $s + s^{-1}$ of the UHMW-PE fibers and reciprocal irradiation dose $1/R$ is obtained. The tensile strength and failure elongation decrease with the

increase of absorbed dose, and the tensile modulus increases with the increase of absorbed dose. The samples are irradiated in air, vacuum, and acetylene atmospheres, separately. The radiation effects, such as crosslinking fraction and mechanical properties of UHMW-PE fibers, are the most significant in acetylene atmosphere in comparison with in air and in vacuum. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1761–1764, 2005

Key words: crosslinking; electron beam irradiation; polyethylene fibers

INTRODUCTION

Ultra high molecular weight polyethylene fibers (UHMW-PE fibers) are one of the special fibers since the invention of carbon fibers, boron fibers, and aromatic synthetic fibers. The strength and modulus of UHMW-PE fibers are very high due to the structure of the linear chain. The tensile strength of the fibers is 3 ~ 3.5GPa. The modulus of the fibers is 100 ~ 125GPa. The density of the fibers is 0.97 g cm⁻³. The strength of the fibers is 10 times higher than that of steel, 2 times higher than that of carbon fibers, and 1.4 times higher than that of aromatic synthetic fibers. UHMW-PE fibers are one of the reinforced fibers in advanced composite materials.^{1–3}

These fibers have advanced excellent characteristics, such as UV radiation resistance, chemical corrosion resistance, impact resistance, high absorption of energy, low dielectric constant, and high transmittance of electromagnetic waves.^{4–6} The fibers can be improved by the self-crosslinking of the fibers or by mixing with other fibers. In recent years, radiation crosslinking of UHMW-PE fibers and films has been

extensively investigated in different electron irradiation atmospheres, and good results have been obtained^{7–15}. The crosslinking of UHMW-PE fibers by means of electron beam irradiation and the structure and mechanical properties of the fibers in different irradiation atmospheres will be discussed in this article.

METHODS

Sample preparation

DSM Fiber Intermediates B.V., the Netherlands, supplied the ultra high molecular weight polyethylene fibers (UHMW-PE fibers, DYNEEMA SK66). Approximately 100m of fibers are wound on a 48 mm diameter and 330 mm length cotton cloth phenolic antioxidant rod. The fibers are warped firmly with a stress of 16N. Then the fibers are placed in a 50 mm diameter glass tube, fitted with a rubber joint for inserting the sample and a glass tap evacuating the tube and introducing gas. The tube is evacuated to less than 6×10^{-2} Pa, filled with acetylene after evacuating, or filled with air until irradiation.

The glass tube with the fibers is placed horizontally in the dose uniform range of electron beam generated by a BF-5 4MeV linear electron accelerator. The dose ratio is 100Gy s⁻¹. The glass tube is rotated around its longitudinal axis by a motor with the rotation speed of

Correspondence to: C. Gao (chunlinggao@sina.com), L. Xie (xielq@bnu.edu.cn).

100r min⁻¹ to ensure uniform irradiation. Revolving samples are irradiated multiple times: 100kGy per time with a stopping interval for 2 ~ 3 min to prevent the rise of temperature during irradiation. The final integrated dose is 1000kGy. After irradiation, the fibers, still kept in the glass tube, are annealed for 1h at 85°C in a vacuum and then kept in a dry container at room temperature.

Gel fraction measurements

An empty 50mm × 25mm stainless steel reticulated pocket is kept in boiling xylene for 5 ~ 10 min and is weighed immediately to obtain a wet weighing w_1 of the pocket. Then being dried at 150°C, the dry weight w_2 of the empty pocket is obtained. Approximately 2m of fibers placed in above pocket is to obtain a weight w_3 , then the pocket is immersed in xylene with antioxidant of 0.1% at nitrogen atmosphere and refluxed for 36 h. After extraction, it is washed in boiling fresh xylene for 5 ~ 10min, and a wet weight w_4 is obtained, Then being dried at 100°C for 12 h, a dry weight w_5 of the sample with pocket is obtained. The gel fraction is defined to be gel = $(w_5 - w_2) / (w_3 - w_2) \cdot 100\%$.

Measurement of swelling ratio

The swelling ratio (SR) is calculated by the following equation^{16,17}:

$$SR = 1 + \frac{(w_4 - w_1) - (w_5 - w_2) \rho_p}{w_5 - w_2} \frac{\rho_p}{\rho_s} \quad (1)$$

where ρ_p is the density of the polymer (PE fibers), 0.908 g cm⁻³ at 120°C; and ρ_s is the density of the solvent, 0.768 g cm⁻³ at 120°C.

The average molecular weight \bar{M}_c of a crosslinking net chain is calculated by the Flory–Rehner equation¹⁸:

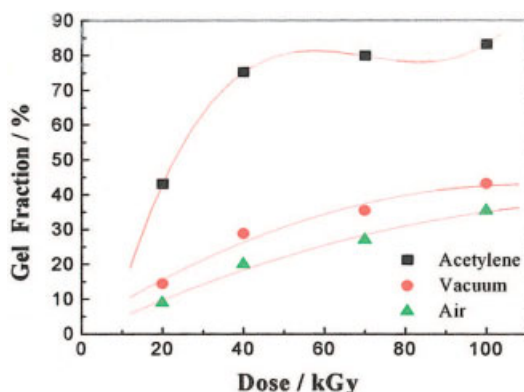


Figure 1 Gel fraction versus dose. EB irradiation in different atmospheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

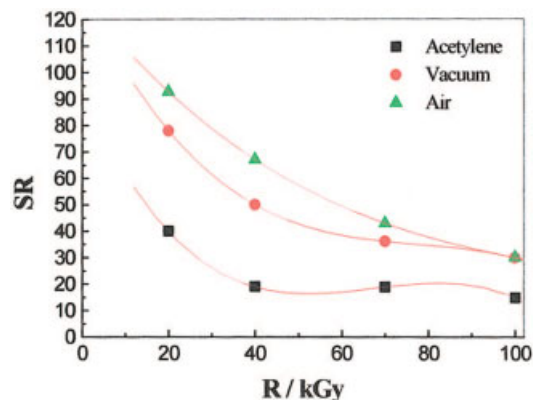


Figure 2 Swelling degree versus dose. EB irradiation in different atmospheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\ln(1 - \varphi_2) + \varphi_2 + \chi_1 \varphi_2^2 = \frac{\rho_p V_s}{\bar{M}_c} \left(\frac{\varphi_2}{2} - \sqrt[3]{\varphi_2} \right) \quad (2)$$

where V_s is the mole volume of the solvent, xylene of 138 cm³ mol⁻¹ at 120°C; ρ_p is the density of the polymer (PE fibers), 0.908 g cm⁻³ at 120°C; φ_2 is the volume fraction of the polymer, $\varphi_2 = 1/SR$; and χ_1 is the interaction parameter between the polymer and the solvent (i.e., Huggins parameter, $\chi_1 = 0.33 + 0.55\varphi_2$ at 120°C).

Mechanical measurement

Mechanical measurements were carried out using a Sintech 2/DL Tester with a test speed of 50 mm min⁻¹ made by TM company, USA. The average value of each sample is obtained from 5 bunches of the fibers.

RESULTS AND DISCUSSION

Gel fraction measurement

It was found that the gel fraction of the unstrained sample increases with the increase of dose in the dose range of 0 ~ 1000kGy in a vacuum. The gel fraction increases faster in the low dose range (less than 200kGy) than in the high dose range (more than 200kGy).

Figure 1 shows the gel fraction of a sample irradiated in air, which is lower than that in a vacuum or acetylene atmosphere. With the dose of 100kGy, the gel fraction appears 36% in air, 44.17% in vacuum, 83.51% in acetylene atmosphere. Crosslinking is resisted by oxygen in air; degradation is increased, so that the gel fraction is reduced. Crosslinking and degradation take place in UHMW-PE fibers in a vacuum. Crosslinking density is enhanced in an acetylene atmosphere due to reaction between acetylene and rad-

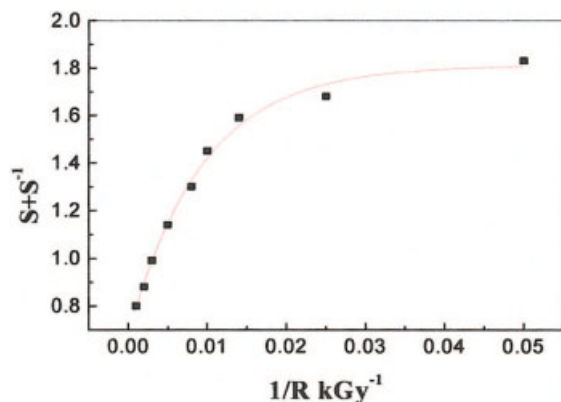


Figure 3 Charlesby–Pinner plot, $s + s^{1/2}$, where s is the sol-fraction versus reciprocal irradiation dose $1/R$ at vacuum. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

icals formed during irradiation; therefore, gel fraction is increased.^{19,20}

Influence of dose on swelling degree

Figure 2 shows the relation of swelling degree versus dose in different irradiation atmospheres. For the same reason as discussed above the gel fraction in air is low and the swelling degree is high; in acetylene the gel content is high, and the swelling degree is low.

Figure 3 shows the curve of $s + s^{1/2}$ for the unstressed sample of the UHMW-PE fibers versus the reciprocal irradiation dose $1/R$ in the dose range of 0 ~ 1000 kGy at vacuum. It is a convex curve in the Charlesby–Pinner plot for the UHMW-PE fibers. The plot is similar to the curve in the Charlesby–Pinner plot for the polydisperse UHMWPE, obtained by Dijkstra et al.¹¹

Figure 4 shows the curve of $s + s^{1/2}$ versus the reciprocal irradiation dose $1/R$ in the different atmo-

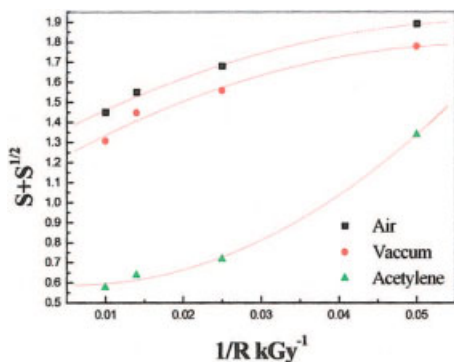


Figure 4 The curve of $s + s^{1/2}$ versus reciprocal irradiation dose $1/R$ in the different atmospheres during irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

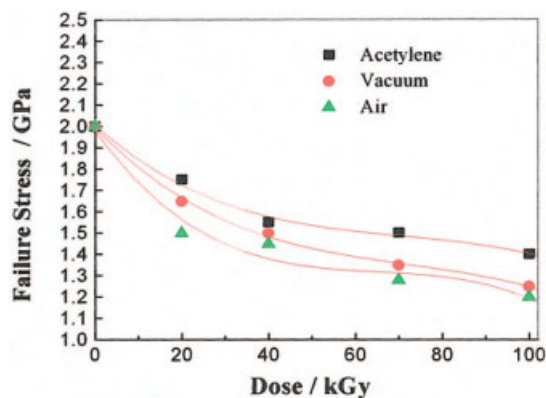


Figure 5 Failure stress versus dose. EB irradiation in different atmospheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spheres during irradiation. It is explained that the relation between $s + s^{-1}$ of the UHMW-PE fibers and the reciprocal irradiation dose $1/R$ in the different atmospheres is deviated for the Charlesby–Pinner equation.¹¹

The average molecular weight \bar{M}_c of the crosslinked net is calculated by eq. (2); it decreases with the increase of the absorbed dose. In acetylene \bar{M}_c decreases with the increase of the dose rapidly when the dose is less than 40kGy; \bar{M}_c decreases slowly with the increase of the dose when the dose is more than 40kGy. The point of the dose 40kGy is an inflection point for the change of \bar{M}_c to the dose in acetylene. The inflection point in vacuum and in air is 70kGy and 100kGy, respectively. According to eq. (2), if \bar{M}_c is $3.3 \times 10^5 \text{ g mol}^{-1}$, the dose is 20kGy in acetylene, 70kGy in vacuum, and 100kGy in air. It means that the dose for crosslinking in acetylene is the lowest.

Influence of radiation crosslinking on mechanical properties

Figure 5 shows the failure stress, which decreases with the increase of the absorbed dose.

Figure 6 shows the tensile modulus, which increases with the increase of the absorbed dose.

It has been observed experimentally that the failure elongation decreases with the increase of the absorbed dose. In the dose range of 0 ~ 100kGy, the failure elongation varies from 3.11% to 2.07% in acetylene, to 1.95% in vacuum, and to 1.81% in air. The above experimental results of mechanical properties, such as failure stress, tensile modulus, and failure elongation, change with dose and different irradiation atmospheres. The ratio of crosslinking to degradation of the fibers increases with the increase of the dose, but decreases progressively with the atmosphere of air, vacuum, and acetylene.

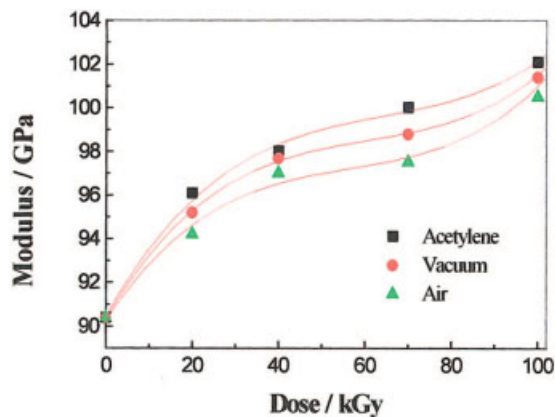


Figure 6 Modulus versus dose. EB irradiation in different atmospheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

1. The gel fraction of the UHMW-PE fibers increases with the increase of the absorbed dose at 4MeV electron beam irradiation in air, vacuum, and acetylene atmospheres. The gel fraction in acetylene is the highest among the above three atmospheres because of the $C\equiv C$ structure of acetylene.
2. After irradiation, the swelling ratio and average molecular weight of the crosslinked net of the samples decrease with the increase of the absorbed dose. The swelling ratio in acetylene atmosphere is the lowest among the different atmospheres.
3. The tensile strength depends on the failure stress, which decreases with the increase of the

absorbed dose. The tensile modulus increases with the increase of the absorbed dose. The failure elongation decreases with the increase of the absorbed dose. When the samples are irradiated in air, vacuum, and acetylene atmospheres, the above results indicate that the radiation effect in acetylene atmosphere is the most significant in comparison with that in air and in vacuum.

References

1. Zhang, Y. *Eng Polym Applicat* 1991, 3, 52.
2. Matsuda, H. S. *CHEMTECH* 1988, 18, 310.
3. Porter, R. S. *Polym Eng Sci* 1994, 34, 266.
4. Van Dingenen, J. L. *J Mater Desi* 1989, 10, 101.
5. Van Grop, E. H. *Chemiefasern/Textilind* 1990, 40, E21.
6. Kirschbaum, R. *Chemiefasern/Textilind* 1986, 36, E123.
7. Bhateja S. K.; Andrews, E. H. *Polymer* 1983, 24, 160.
8. Woods, D. W.; Busfield, W. K.; Ward, I. M. *Plast Rubber Process Appl* 1985, 5, 157.
9. Sawatari, C.; Nishikido, H.; Matsuo, M. *Colloid Polym Sci* 1988, 266, 316.
10. Streicher, R. M. *Plast Rubber Process Appl* 1988, 10, 221.
11. Dijkstra, D. J.; Hoogsteen, W.; Pennings, A. J. *Polymer* 1989, 30, 866.
12. Dijkstra, D. J.; Pennings, A. J. *Polym Bull* 1987, 17, 507.
13. Woods, D. W.; Ward, I. M. *Plast Rubber Compos Process Appl* 1992, 18, 255.
14. Klein, P. G.; Gonzalez-Orozco, J. A.; Ward, I. M. *Polymer* 1991, 32, 1732.
15. Klein, P. G.; Gonzalez-Orozco, J. A.; Ward, I. M. *Polymer* 1994, 35, 2044.
16. High Molecular Group, Chem Depart of Peking Univ. *High Molecular Phys Experiment*; Peking Univ Publishing House: Peking, 1983; p 184.
17. Van Aerle, N. *Polym Commun* 1988, 29, 128.
18. Hikmet, R. *Colloid Polym Sci* 1987, 265, 185.
19. Klein, P. G. *J Polym Sci Part B: Polym Phys* 1987, 25, 1359.
20. Jones, R. A. *J Polym Sci Part B: Polym Phys* 1993, 31, 807.