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## Radiation effects of UHMW-PE fibre on gel fraction and mechanical properties

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## ABSTRACT

The effect of gamma ray irradiation on ultra-high molecular weight polyethylene (UHMW-PE) fibre was investigated for the change of gel fraction, mechanical properties, and morphology of crystallites. In the case of irradiation in air, the oxidation was limited to the fibre surface where the gel fraction decreased by chain scission, and the depth of the oxidation area from the surface was estimated to be 2  $\mu\text{m}$ . Tensile tests showed similar stress–strain curves for irradiation in vacuum or in air, but the elongation at break decreased more obviously for irradiation in air. The oxidation products, such as carboxylic acids, were detected by FTIR measurement. However, the DSC and XRD analyses indicated little change of crystallinity on irradiation in vacuum or in air. The oxidation was limited to a thin surface area on irradiation in air due to a low migration rate of the radicals trapped in the crystallite in the UHMW-PE fibre.

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### 1. Introduction

UHMW-PE fibre, generated by gel-spinning processing at high temperature, has an excellent tensile strength and modulus. However, the chemically inert surface limits its application in fibre reinforced plastics (FRP) (Smith et al., 1981; Penning et al., 1994). Many attempts have been made to improve its interfacial adhesion by chemical etching, flame-oxidation, plasma treatment, radiation treatment, etc. (Intrater et al., 2006; Berger et al., 2003; Wang et al., 2006). Radiation modification has been considered to be a favorable method because of its high penetration depth and uniformity. Our previous work (Zhao et al., 2010) revealed that the free radicals trapped in the fibre have a long lifetime due to the large size of the crystallites.

The purpose of this work is to investigate the radiation modification and radiation damage of UHMW-PE fibre. The long living trapped radicals might be applied for surface modification by oxidation or graft-polymerization after irradiation. From the viewpoint of surface modification, radiation-induced oxidation and a change in the mechanical property of the fibre were studied by various techniques and analysis.

### 2. Experimental

UHMW-PE fibre (TYZ Safetex FT-103, size of 3.6 Denier) was purchased from Beijing Tongyizhong Advanced Material Company (Beijing, China). The fibre was soaked in heptane at room temperature for 24 h, then washed with acetone and dried at 60 °C. The fibre samples were sealed off in glass tubes after evacuation to  $10^{-2}$  Pa for irradiation in vacuum, and wrapped by aluminum foil for irradiation in air. Irradiation was carried out at room temperature by Co-60  $\gamma$ -ray at a dose rate of 0.73 Gy/s up to 30–180 kGy. After irradiation, some samples were annealed at 135 °C for 2 h in vacuum.

Gel fraction measurement was performed using xylene solvent, and the soluble fraction was extracted for 36 h at the boiling temperature of around 140 °C. In order to prevent fibre oxidation during extraction, a specific antioxidant was added to the xylene at 0.5 wt%. The residual gel components were dried under vacuum at 70 °C for 48 h. FTIR spectra were observed at room temperature using a Nicolet-560 spectrometer. A specimen of the UHMW-PE fibre was sliced into thin sections of 20  $\mu\text{m}$ , and 1.0 mg was pressed into a potassium bromide disc with a diameter of 15 mm for scanning transmission spectroscopy. XRD measurement was performed using a D/max-RB diffractometer and Cu  $K_{\alpha}$  ( $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and 150 mA. The UHMW-PE fibre in the form of a bundle was set perpendicular to the direction of rotation in the XRD measurement. DSC (Perkin-Elmer DSC-822e) measurement was performed with a heating rate of 10 °C/min

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from  $-20$  to  $180$  °C in a nitrogen gas flow of 30 mL/min. The crystallinity was calculated from the enthalpy ( $\Delta H_m$ ) of melting of the crystallites, using  $\Delta H_m = 295$  J/g for the crystallites. Mechanical properties, such as tensile strength, elongation at break, and yield strength, were measured using a single fibre strength tester (LLY-06E).

### 3. Results and discussion

#### 3.1. Radiation effect on gel fraction and crystallinity

The average cross-sectional area of the UHMW-PE fibre was calculated to be  $4.0 \times 10^{-6}$  cm<sup>2</sup> based on 3.6 Denier (3.6 g/9000 m) and a density of 1.00 g/cm<sup>3</sup>. The cross-sectional diameter of the UHMW-PE fibre is around 23  $\mu$ m when the shape of the cross-section is circular. The fibre was crosslinked by a chemical agent during fibre processing which results in a very high fibre gel fraction.

The changes in the gel fraction of UHMW-PE on irradiation in vacuum and in air are shown in Fig. 1. The gel fraction of the initial fibre was found to be 98% by extraction of the sol component in boiling xylene. The increase in the gel fraction is small even for crosslinking by irradiation in vacuum. Moreover, chain scission occurs via oxidation on irradiation in air, and the gel fraction decreases with dose, due to a breakdown of the network structure of the crosslinked UHMW-PE fibres as a result of chain scission.

However, at doses higher than 80 kGy, it is interesting to note that the decrease in the gel fraction saturates to 68–70%. Annealing of the UHMW-PE fibres after irradiation in air gives a relatively higher gel fraction, indicating an additional crosslinking via combination of the polymer chain radicals that are formed by radiation or by decomposition of oxidative products such as peroxides produced by radiation oxidation.

If the oxidation occurred throughout the fibre, chain scission would proceed more severely and the gel fraction should decrease more promptly with dose and may reach zero at around 280 kGy. The fact that the gel fraction tends to become constant above 80 kGy means that the chain scission proceeds in an area of about 30% of the fibre near the surface (Daly and Yin, 1998). On the one hand, during storage in air, most of the alkyl radicals in the irradiated UHMW-PE fibre will react with oxygen at the surface of crystallites, since the alkyl radicals trapped in crystallites move to the surface by radical migration (Zhao et al., 2010). On the other

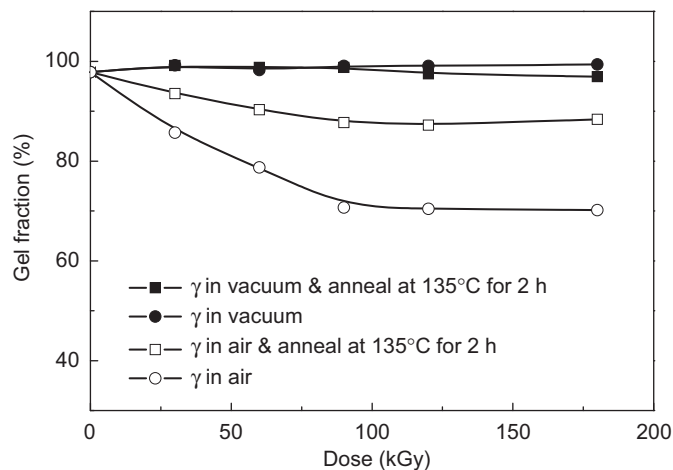


Fig. 1. Change of gel fraction as a function of dose for UHMW-PE fibre irradiated in vacuum or air, and annealed at 135 °C for 2 h after irradiation.

hand, it is easier for oxygen to penetrate into an amorphous region than into a crystalline or inter-phase between crystalline and amorphous regions. Therefore, the oxidation was limited to a thin surface area on irradiation in air due to the large size of crystallites and a low migration rate of the radicals trapped in the crystallites in the UHMW-PE fibre. According to the proposed model, therefore, the surface 30% of the fibre is primarily amorphous. That is, the surface 30% of the fibre, primarily in an amorphous region, is oxidized with subsequent chain scission, and the inner part of 70% is not oxidized, as illustrated in Fig. 2.

For any polymer material, oxidation is limited to the surface layer when the material is of a large size or a thick sheet when irradiated in an oxygen atmosphere. For sheet material, the oxidation layer, that is, the depth of oxidation from surface ( $L$  [mm]), is determined by the following equation (Seguchi, et al., 1981):

$$L = (DS/\Phi)^{1/2} \times (P/I)^{1/2}, \quad (1)$$

where  $D$  (cm<sup>2</sup>/s) and  $S$  (mol/cm<sup>3</sup>/atm) are diffusion coefficient and solubility of oxygen in polymer material, respectively.  $\Phi$  (mol/cm<sup>3</sup>/Gy) is the oxygen consumption coefficient by radiation oxidation,  $P$  (atm) is oxygen partial pressure during irradiation, and  $I$  (Gy/s) is the dose rate.  $D$ ,  $S$ ,  $\Phi$  are intrinsic values for each polymer material. For low density polyethylene, for example,  $L$  is 50–100  $\mu$ m when a thick sheet is irradiated in air at room temperature with a dose rate of 3 Gy/s. For a fibre sample with a cylindrical shape, Eq. (1) could be applied in the case where  $L$  is relatively small.

For UHMW-PE fibre, the  $c$ -axis of the crystallites is aligned with the fibre direction and the degree of crystallinity is higher than 80%. Molecules in the amorphous region are stretched along the fibre axis, so that molecular motion is restricted greatly. Therefore,  $D$  and  $S$  for oxygen in the fibre are very low, and  $D \times S$  could be estimated to be of the order of  $10^{-4}$  of that for low density polyethylene. The oxygen penetrates into the amorphous region where the oxidation takes place and chain scission occurs. The balance between the oxygen penetration rate and the oxygen consumption rate during irradiation determines the oxidation depth from the surface. The oxidation depth can be controlled by selection of the oxygen pressure during irradiation [ $P$ ], the dose rate [Gy/s], and also the irradiation temperature, because the diffusion coefficient  $D$  is temperature dependent.

Fig. 3 shows the FTIR spectra of UHMW-PE fibre irradiated in vacuum or in air to a dose of 180 kGy, and annealed after irradiation. The FTIR spectra were normalized. The absorption bands at 1463 and 1474 cm<sup>-1</sup> are assigned to the symmetric CH<sub>2</sub>-deformation vibration in the crystal. The band at 717 cm<sup>-1</sup> is due to the in-phase CH<sub>2</sub>-rocking vibration and the 730 cm<sup>-1</sup> band is due to the out-of-phase CH<sub>2</sub>-rocking vibration. The intensity of the bands at 717 and 730 cm<sup>-1</sup> increased after irradiation in vacuum or in air, but decreased by the annealing. The absorption bands at 1700–1735 cm<sup>-1</sup> are assigned to carbonyl containing

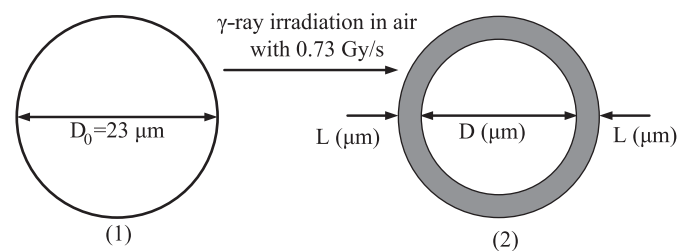
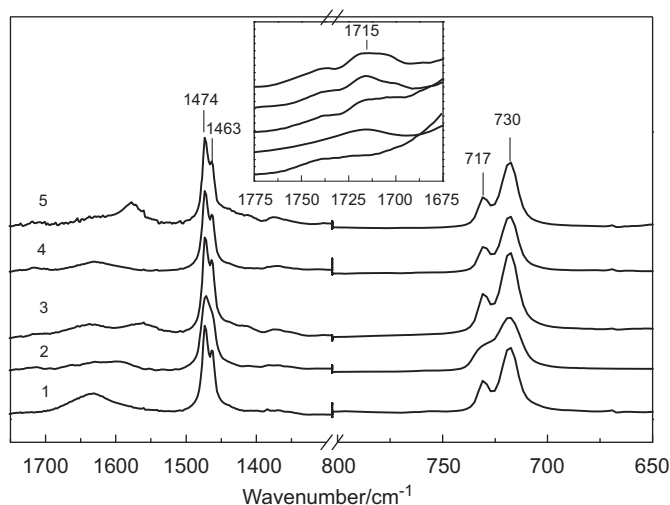
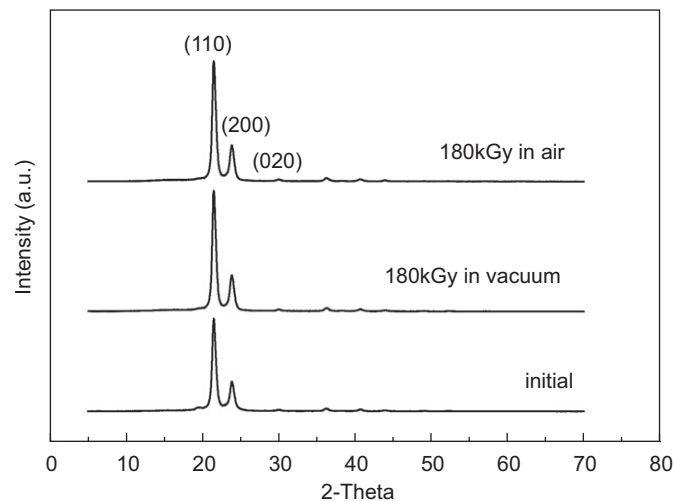


Fig. 2. A model of UHMW-PE fibre by radiation oxidation: (1) Cross-section of initial fibre,  $D_0$ : diameter of the initial fibre (23  $\mu$ m); (2) Cross-section of oxidized fibre by irradiation in air,  $D$ : diameter of non-oxidized part (19  $\mu$ m),  $L$ : depth of oxidation layer (2  $\mu$ m).



**Fig. 3.** FTIR spectra of UHMW-PE fibre irradiated in vacuum and in air. 1: Initial (0 kGy), 2: 180 kGy in vacuum and annealed at 135 °C for 2 h, 3: 180 kGy in vacuum, 4: 180 kGy in air and annealed at 135 °C for 2 h, 5: 180 kGy in air. Inset: enlarged area of the carbonyl compounds absorption.



**Fig. 5.** XRD patterns of UHMW-PE fibre irradiated up to 180 kGy in vacuum and in air.

XRD patterns as shown in Fig. 5. The diffraction peaks at  $2\theta=21.5^\circ$ ,  $23.9^\circ$ , and  $30.0^\circ$  are assigned to the diffraction planes (1 1 0), (2 0 0), and (0 2 0) of the orthorhombic unit cell of polyethylene (the lattice parameters  $a=7.41 \text{ \AA}$ ,  $b=4.96 \text{ \AA}$ , and  $c=2.54 \text{ \AA}$ ) (Bakshi et al., 2007; Sui et al., 2009).

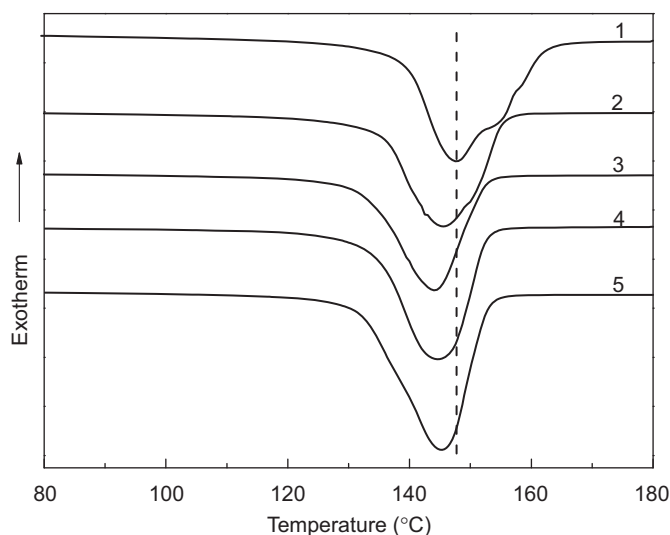
There was almost no change in  $2\theta$ , the half-height width of the diffraction peak, and the space between different diffraction planes on irradiation in vacuum or in air. Although there is a slight shift of the crystallite size ( $L_{110}$ ) from 14.7 to 15.5 nm calculated by the XRD patterns, the deviation might be caused by the distribution of fibre orientations that are not exactly parallel to the z-axis of crystallites in the experiment. In summary, the crystalline structure or size does not change on irradiation in vacuum or in air.

### 3.2. Radiation effect on mechanical properties

Fig. 6 shows the results of tensile tests on a UHMW-PE monofilament. Fig. 6(a) shows the stress–strain curves for the initial and irradiated fibre samples. The data for the tensile strength (b), elongation at break (c), and yield strength (d) are obtained from such measurements by averaging the data of 50 mono-filaments. For irradiation in vacuum, the tensile strength, elongation at break, and yield strength decrease slightly or remain almost unchanged up to 100 kGy. However, these properties decrease substantially with dose for irradiation in air.

The decrease in the tensile strength, elongation, and yield strength on irradiation in air can be explained by chain scission following radiation oxidation. The oxidation region is 30% of the fibre cross-section and at the surface, and the inside region of the fibre undergoes crosslinking without oxidation. In the tensile tests, cracks are formed at the surface and progress into the inside of the fibre. Further, it was observed that the tensile properties of the fibre irradiated in air changed scarcely on annealing at 135 °C for 2 h.

On storage for a long time (275 days) in air after irradiation in air, the tensile strength of the fibre decreased by 20% or more. This is due to post-irradiation oxidation of the residual free radicals trapped in the crystallites. The alkyl radicals trapped in the crystallites have a long life, and migrate slowly to the fibre surface (Zhao et al., 2010). During storage in air, the radicals react with oxygen to form oxidation products at the surface of the crystallites.

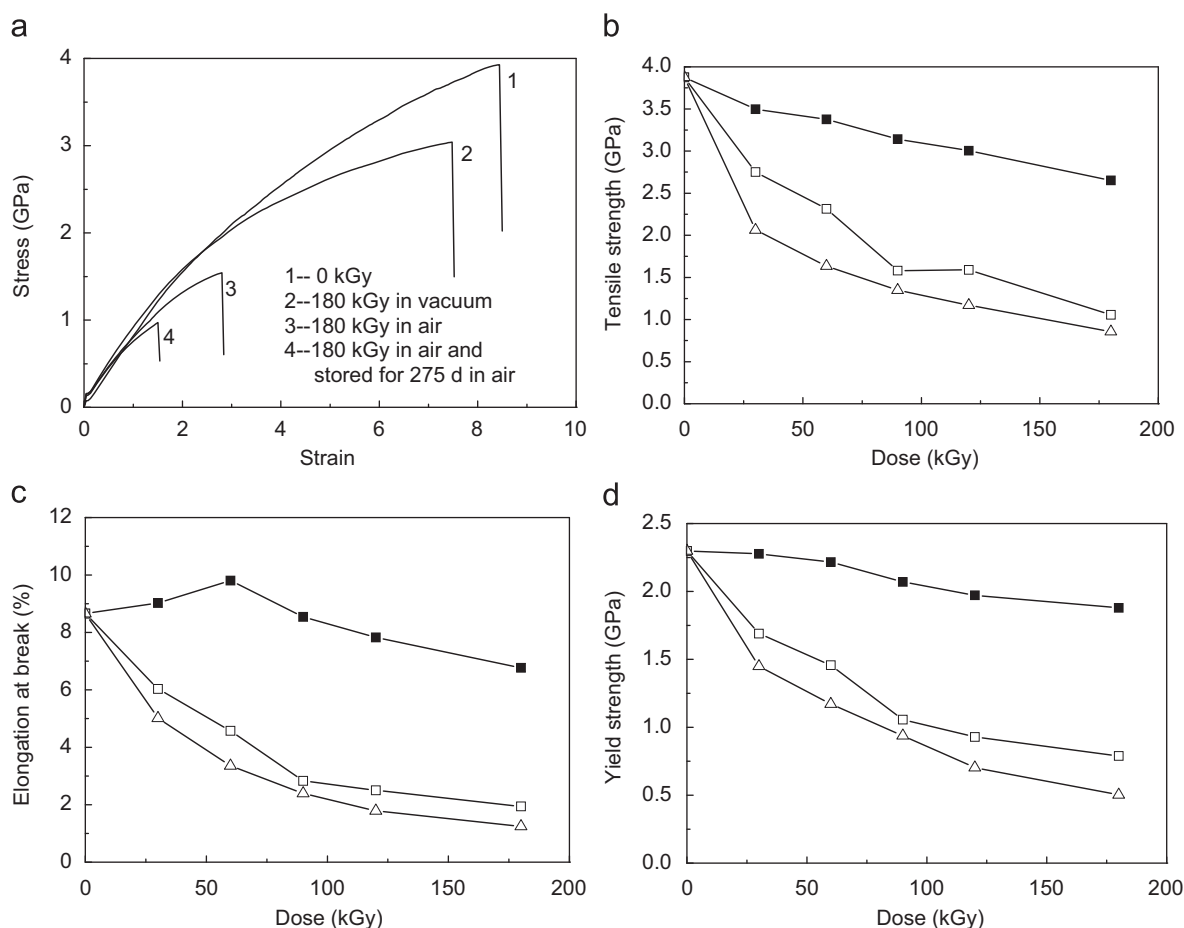


**Fig. 4.** DSC endothermic curves of irradiated UHMW-PE fibre. 1: Initial, 2: 180 kGy in vacuum, 3: 180 kGy in vacuum and annealed at 135 °C for 2 h, 4: 180 kGy in air, 5: 180 kGy in air and annealed at 135 °C for 2 h.

compounds (mainly carboxylic acid:  $\text{HO-C=O}$ ). The number of carbonyl groups presents increases with dose on irradiation in air. However, the intensity of the carbonyl peak was not high, and tended to decrease on annealing. The FTIR results provide additional support for the conclusion that the oxidation is limited to the surface layer in the case of irradiation in air.

Fig. 4 shows the DSC endothermic curves for UHMW-PE fibre irradiated in vacuum or in air, and annealing after irradiation. The melting point decreased slightly after irradiation, maybe due to the formation of defects in the crystallites on irradiation (Costa et al., 2002). However, the endothermic peak area ( $\Delta H$ ) remained almost unchanged after irradiation at different doses in vacuum or in air. This means that the crystallinity was scarcely changed on irradiation in vacuum or in air.

We further investigated the radiation effect on the crystal structure of UHMW-PE fibre by XRD measurement. The structural parameters of crystals in UHMW-PE fibres were obtained from the



**Fig. 6.** Change of tensile properties of UHMW-PE fibre by irradiation in vacuum and in air: (a) stress–strain curves of initial fibre and irradiated at 180 kGy, (b) tensile strength, (c) elongation at break, (d) yield strength. (■) Irradiated in vacuum; (□) irradiated in air; (△) irradiated in air and stored for 275 days.

#### 4. Conclusion

Radiation effects for UHMW-PE fibre on chemical reactions, polymer morphology, and mechanical properties were compared for irradiation in vacuum or in air. Crosslinking took place on irradiation in vacuum, but led to almost no change morphology and mechanical properties up to 180 kGy. In contrast, the irradiation in air led to chain scission by oxidative degradation and a decrease in the tensile properties. Especially, oxidation proceeded only at the surface layer of the UHMW-PE fibre within 2  $\mu\text{m}$  thickness for irradiation with a dose rate of 0.73 Gy/s, and crosslinking took place inside of the fibre. This means that the surface layer could be modified by radiation oxidation, and the thickness of the oxidized layer could be controlled by a choice of the irradiation conditions. The structure and morphology of the crystallites were scarcely changed by irradiation in air; however, the tensile properties were influenced by the surface oxidation.

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#### References

- Bakshi, S.R., Tercero, J.E., Agarwal, A., 2007. Synthesis and characterization of multiwalled carbon nanotube reinforced ultra high molecular weight polyethylene composite by electrostatic spraying technique. *Composites, Part A* 38, 2493–2499.
- Berger, L., Kausch, H., Plummer, C., 2003. Structure and deformation mechanisms in UHMWPE-fibres. *Polymer* 44, 5877–5884.
- Costa, L., Jacobson, K., Bracco, P., Brach del Prever, E.M., 2002. Oxidation of orthorhombic UHMW-PE. *Biomaterials* 23, 1613–1624.
- Daly, B.M., Yin, J., 1998. Subsurface oxidation of polyethylene. *J. Biomed. Mater. Res.* 42, 523–529.
- Intrater, R., Hoffman, A., Gouzman, I., Grossman, E., Lempert, G., 2006. Effect of imaging technique on the observed surface morphology of oxygen plasma etched polyethylene fibers. *Polym. Degrad. Stab.* 91, 1948–1953.
- Penning, J., Pras, H., Pennings, A.J., 1994. Influence of chemical cross-linking on the creep-behavior of ultra-high-molecular-weight polyethylene fibers. *Colloid. Polym. Sci.* 272, 664–676.
- Seguchi, T., Hashimoto, S., Arakawa, K., Hayakawa, N., Kawakami, W., Kuriyama, I., 1981. Radiation induced oxidative degradation of polymers—I. Oxidation region in polymer films irradiated in oxygen under pressure. *Radiat. Phys. Chem.* 17, 195–201.
- Smith, P., Lemstra, P.J., Booy, H.C., 1981. Ultra-drawing of high-molecular-weight polyethylene cast from solution. 2. Influence of initial polymer concentration. *J. Polym. Sci. Part B Polym. Phys.* 19, 877–888.
- Sui, G., Zhong, W.H., Ren, X., Wang, X.Q., Yang, X.P., 2009. Structure, mechanical properties and friction behavior of UHMWPE/HDPE/carbon nanofibres. *Mater. Chem. Phys.* 115, 404–412.
- Wang, J., Liang, G., Zhao, W., Lu, H., Zhang, P., 2006. Studies on surface modification of UHMWPE fibers via UV initiated grafting. *Appl. Surf. Sci.* 253, 668–673.
- Zhao, Y.N., Wang, M.H., Tang, Z.F., Wu, G.Z., 2010. ESR study of free radicals in UHMW-PE fiber irradiated by gamma rays. *Radiat. Phys. Chem.* 79, 429–433.