polymer communications

Radiation crosslinking of polytetrafluoroethylene

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Polytetrafluoroethylene (PTFE) is considered to be a typical radiation degradative polymer. In this work the polymer was crosslinked by means of radiation at $335 \pm 5°C$ under vacuum. Crosslinked PTFE showed a great improvement in high temperature properties and radiation stability.

(Keywords: PTFE; radiation; crosslinking)

Introduction

Polytetrafluoroethylene (PTFE), owing to its superior high temperature properties and chemical resistance, is widely used in many industrial fields. Nevertheless, its cold creeping and radiation sensitivity often limit its application to a certain extent. Previous research[1–4] on the effects of radiation on PTFE has revealed that when irradiation is performed at temperatures below the melting point of PTFE (327°C), the predominant radiation-induced change in molecular structure is scission of molecular chains; an irradiation dose of several kilogray, which is generally thought to have little effect of many other radiation degradative polymers, can lead to PTFE losing most of its useful mechanical properties. The unusual radiation sensitivity of PTFE was thought to result from its high crystallinity and high stability of radiation-induced macromolecular radicals[5,6]. Therefore the only way found to crosslink PTFE by radiation was to change the molecular structure of PTFE by, for example, copolymerizing TFE with a certain amount of hexafluoropropylene (5–20%). The copolymer thus formed, perfluoro-polyethylene-propylene (FEP) was found to be crosslinked by radiation under vacuum at a temperature higher than its glass transition temperature[7,8]. To date, there is no published work describing an effective method by which PTFE can be crosslinked through high energy radiation.

Research work attempting to modify PTFE by high energy radiation was carried out in our laboratory in the 1970s. After almost 10 years we finally found a very strict condition under which the dream of radiation crosslinking of PTFE becomes reality. Crosslinked PTFE showed a marked improvement in the properties of radiation stability and cold creeping. We have now decided to publish results obtained 13 years ago regarding this condition, and hope that scientists and technologists all over the world engaged in this field will benefit from them.

Experimental

The samples used in this work were from commercial PTFE sheet produced by Shanghai Institute of Organic Fluoro-materials, P. R. China.

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Irradiation was performed by using a 20 000 Ci Co-60 source; absorbed dose was controlled in the range of 0–100 kGy. High temperature irradiation was carried out in a heater made by ourselves and the temperature was controlled at $335 \pm 5°C$. Samples to be irradiated were sealed in glass tubes under vacuum, except where stated otherwise.

Results and discussion

Conditions under which PTFE can be crosslinked. During investigations of the radiation effects of PTFE, we often noted that not only atmosphere but also irradiation temperature could markedly affect the radiation stability of PTFE. By increasing the irradiation temperature, it was possible to reduce the degree of deterioration of mechanical properties of the irradiated polymer, as shown in *Figures 1* and *2*. As a result of research on the temperature effect of radiation stability of PTFE, we finally found that when irradiation was performed at a temperature of $335 \pm 5°C$ in an oxygen-free atmosphere, radiation caused the formation of crosslinking structure in PTFE if the absorbed dose was within the range 2–30 kGy.

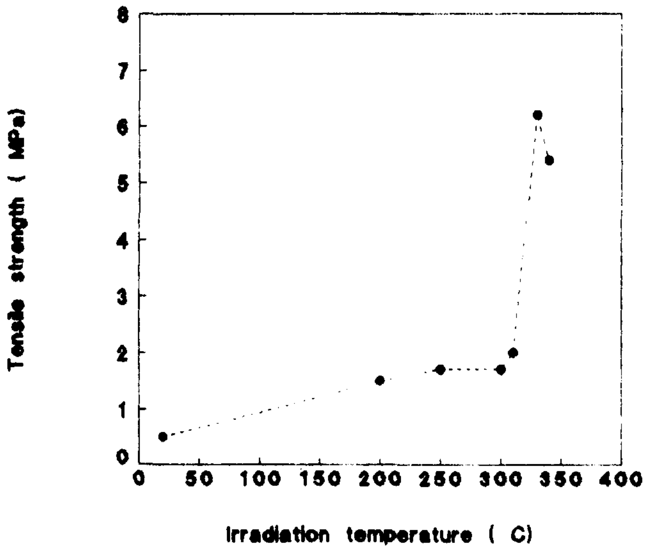

Figure 1 Tensile strength at 200°C of PTFE (absorbed dose 20 kGy)

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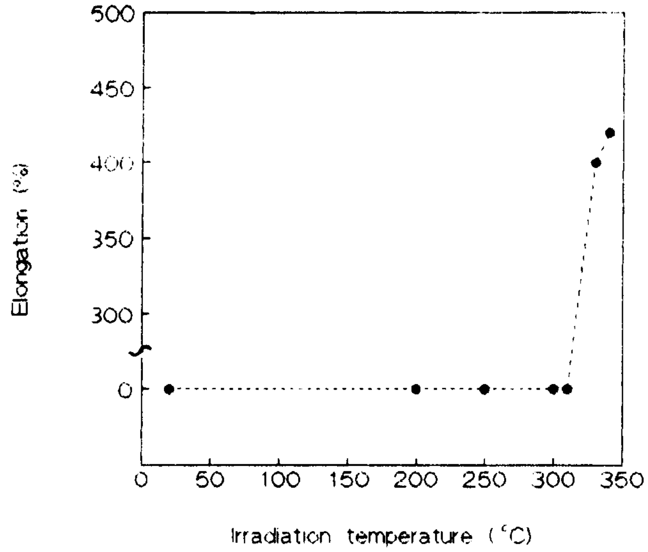

Figure 2 Elongation at 200°C of PTFE (absorbed dose 20 kGy)

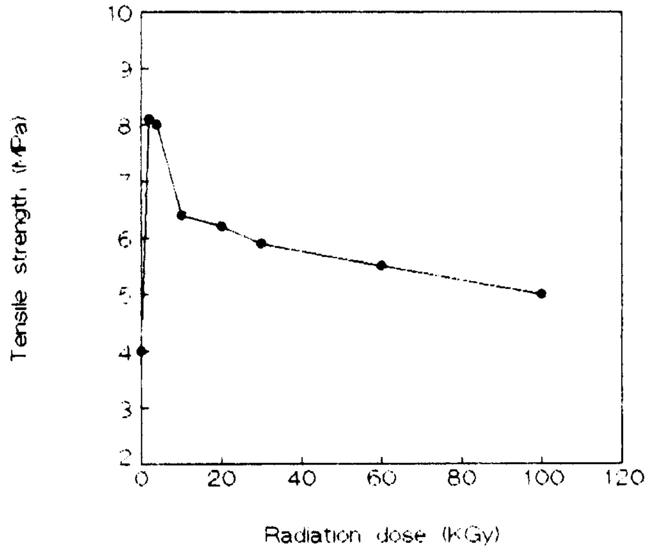

Figure 3 Effect of radiation dose on tensile strength at 200°C of PTFE irradiated at 330°C

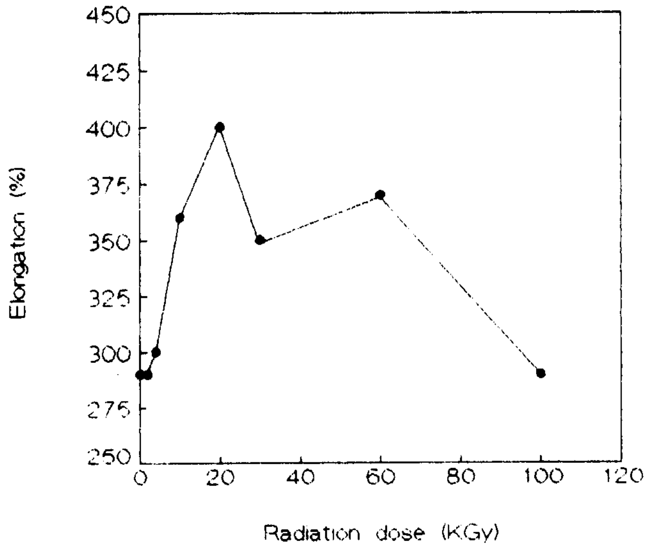

Figure 4 Effect of radiation dose on elongation at 200°C of PTFE irradiated at 330°C

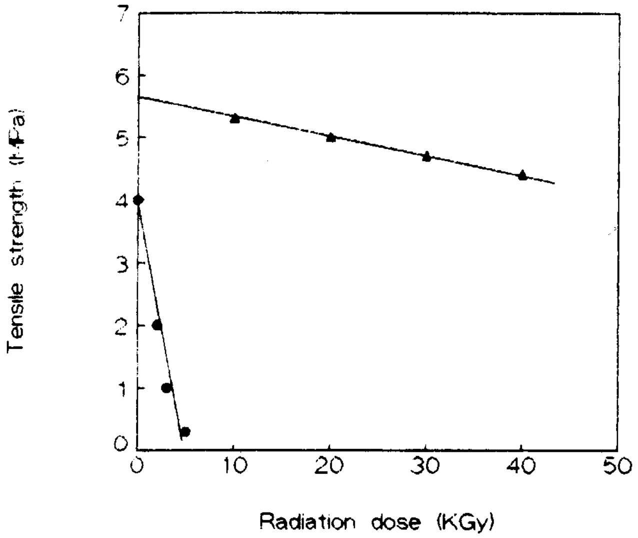

Figure 5 Effect of irradiation on tensile strength of PTFE: ●, uncrosslinked PTFE; ▲, crosslinked PTFE

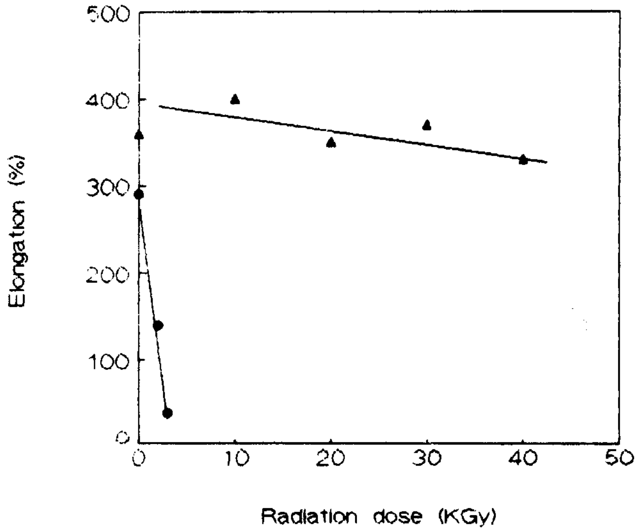

Figure 6 Effect of irradiation on elongation of PTFE: ●, uncrosslinked PTFE; ▲, crosslinked PTFE

Mechanical properties of crosslinked PTFE. *Figures 3* and *4* show the mechanical properties at 200°C of PTFE crosslinked at 330°C with 20 kGy dose. It is clear that under such conditions the radiation behaviour of PTFE is quite different to that of PTFE irradiated at ambient temperature. Both tensile strength and elongation at 200°C show an initial increase followed by a decrease with increasing irradiation dose. The maximum values were observed to occur at 2 kGy for tensile strength and 20 kGy for elongation. The marked improvement in high temperature performance of PTFE evidently indicates the formation of three-dimensional network structures in PTFE.

Improvement in radiation stability of PTFE. PTFE was well known to be a typical radiation degradative polymer as early as the 1960s. *Figures 5* and *6*, however, show an unusual feature of the radiation behaviour of the polymer. The values of high temperature tensile strength and elongation of uncrosslinked PTFE are observed to drop sharply, even in the dose range below 5 kGy, which agrees with many previous reports. For crosslinked samples (330°C, 10 kGy), although the increase in radiation dose causes the gradual reduction of tensile strength and elongation, the degree of decrease is much less than that of uncrosslinked samples. PTFE samples that have absorbed up to 100 kGy radiation dose can retain 138% of the tensile strength and 100% of the elongation, which is generally thought to be incredible for PTFE.

Conclusion

These results clearly indicate that when irradiation is performed at 335 ± 5°C under an oxygen-free atmosphere, the radiation crosslinking of PTFE can be achieved. Detailed research on the characterization of crosslinked PTFE will be published soon.

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