Radiation stability of perfluoroethylene–propylene copolymer

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The gel content of crosslinked perfluoroethylene–propylene copolymer was obtained by extraction with fluoro-chloro oil. It was then treated by the Charlesby–Pinner equation. The results obtained revealed that both the gelation dose and the ratio of fracture to crosslinking density decreased with increasing irradiation temperature.

(Keywords: FEP; radiation; crosslinking; scission; gelation dose)

Introduction

Perfluoroethylene–propylene copolymer (FEP) has outstanding properties of heat resistance, chemical resistance and processability. In comparison with poly(tetrafluoroethylene) (PTFE), FEP contains ~80–90% tetrafluoroethylene units in its backbone chain. Though most of its structural units are the same as in PTFE, which is well known to be a typical radiation degradative polymer, FEP was reported to be able to form crosslinking structures when exposed to ionizing radiation at temperatures above its glass transition temperature (T_g, ~80–90°C) and in the absence of oxygen[1,2]. Since the measurement of any solution property of FEP is extremely difficult and basic relationships with molecular weight have not yet been established, previous studies have relied upon the semiquantitative indications of changes in melt viscosity and zero strength time (ZST). In this work, the observation of the radiation-induced formation of the gel shown by extracting the crosslinked polymer with an oligomer of trifluorochloroethylene (fluoro-chloro oil) provides the most direct and quantitative evidence for the formation of crosslinking structures in irradiated FEP. It also makes it possible to estimate the gelation dose and the ratio of scission to crosslinking density of the polymer.

Experimental

The FEP samples used were commercially produced and contained 14 mol% hexafluoropropylene units. Sheet samples were obtained by pressing under 270°C.

Irradiation was carried out with a 259 × 10^{13} Bq ^{60}Co source. Unless stated otherwise, all samples were irradiated under 0.2 Pa. High temperature radiation was carried out using a heater which controlled the temperature to within ±5°C.

The gel content was obtained by extracting the crosslinked sample with fluoro-chloro oil at 250°C.

Results and discussion

In earlier work of radiation effects on FEP carried out by Bowers *et al.*[1] and Florin and Wall[2], the increase in ZST and decrease in melt viscosity were thought to prove the formation of crosslinking structures in irradiated FEP. In this work, by examining the changes in gel content, the most direct evidence for the formation of a network structure, the effect of irradiation temperature on the crosslinking of FEP, was studied. The results shown in *Figure 1* reveal that the radiation behaviour of FEP is radiation temperature dependent. In the temperature range below the T_g (~90°C) no gel could be observed, whereas above the T_g the gel content was seen to increase with increasing radiation dose, which agrees with the results reported by Bowers *et al.*[1] and Florin and Wall[2].

For a radiation crosslinkable polymer, assuming the initial molecular weight distribution is random, the degree of crosslinking is proportional to the radiation dose and crosslinking within a molecule may be neglected. Charlesby and Pinner[3] treated the random crosslinking of polymers using Flory's probability method[4] and established an equation relating the sol fraction S to the radiation dose R (in Mrad):

$$S + S^{1/2} = p_0/q_0 + 1/qu_1R \qquad (1)$$

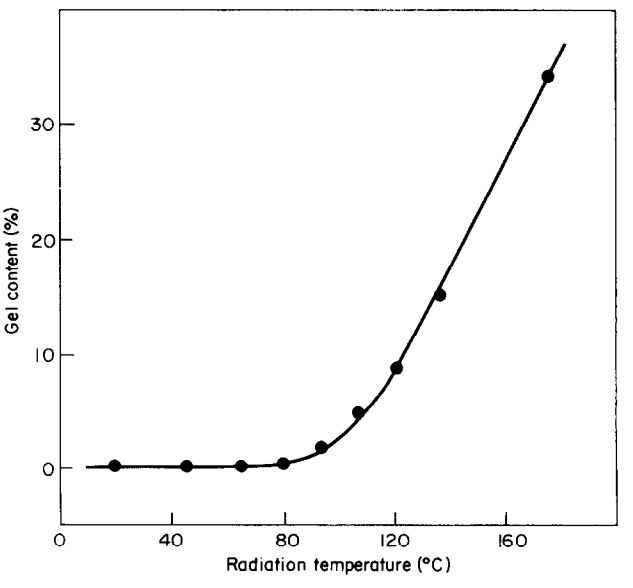

Figure 1 Relationship between gel content of irradiated FEP and radiation temperature

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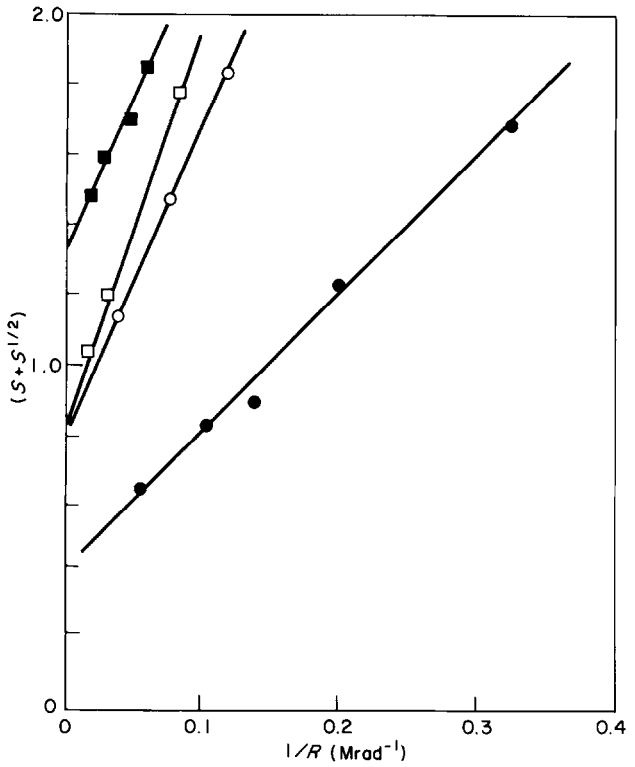

Figure 2 Relationship between $(S + S^{1/2})$ and $1/R$ for FEP irradiated at different temperatures: (■) 150°C; (□) 210°C; (○) 220°C; (●) 240°C

where p_0 and q_0 are fracture and crosslinking density, i.e. the fraction of monomer units in the polymer chains which take part in scission and the crosslinking reaction respectively, and u_1 is the initial number-average degree of polymerization.

Table 1 Values of p_0/q_0 and gelation dose of FEP irradiated at different temperatures

Irradiation temperature (°C)	p_0/q_0	Gelation dose (Mrad)
150	1.35	12.3
210	0.85	10.0
220	0.80	8.0
240	0.42	2.5

Figure 2 shows plots of $(S + S^{1/2})$ *versus* $1/R$ for FEP crosslinked at different temperatures. The good linear relationship observed here indicates that in the temperature range examined, the above assumptions are appropriate for the crosslinking of FEP. From the slopes and the intercepts of the lines in *Figure 2*, the ratio p_0/q_0 and the gelation dose of FEP can be calculated. The results are shown in *Table 1*.

Since the number-average molecular weight of the FEP used was not known, the G values for crosslinking and scission could not be obtained. The decrease in p_0/q_0 and gelation dose with increasing irradiation temperature, however, reveal that an increase in irradiation temperature may not only change the radiation behaviour of FEP from predominantly degradation to forming a network structure, but also favours radiation-induced crosslinking reactions.

References

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