

The Use of Crosslinking Promoters in the γ -Radiolysis of Poly(tetrafluoroethylene-co-perfluoromethylvinyl ether). II.

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Received 8 May 1998; accepted 2 June 1999

ABSTRACT: Incorporation of 0.5 mol % of nitrile and bromine functionalities was found to enhance the radiation crosslinking of the copolymer of tetrafluoroethylene-co-perfluoro(methylvinyl ether) (TFE/PMVE) by a factor of 2 for γ -irradiations carried out at room temperature to doses in the range 0–50 kGy. The functional groups, nitrile, perfluorophenyl, and hydrogen were found to greatly enhance crosslinking well below the glass transition temperature of TFE/PMVE (276 K). Increased amounts of gel formation as well as improved tensile properties were obtained for irradiations carried out below the T_g of the polymers containing functionalized monomers. These functional groups appear to be acting as catalysts for the radiation crosslinking of TFE/PMVE but they do not get incorporated into the crosslink. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1447–1452, 2000

Key words: poly(tetrafluoroethylene-co-perfluoromethylvinylether); crosslinking promoters; γ -radiolysis; radical yields; gel content; tensile properties

INTRODUCTION

The outstanding chemical and thermal inertness of perfluoroelastomers, such as TFE/PMVE, is attributed to the high stability of the C—F bond.¹ As with all elastomers, TFE/PMVE must be crosslinked into a stable three dimensional network to obtain good thermal and mechanical properties. The chemical inertness of TFE/PMVE makes conventional chemical crosslinking difficult, but this can be overcome by randomly incorporating a small amount of a functionalized monomer into the polymer during polymerization. Further reaction of the functional groups with a

suitable reagent crosslinks the polymer chains. These crosslinkable comonomers contain functional groups such as nitrile, bromine, hydrogen, and perfluorophenyl. The chemical crosslinking of perfluoroelastomers has been reviewed in detail by Logothetis.^{2,3}

The effects of these functional groups on the radiation crosslinking of TFE/PMVE were investigated first by Logothetis.⁴ He used electron beam irradiations and he studied the chemical and physical properties of the crosslinked polymers. Logothetis found that at high doses (\approx 150 kGy) these functional groups did not significantly enhance the radiation crosslinking at room temperature. Interestingly, FTIR analyses indicated that the nitrile functionality was not affected by radiolysis and remained in the polymer after a dose of 120 kGy.

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Journal of Applied Polymer Science, Vol. 75, 1447–1452 (2000)
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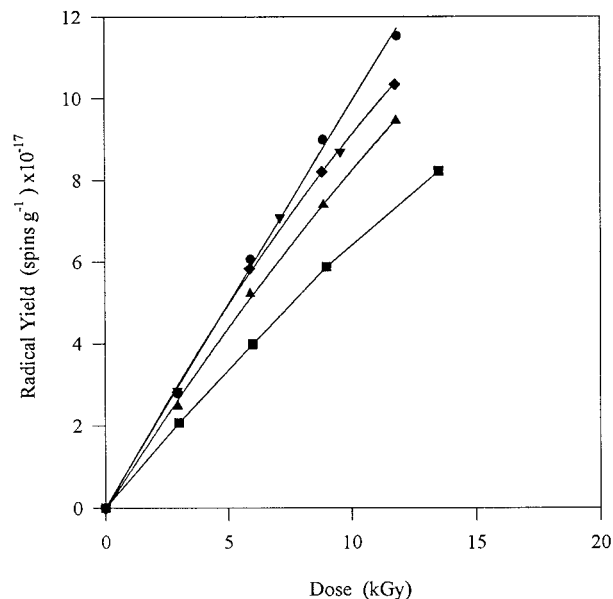


Figure 1 Radical yields determined from ESR measurements of the γ -irradiated TFE/PMVE elastomers at 77 K; (■) neat, (▲) Bromine, (▼) Perfluorophenyl, (◆) Hydrogen, (●) Nitrile.

In this study, the effect of nitrile, bromine, perfluorophenyl and hydrogen functional groups will be further investigated and the relative crosslinking efficiencies of the functionalities compared. In addition, the effect of these functionalities on the radiation chemistry of TFE/PMVE at various temperatures will be explored.

EXPERIMENTAL

The TFE/PMVE used in this study and the method of sample preparation that was adopted have been described in Part 1.⁵ Elastomers containing 0.5 mol % of the functional groups; nitrile, bromine, perfluorophenyl, and hydrogen were similarly synthesized. Details of the γ -irradiations and temperature controls have been described elsewhere.⁶ ESR measurements and sol/gel analysis have also been described in Part 1.⁵

RESULTS AND DISCUSSION

Room Temperature γ -Irradiation

The formation of chain ends, crosslinks and volatile products is believed to proceed via the forma-

tion of radical intermediates and is therefore of interest in the investigation of the effects of crosslinking promoters on the radiolysis of TFE/PMVE.^{7,8} The introduction of the functionalized monomers into TFE/PMVE increased the radical yields by approximately 40 percent at 77 K (Fig. 1). This large increase was surprising as the functionalized monomers were present only in a concentration of 0.5 mol %. It could therefore be assumed that direct cleavage at the functional groups, and subsequent formation of radical species could not be the source of this increase. Logothetis also showed that the functional groups were not altered during radiolysis.⁴ A likely reason for the increased radical response was the trapping of radical species such as fluorine radicals, by the functionalities. The fluorine radicals would otherwise recombine with polymeric radicals thus lowering the total radical yield. Previous studies have shown the recombination of fluorine radicals with polymeric radicals to be an important reaction during radiolysis at room temperature.⁹ The $G(R)$ values for total radical production, $G(R)$, were determined from the initial slopes from Figure 1 and are given in Table I. All of the functionalized elastomers gave similar radical yields at 77 K with an average $G(R)$ of 1.5. The neat TFE/PMVE, which has the lowest radical yield, is also the most concave to the abscissa, which indicates a higher rate of radical recombination especially at the higher doses.

All of the elastomers crosslinked readily upon radiolysis at room temperature, giving a maximum of 90–95% gelation after a dose of 200 kGy. This was accompanied by an increase in the glass transition temperatures of the elastomers (Fig. 2). Comparison of the gel contents for the nitrile (Fig. 3A) and hydrogen (Fig. 3B) functionalized elastomers with the neat elastomer are shown as

Table I Effect of Functionalities on the Radical Production at 77 K and the Dose for Gelation at Room Temperature

Functionality	G (Radical)	Gel Dose (kGy)
Neat	1.1	16
Nitrile	1.5	7
Bromine	1.4	7
Perfluorophenyl	1.6	14
Hydrogen	1.5	16

a function of radiation dose. The increased efficiency of crosslinking in the nitrile functionalized elastomer is clearly seen in Figure 3A which shows a higher gel content at doses lower than 100 kGy. The higher gelation was only maintained at low irradiation doses as all the elastomers gave similar gel contents at 200 kGy. The hydrogen functionalized elastomer failed to enhance crosslinking, producing a similar gel content compared to the neat elastomer (Fig. 3B). The doses for gelation determined from the Charlesby-Pinner relationship¹⁰ are given in Table I. Incorporation of the nitrile and bromine functionalities enhanced crosslinking and reduced the dose for gelation by 50%. However no change in the dose for gelation was observed with the incorporation of the perfluorophenyl, and hydrogen functionalities.

The tensile strengths of the neat, nitrile and perfluorophenyl containing elastomers are shown in Figure 4. Incorporation of the nitrile and bromine functionalities increased the tensile strength at break from 8.2 MPa to approximately 15 MPa which was attributed to preferential aggregation of the carboxylate end groups around these functionalities. Carboxylate end groups are present in the elastomer and originate from hydrolysis of the sulphate initiator chain ends.³ The

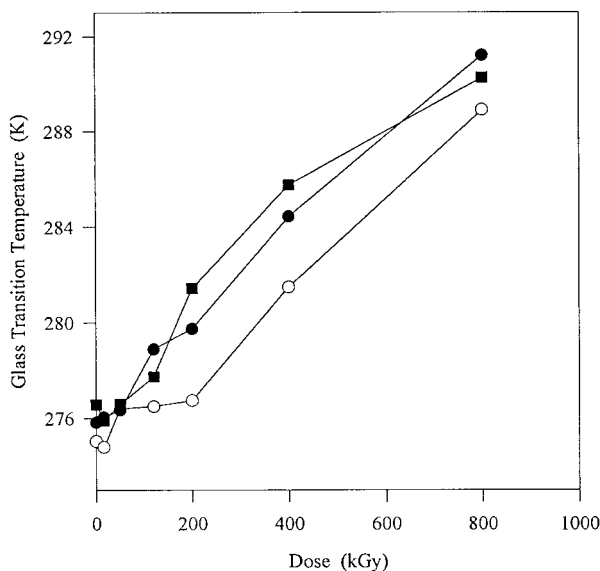


Figure 2 Glass transition temperature measurements of the elastomers as a function of dose determined by DSC; neat (●), nitrile (○), and perfluorophenyl (■). The elastomers were γ -irradiated at room temperature.

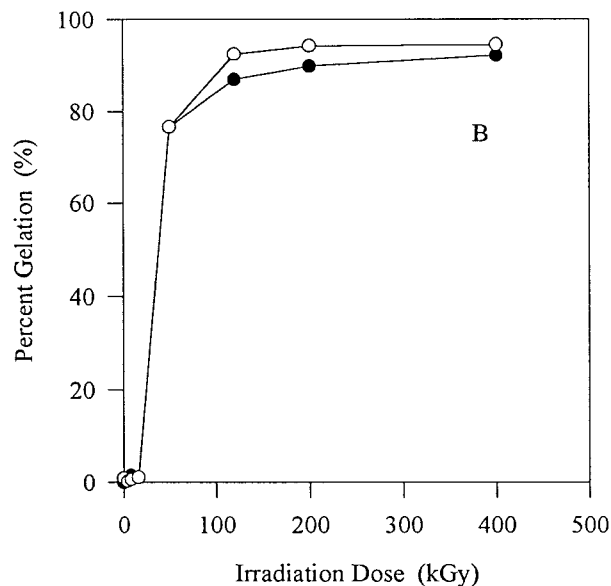
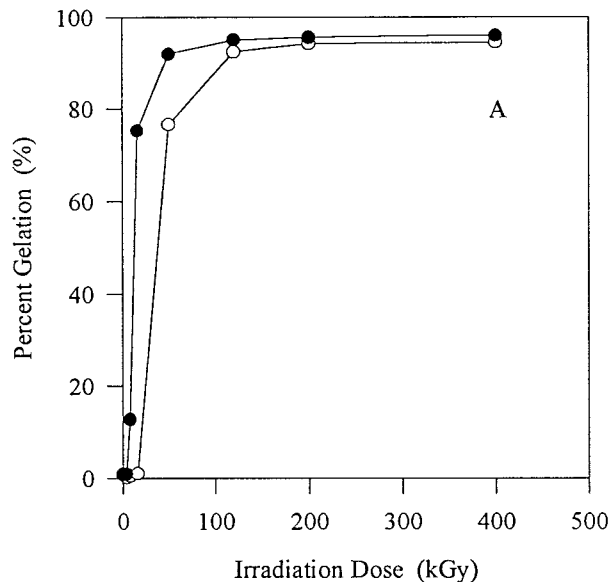


Figure 3 The variation of the gel content with the radiation dose for the neat elastomer (○) and an elastomer containing A) a nitrile (●) or B) a hydrogen (●) functionality.

perfluorophenyl and hydrogen elastomers showed almost identical tensile properties compared to the neat elastomer, both before and after irradiation. The tensile strengths at break of the elastomers dropped to half of their original value at a dose of 16 kGy. This was mirrored with an increase in the ultimate elongation in the same dose range. This has been attributed to the radiolytic destruction of the carboxylate end groups.¹¹

Ultimate elongation measurements can yield relative information on network architecture of elastomers.¹² The ultimate elongation of an ideal elastomer reflects the smallest inter crosslink distance, since the polymer chain will continue to stretch until it reaches a crosslink site which results in chain rupture.^{13,14} The ultimate elongation is therefore no longer affected by main chain

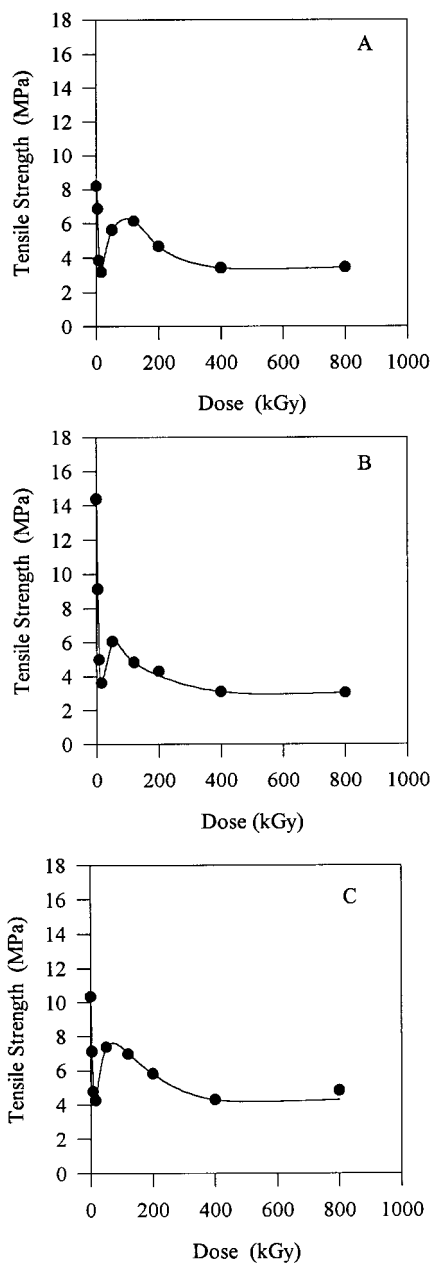


Figure 4 The tensile strength at break of A) neat, B) nitrile, and C) perfluorophenyl elastomers as a function of radiation dose.

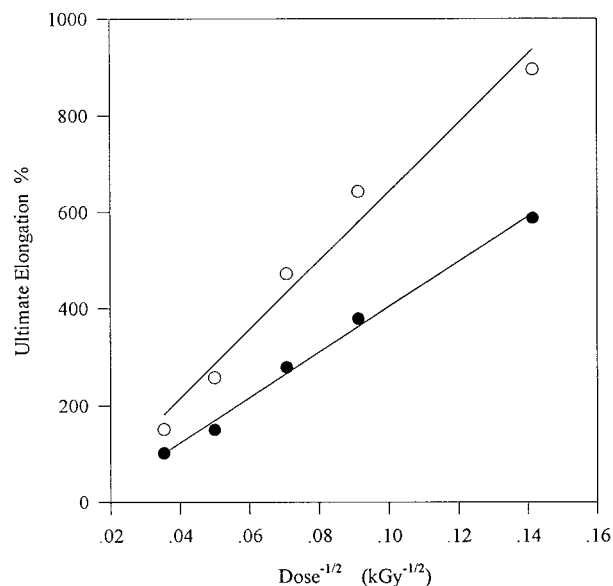


Figure 5 The ultimate elongation vs the reciprocal square root of the radiation dose for the neat (○) and nitrile (●) elastomers. Comparison of the slopes reflects the relative crosslinking efficiency.

scission after the formation of an infinite network as the smallest inter crosslink distance remains constant. Main chain scission only affects the dose at which the gel is formed, after which the ultimate elongation becomes dependent on the crosslink density. If we assume that all of the carboxylate end groups have disappeared after a dose of 50 kGy, a comparison of the crosslinking efficiencies determined from the ultimate elongation measurements is therefore possible. A plot of the ultimate elongation versus the reciprocal square root of the irradiation dose is shown in Figure 5 for the nitrile and neat elastomers in the dose range of 50 to 800 kGy. The slopes for all the elastomers are given in Table II and reflect the relative crosslinking efficiencies. The crosslinking efficiencies were determined from the reciprocal square of the slopes, and are normalized to the neat elastomer. Comparison of the crosslinking efficiencies shows that the perfluorophenyl and hydrogen elastomers did not promote crosslinking under these conditions. In contrast, incorporation of the nitrile and bromine functionalities increased the crosslinking efficiency by a factor of 2.3 and 1.9 respectively.

Variable Temperature γ -Irradiation

The effect of temperature on the γ -radiolysis of TFE/PMVE has been investigated⁶ and was

shown to have a dramatic effect on the governing radiolytic processes. Figure 6 shows the gel content of the elastomers γ -irradiated to 150 kGy as a function of radiolysis temperature. All of the elastomers gave 90 to 95% gel when irradiated above 273 K but showed a varied response below the T_g . The neat elastomer produced no gel when irradiated at 77 K and 195 K. This was attributed to a reduction of crosslinking as well as a shift to a higher dose for gelation in this temperature range. The introduction of nitrile, perfluorophenyl, and hydrogen functionalities in TFE/PMVE yielded high amounts of gel in this temperature range and therefore lowered the dose for gelation. Promotion of crosslinking below the glass transition temperature of 276 K was surprising because of the limited chain mobility that exists in the glassy state. Interestingly, the bromine functionality, which promoted crosslinking at room temperature, did not enhance crosslinking below the glass transition temperature.

Figure 7 shows the effect of irradiation temperature on the tensile properties for the nitrile, bromine, and the neat elastomers. The tensile properties for all the elastomers were similar for irradiations carried out above the T_g . However, below the T_g the mechanical properties were strongly influenced by the type of functionality incorporated into the polymer. The drop in tensile strength and the increase in the ultimate elongation from 77 K to 195 K for the neat elastomer are attributed to the predominance of main chain scission. Crosslinking becomes more predominant as the irradiation temperature approaches the T_g , where main chain mobility is achieved. The nitrile functionalized elastomer successfully promoted crosslinking well below the T_g as shown by

Table II Gradients Obtained from Figure 5 for All the Elastomers

Functionality	Slope (kGy) ^{1/2}	Relative Crosslinking Efficiency
No functionality	71.24	1.0
Nitrile	46.76	2.3
Bromine	51.90	1.9
Perfluorophenyl	64.62	1.2
Hydrogen	64.20	1.2

The relative crosslinking efficiencies are calculated from the reciprocal square of the slopes and are normalized to the neat TFE/PMVE elastomer.

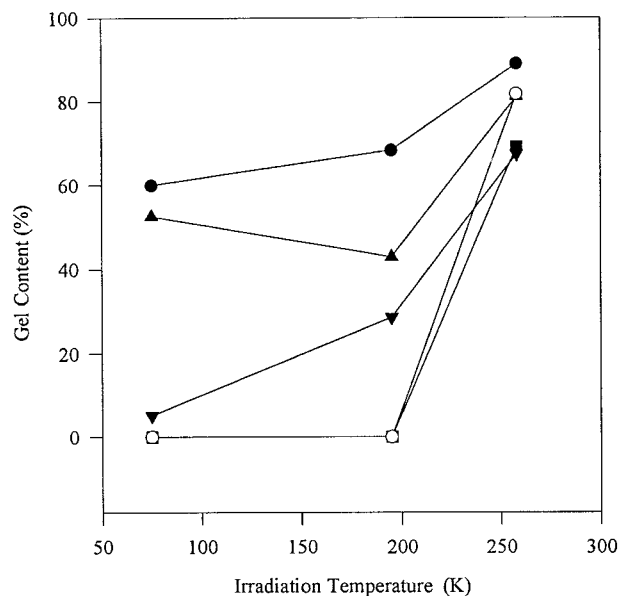


Figure 6 Gel content of nitrile (●), bromine (■), perfluorophenyl (▲), hydrogen (▼) and neat (○) elastomers γ -irradiated to a dose of 150 kGy at various temperatures below the glass transition temperature (273 K).

the significantly higher tensile strengths and lower elongations of the polymers. The large drop in tensile properties at 195 K seen in the neat elastomer was not observed. Similar results were also obtained for the perfluorophenyl and hydrogen functionalized elastomers. The bromine functionalized elastomer showed a small increase in the ultimate elongation at 195 K but was not as large as that observed for the neat elastomer.

CONCLUSIONS

The nitrile and bromine functionalities enhanced the radiation crosslinking of TFE/PMVE at room temperature by a factor of two over the dose range 0–50 kGy whereas the perfluorophenyl and hydrogen moieties had little impact. The mechanism for the enhancement of crosslinking is not fully understood but it does appear that the nitrile and bromine groups act as catalysts for crosslinking. Logothetis⁴ has shown the nitrile functionality to remain unaltered during irradiation, which explains why the increased radiation response persists throughout the dose range.

The nitrile and perfluorophenyl functionalities greatly enhanced crosslinking and reduced the dose for gelation well below the glass transition

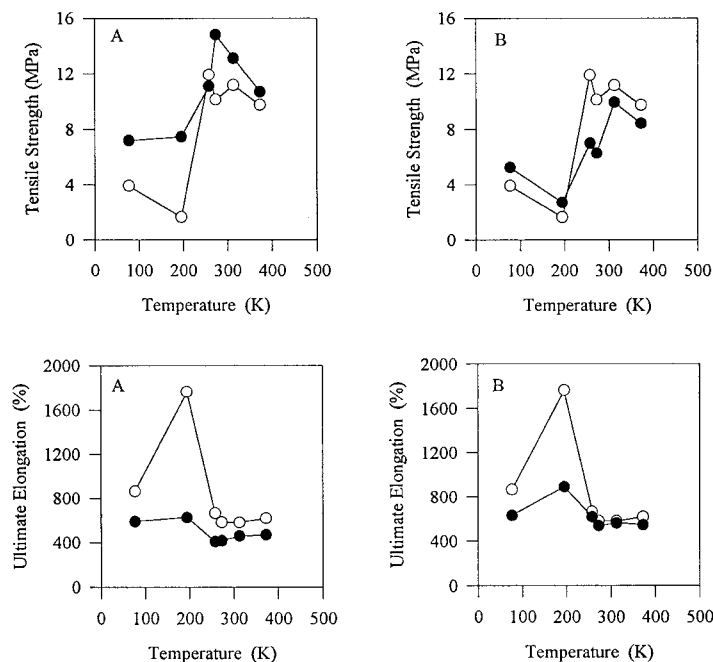


Figure 7 The variation of the tensile strength at break and ultimate elongation with the irradiation temperature for the neat elastomer (○) and an elastomer containing A) a nitrile (●) or B) a bromine (●) functionality. All the elastomers were γ -irradiated to 150 kGy.

temperature, despite the limited chain mobility. Below room temperature, the following relative crosslinking efficiencies were determined: nitrile > perfluorophenyl > hydrogen > bromine.

The authors wish to thank the Australian Research Council and the Australian Institute of Nuclear Science and Engineering for financial support and Dr. John Lyons for his helpful discussions.

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