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

J. S. FORSYTHE,¹ D. J. T. HILL,¹ A. L. LOGOTHETIS,² P. J. POMERY,¹ A. K. WHITTAKER³

¹ Polymer Materials and Radiation Group, University of Queensland, St Lucia, Q. 4072, Australia

² DuPont Dow Elastomers L.L.C., DuPont Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

³ Centre for Magnetic Resonance, University of Queensland, St Lucia, Q. 4072, Australia

Received 26 January 1998; accepted 5 September 1998

ABSTRACT: Incorporation of 1 wt % of triallyl isocyanurate (TAIC) significantly enhanced the radiation crosslinking of the perfluoroelastomer, poly(tetrafluoroethyleneco-perfluoromethylvinyl ether) (TFE/PMVE). The dose for gelation was lowered by 70% with the presence of TAIC. The additive also improved the tensile properties of TFE/ PMVE both before and after crosslinking by irradiation. Higher radical yields were obtained with the presence of TAIC at 77 K, indicating the crosslinking promoter was acting as a radical trap. ESR studies showed that radiolysis of TAIC and subsequent photobleaching cleaved an allyl branch from the ring structure. Upon thermal annealing, an allyl radical on the TAIC molecule was observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 169–175, 1999

Key words: poly(tetrafluoroethylene-*co*-perfluoromethylvinylether); crosslinking promoters; gamma radiolysis; tensile properties; gelation; radicals

INTRODUCTION

It has been known for some time that crosslinking promoters may be used to amplify the radiation crosslinking of polymeric materials, or indeed, to allow crosslinking in an otherwise radiation degradative polymer.¹ Crosslinking promoters also lower the required irradiation doses, minimizing some of the adverse effects of ionizing radiation, such as chain scission.

Cross et al.² investigated the addition of small amounts of added triallyl cyanurate (TAC) on the radiation crosslinking of polyethylene, polymethyl acrylate, and polyvinyl acetate. Low concentrations of TAC effectively enhanced crosslinking at low irradiation doses, while comparatively

Journal of Applied Polymer Science, Vol. 73, 169-175 (1999)

higher TAC concentrations resulted in an inhibited response to crosslinking. However, with increased irradiation doses, higher TAC concentrations showed an overall increase in the crosslink density. The dose rate did not significantly affect the dose for gelation, suggesting the reaction was not diffusion controlled. These observations also indicated that homopolymerization and hydrogenation of the double bonds of TAC were not important. Calculations showed that for up to 5% added TAC, an average of 2.5 polymer chains were linked to each TAC molecule. Sequential addition of polymeric chain radicals to each of the allyl groups of TAC and formation of a bridged crosslink network was proposed.

Crosslinking promoters have also been successfully used in the radiation crosslinking of fluoropolymers. Miller et al.³ used crosslinking promoters such as mixtures of trimethylolpropane trimethacrylate (TMPTM) and triallyl isocyanurate (TAIC) for the radiation crosslinking of the

Correspondence to: D. J. T. Hill.

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/020169-07



Figure 1 Structure of TFE/PMVE random copolymer. The ratio of TFE:PMVE is 2:1.

fluoroelastomer, Viton[®] GLT. An apparent synergy between TMPTM and TAIC was observed for the crosslinking of the fluoroelastomer, but neither the nature of this effect nor the mechanism for crosslinking were disclosed. TAIC has also been used successfully in the radiation crosslinking of TFE/propylene encapsulated wire.⁴

Logothetis⁵ incorporated 3 wt % TAIC into TFE/PMVE copolymer (Fig. 1) that also contained nitrile and iodine, and found the crosslinking promoter to increase the crosslinking efficiency and to significantly improve the tensile properties at an irradiation dose of 150 kGy. In this article we further investigate the action of the crosslinking promoter, TAIC, on the radiation crosslinking of TFE/PMVE copolymer containing no reactive functionalities.

EXPERIMENTAL

Materials

TFE/PMVE was supplied by Du Pont Dow Elastomers L.L.C., and was synthesized using an emulsion polymerization continuous reactor employing an ammonium persulfate free radical initiator.⁵ The fluoroelastomer contained 33 mol % PMVE units, was fully amorphous, and had a glass transition temperature of 276 K. TFE/ PMVE containing 1 wt % TAIC was also obtained from Du Pont Dow Elastomers L.L.C. The mixture was made by fluxing the polymer in a tworoll shear mill at 333–343 K , followed by slow TAIC addition while maintaining a smooth band. TAIC used in the ESR studies was obtained from Aldrich Chemical Company, and was used without any further purification.

Sample Preparation

The TFE/PMVE and TFE/PMVE/TAIC crumb were compression molded between stainless steel plates with Mylar[®] backing sheets at a tempera-

ture of 393 K under a nitrogen atmosphere. Sheets of approximately 1.5-mm thickness were compressed for the tensile tests using dogbones with a gauge length of 15 mm.

Radiolysis

Dogbones were placed in glass tubes and evacuated to a pressure of 10^{-4} Pa for 24 h. The glass tubes were sealed and irradiated using a 60 Co γ -source at the Australian Institute of Nuclear Science and Engineering at a dose rate of 1.9 kGy h^{-1} at room temperature. The glass tubes were opened and the TFE/PMVE samples placed in a vacuum oven at 323 K to expell evolved volatiles. Irradiations in all of the electron spin resonance (ESR) studies were conducted using a Co-60 AECL Gammacell at a dose rate of 1.5 kGy h^{-1} .

Method

Tensile measurements were conducted on an Instron Series IX Automated Materials Testing System 1.23. A crosshead speed of 500 mm/min was used at a temperature of 297 K. Tensile measurements were averaged from four or five identical tests. A Perkin-Elmer Differential Scanning Calorimeter DSC7/TAC7 was employed with a heating range of 223 to 323 K at a scanning rate of 40 K min⁻¹ to determine the glass transition temperatures. Results from two identical DSC scans were averaged to yield the T_{e} .

The sol/gel determinations were performed on molded samples of approximately 1.5-mm thickness with a length of 10 mm and width of 5 mm. Samples were preweighed and placed in stainless steel mesh bags. These were then placed in a soxhlet apparatus from which Freon[®] FC-77 (a mixture of perfluorinated octanes) vapors could condense, thus immersing the sample. The Freon solvent was allowed to drain and refill the soxhlet at regular 10-min intervals during a 48-h period. The samples were dried in a vacuum oven at 353 K and weighed to constant weight. The gel content was determined from the ratio of the weight of the dried extract to the original weight.

ESR studies were performed using a Bruker ER-200D X-band spectrometer. Samples were placed in quartz tubes and sealed at a reduced pressure of 10^{-4} Pa and irradiated at 77 K. TAIC was degassed using five freeze-thaw cycles before being similarly irradiated. Radical yields were measured at 77 K using a liquid nitrogen insert in the ESR spectrometer. Thermal annealing experiments were performed using a variable temperature accessory. ESR samples were annealed at the desired temperature until there was no observed drop in the radical yield. Photo bleaching experiments were carried out *in situ* at 77 K using an Oriel UV lamp model 66021 fitted with a 560 nm filter.

RESULTS AND DISCUSSION

Significant improvements in the tensile properties were obtained for irradiated TFE/PMVE/ TAIC over the entire dose range. The ultimate elongation, stress at break, and the stress at 100% elongation all indicated an enhancement of crosslinking (Fig. 2). The ultimate elongation [Fig. 2(A)] of the TFE/PMVE/TAIC remained consistently lower than TFE/PMVE, indicating a higher crosslink density. TFE/PMVE/TAIC showed a significantly higher stress at break [Fig. 2(B)] and stress at 100% elongation [Fig. 2(C)] over the entire dose range. The stress at break and stress at 100% elongation of unirradiated TFE/PMVE/TAIC were also significantly higher than TFE/PMVE. A comparison of the tensile properties of the irradiated materials at 120 kGy is shown in Table I. The glass transition temperature of unirradiated TFE/PMVE/TAIC (281.6 K) was significantly higher than TFE/PMVE (275 K) (Fig. 3). Upon irradiation, TFE/PMVE/TAIC gave consistently higher glass transition temperatures compared to TFE/PMVE.

Figure 4 shows the effect of added TAIC on the gel behavior of TFE/PMVE. At comparatively low doses, there was a significant increase in the amount of gelation. The dose of gelation, determined by the Charlesby-Pinner relationship,⁶ dropped by 70% with the introduction of TAIC in TFE/PMVE (Table I). However, TFE/PMVE/TAIC showed a decreased response to gelation at higher irradiation doses, producing only 85% gel at 200 kGy compared to 94% gel for TFE/PMVE at the same irradiation dose.

The significant improvements in the tensile properties and increase in the glass transition temperatures of TFE/PMVE when TAIC is incorporated is perhaps attributed to increased aggregation of the carboxylate end groups to form ionomers that act as crosslinks. The carboxylate end groups are formed from the hydrolysis of the sulphate initiator chain ends and form ionomeric crosslinks with Mg^{2+} , which is added as $MgSO_4$ to coagulate the emulsion polymerization.^{7,8} TAIC



Figure 2 Tensile properties of TFE/PMVE (\bullet) and TFE/PMVE/TAIC (\bigcirc); (A) ultimate elongation, (B) tensile stress at break, (C) stress at 100% elongation.

acts as a plasticizer to the polymer and the combination of shear, heat, and plasticization during milling, allows a more efficient formation of ionomeric aggregates. The improvement of tensile properties therefore takes place when TAIC is milled in the fluoroelastomer.

Irradiated TFE/PMVE/TAIC showed improved tensile properties (Fig. 2 and Table I) and higher glass transition temperatures, which is consistant with a more efficient crosslinked network. A previous study of the mechanical properties of γ -irradiated TFE/PMVE indicated that the ionomeric crosslinks were destroyed at doses less than 16 kGy.⁹ Decarboxylation of the ionomeric

Properties	TFE/PMVE	TFE/PMVE/TAIC	TAIC
Gel Dose (kGy) ^a	16	5	
Ultimate elongation % ^b	643.2	463.0	
Stress at break (Mpa) ^b	6.1	17.1	
Stress at 100% elongation ^b	0.9	3.41	
G (radical) ^c	1.1	2.2	1.7

Table I Comparison of the Properties of TFE/PMVE and TFE/PMVE/TAIC

^a Gelation dose for irradiations carried out at room temperature.

^b Tensile tests for dogbones irradiated to 120 kGy.

^c Radical yields measured at 77 K.

crosslinks upon irradiation would lead to the formation of chain end radicals, which would readily be scavenged by, and endlink with, the electron rich allyl functionalities on the TAIC molecule. The trifunctionality of TAIC molecules could provide sites for three successive chain-end radical additions, forming a bridged, crosslinked network. This mechanism also explains the comparatively large amount of gelation that occurs at low doses, as well as the 70% decrease in the dose for gelation. The lower gel content of TAIC/TFE/ PMVE at higher irradiation doses may be attributed to the radiation sensitivity of the TAIC molecule.

Triallylisocyanurate is a well-known radical trap and is used extensively as a crosslinker molecule in the chemical curing of fluoroelas-tomers.^{10–12} Chemical crosslinking proceeds via the formation of a bridged crosslinked network by the



The ESR spectra of TFE/PMVE [Fig. 5(A)] and TFE/PMVE/TAIC [Fig. 5(B)] γ -irradiated at 77 K are similar in shape, and were very broad and featureless, which made elucidation of the spectra



Figure 3 Glass transition temperature measurements determined by DSC of TFE/PMVE (\bullet) and TFE/PMVE/TAIC (\bigcirc).



Figure 4 Percent gelation as a function of γ -irradiation dose of TFE/PMVE and TFE/PMVE/TAIC.



Figure 5 ESR spectra of (A) TFE/PMVE and (B) TFE/ PMVE/TAIC γ-irradiated and acquired at 77 K.

difficult. This is attributed to the large anisotropy of the fluorine hyperfine coupling tensor, as well as the lack of orientation of the sample.¹⁵

The effectiveness of TAIC as a radical trap is clearly demonstrated by the 100% increase in the radical yield at 77 K when TAIC is present in the elastomer (Fig. 6). It is interesting to note that there were linear increases in the radical yields over the entire dose range for both TAIC and TFE/PMVE/TAIC, while the radical concentration for TFE/PMVE was concave to the abscissa. G-values for the total radical production at 77 K obtained from the initial slopes of the radical yields in Figure 6 are given in Table I. The ESR spectra of irradiated TFE/PMVE [Fig. 5(A)] and TFE/PMVE/TAIC (Fig. 5(B)] at 77 K are identical, which indicated that the same radical species were present in both systems.

The nonlinearity of the radical yield, especially at higher doses, for the neat elastomer indicated a

higher rate of cage recombination. This was effectively reduced with the presence of TAIC in the elastomer. The F atom is isosteric with the hydoxy group OH,¹⁶ so limited mobility at 77 K would be expected. The F·radical may, therefore, preferentially migrate to and be scavenged by the electron rich TAIC molecule. Cage recombination reactions of the F·radicals with polymeric radicals would, therefore, be reduced, effectively increasing the concentration of the polymeric radicals.

Solid-state ¹⁹F-NMR studies of irradiated TFE/ PMVE have indicated Y-linking from recombination of a $-CF_2$ chain end radicals with chain radicals, $-CF_2-C \cdot F - CF_2 - .^{13}$ Formation of saturated chain ends ($-CF_2-CF_3$) by the recombination of chain end radicals $-CF_2$, with F· radicals were also observed. This reaction would therefore compete with the Y-linking of TFE/ PMVE, as both processes involve the recombination of chain end radicals. When TAIC is incorporated in TFE/PMVE, it may increase the crosslinking yield by trapping F· radicals that would otherwise recombine with the polymeric radicals.

The interaction of ionizing radiation with molecules containing allylic functionalities has been previously investigated using ESR. Maas and Volman¹⁷ conducted ESR studies on UV irradiated 2-buten-1-ol at 77 K and identified a five-line spectrum with an average peak separation of 1.50 mT and total spread of 6 mT. Some of the outer peaks showed small splittings of 0.4 mT. The ESR spectrum was assigned to an allyl radical indicat-



Figure 6 Radical yields as a function of radiation dose at 77 K for TFE/PMVE, TFE/PMVE/TAIC, and neat TAIC. γ-Irradiations were carried out at 77 K.



Figure 7 ESR spectra of TAIC γ -irradiated at 77 K (A) measured at 77 K, (B) after photobleaching > 560 nm for 30 min at 77 K, (C) after photobleaching and thermal annealing at 220 K.

ing primary cleavage of the alcohol functionality. Upon heating to 106 K, the five-line spectrum was replaced with four lines with a peak separation of 1.47 mT and a total spread of 4.4 mT. This spectrum was attributed to an α -hydroxyallyl radical. Cochran et al.¹⁸ also obtained a similar five-line ESR spectrum from the photolysis of allyl iodide at 4.2 K.

The ESR spectrum of TAIC, γ -irradiated to 2.11 kGy at 77 K, showed a sharp singlet with a peak to peak width of 0.65 mT and g-value of 2.00359 [Fig.

7(A)]. This ESR spectrum was assigned to a carbonyl radical anion [Fig. 8(A)]. Small unresolved shoulders were also present in the spectrum of TAIC. Photobleaching for 30 min at 77 K using long wavelength visible radiation with a cutoff of 560 nm resulted in a continual reduction in the intensity of the singlet, as well as the formation of four new absorbances on the shoulders of the singlet [Fig. 7(B)]. No change in the radical yield was observed after photobleaching. The outer four lines in the spectrum are believed to be part of a five line spectrum, with the central peak hidden under the large singlet. The five-line spectrum is assigned to the allyl radical:



Figure 8 Proposed mechanism for the γ -radiolysis of TAIC.



The allylic radical couples with the four α -hydrogens on the CH₂ groups producing a five-line spectrum with a 1.3 mT splitting. Coupling with the central β proton provides further splitting of 0.44 mT. The total width of the spectrum was approximately 6.0 mT. It, therefore, appeared that photobleaching (>560 nm) of the carbonyl radical anion at 77 K resulted in radical transfer, and ultimately, cleavage of an allyl radical from the isocyanurate ring as shown in Figure 8. This allylic radical was thermally stable up to 180 K, which was 116.5 K below the melting temperature of TAIC. At 220 K, the five-line spectrum disappeared and was replaced with a four-line spectrum that was also partly masked by the singlet, which had decreased in intensity [Fig. 7(C)]. The four-line spectrum has an average splitting of 1.4 mT and a total width of 4.8 mT, and is assigned to another allylic radical as shown in Figure 8(B).

CONCLUSIONS

The addition of 1% TAIC enhances the radiation crosslinking of TFE/PMVE, which imparts superior mechanical properties to the polymer. Possible mechanisms for the enhancement crosslinking include: (1) TAIC reacts with the chain-end radicals formed after decarboxylation of the carboxylate ends groups. (2) Polymer chain radicals can add to the allyl double bonds of TAIC giving a bridged crosslinked network. (3) TAIC can preferentially trap F·radicals, which would otherwise recombine with polymeric radicals. An increase in polymeric radicals would ultimately increase the yield of Y-linking within the polymer.

The authors wish to thank the Australian Institute of Nuclear Science and Engineering for use of their facilities and Dr. John Lyons for his helpful discussions.

REFERENCES

- 1. Lyons, B. J. Radiat Phys Chem 1995, 45, 159.
- Cross, P. E.; Lyons, B. J. Trans Faraday Soc 1963, 59, 2350.
- Miller, G. A.; Sperling, L. H. Polym Eng Sci 1982, 22, 478.
- 4. Saito, M. Jpn Kokai Tokkyo Koho 1995, 179, 705.
- 5. Logothetis, A. L. J Appl Polym Sci 1997, 63, 147.
- Charlesby, A.; Pinner, S. H. Proc R Soc Lond 1958, 249A, 369.
- 7. Logothetis, A. L. Prog Polym Sci 1989, 14, 251.
- Logothetis, A. L. In Macromolecular Design of Polymeric Materials; Hatada, K.; Kitayama, T.; Vogl, O., Eds.; Marcel Dekker Inc.: New York, 1997, p. 447.
- 9. Forsythe, J. S.; Hill, D. J. T.; Logothetis, A. L.; Seguchi, T.; Whittaker, A. K. Radiat Phys Chem, to appear.
- 10. Apotheker, D.; Finlay, J. B.; Krusic, P. J.; Logothetis, A. L. Rubber Chem Technol 1982, 55, 1004.
- Oka, M.; Tatemoto, M. In Contempory Topics in Polymer Science; Bailey, W. J.; Tsuruta, T., Eds.; Plenum Press: New York, 1984, p. 763.
- Schmiegel, W. W.; Logothetis, A. L. In Polymers for Fibres and Elastomers; ACS Symposium Series 260; American Chemical Society: Washington, DC, 1984, p. 159, vol. 10.
- 13. Forsythe, J. S.; Hill, D. J. T.; Logothetis, A. L.; Seguchi, T.; Whittaker, A. K. Macromolecules, to appear.
- Pacansky, J.; Waltman, R. J.; Jebens, D. Macromolecules 1996, 29, 7699.
- 15. Ovenall, D. W. J Chem Phys 1963, 38, 2448.
- Smart, B. E.In Organofluororine Chemistry: Principles and Commerial Applications; Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds.; Plenum Press: New York, 1994, p. 57.
- 17. Maas, K. A.; Volman, D. H. Trans Faraday Soc 1964, 60, 1202.
- Cochran, E. L.; Adrian, F. J.; Bowers, V. A. J Chem Phys 1961, 34, 1161.