

^{60}Co - γ -ray-Induced Graft Copolymerization of Methylmethacrylate onto EPDM Rubber: Improved Oil Resistivity

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ABSTRACT: Attempts have been made to impart oil resistivity to the surface of nonpolar ethylene-propylene-terpolymer rubber by gamma radiation grafting of methyl methacrylate (MMA) monomer onto this rubber using a simultaneous technique. The effect of monomer concentration on the graft level has been studied. Grafted samples have been characterized using attenuated total reflectance infrared, scanning electron microscopy, energy dispersive X-ray analysis, and optical microscopy. The oil resistivity of the modified vulcanizates has been evaluated and compared with that of nitrile rubber. The effect of multifunctional acrylates on the grafting behavior of this monomer has also been studied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 25–31, 1998

Key words: oil resistivity; graft copolymerization; methylmethacrylate; γ -ray

INTRODUCTION

The surface properties of polymers are important for various applications. These include adhesion, chemical resistivity, and paintability. Therefore, to render a polymer with the optimum bulk mechanical properties suitable for certain applications, its surface may need to be modified. The radiation-induced grafting of vinyl monomers has been found to be an efficient method for this purpose, and many reports have been published by Chapiro,¹ Ratner and Hoffman,² and coworkers, Dworjanyn,^{3,4} Ang et al.⁵ and Garnett et al.⁶ Methacrylic acid has been grafted onto polypropylene, reported by Mukherjee and Gupta,⁷ and graft copolymerization of acrylonitrile onto natural rubber (NR) has also been reported by Claramma et al.⁸ *N*-Vinylpyrrolidone (NVP) and hydroxyethyl methacrylate (HEMA) have been grafted onto EPDM rubber for improved surface wet-

tability using ^{60}Co - γ -radiation (Katbab et al.⁹). CO_2 pulsed laser-induced grafting of acrylamide (AAM) has also been carried out (Mirzadeh et al.^{10,11}) for the purpose of improved biocompatibility.

EPDM rubber has a saturated structure, which is resistive towards ozone deterioration, with excellent bulk mechanical properties. However, this polymer tends to swell in contact with paraffinic oil and aromatic hydrocarbons. On the contrary, nitrile rubber shows good resistance in such media but it suffers from deterioration by ozone cracking. In the present work, methyl methacrylate (MMA) has been graft-polymerized onto the surface of ethylene-propylene-terpolymer (EPDM) rubber by the use of ^{60}Co - γ -radiation as an excitation source, and the percentage of oil absorption of the treated samples has been evaluated and compared with that of commercial nitrile rubber.

EXPERIMENTAL

Materials

The characteristics of the raw EPDM used are shown in Table I. MMA (Merck) was purified by

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Table I Characteristics of the Raw EPDM Rubber

Company	Uniroyal
Trade name	Royalene
Density	0.865 g/cm ³
Mooney viscosity (ML 1 + 4/125°C)	35–49
E/P ratio	68/32

vacuum distillation prior to use, and trimethylolpropane trimethacrylate (TMPTMA) (Merck) was purified by passing through alumina.

Preparation of Vulcanizates

Raw EPDM rubber was premastered by two-rolled mill for 5 min at 75°C and then 5% dicumyl peroxide was added to the rubber and mixing was continued up to 10 min.

The compounded rubber was molded into 1.5 mm thick sheets at 170°C (12 min) using a Daventest compression press. The sheets were cut into 10 × 100 mm strips and then Soxhlet-extracted with a mixture of methanol–toluene (50 : 50) for 15 h. To remove the residual organic solvents, the extracted samples were dried in vacuum to constant weight.

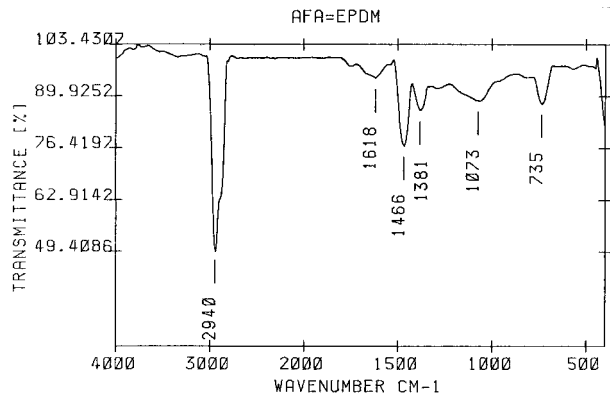


Figure 2 ATR-FTIR spectrum of the unmodified EPDM vulcanizate.

Irradiation Procedure

Graft polymerization was carried out by the mutual method using ⁶⁰Co- γ -ray as the irradiation source. The prepared samples were put into glass tubes containing a monomer–methanol mixture. The dissolved oxygen in the mixture was replaced by nitrogen, and then the tubes were sealed. The tubes were irradiated in a ⁶⁰Co- γ -radiation source at a rate of 0.8 Mrad/h for 30 min. After each exposure, the samples were removed and washed first with warm acetone and then thoroughly extracted with acetone for

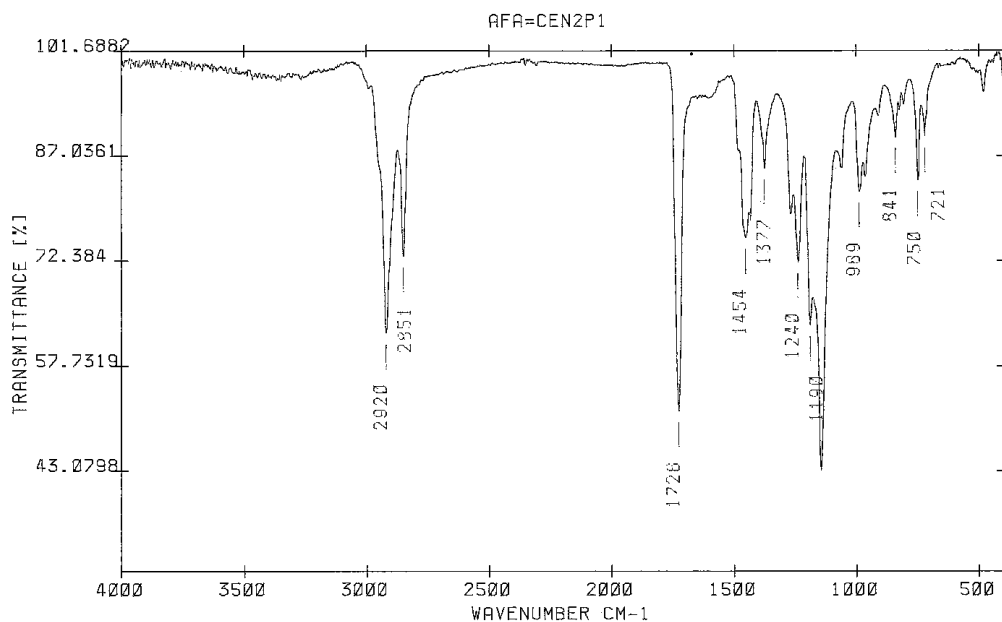


Figure 1 ATR-FTIR spectrum of EPDM vulcanizate modified with MMA (graft degree = 5.0 wt %).

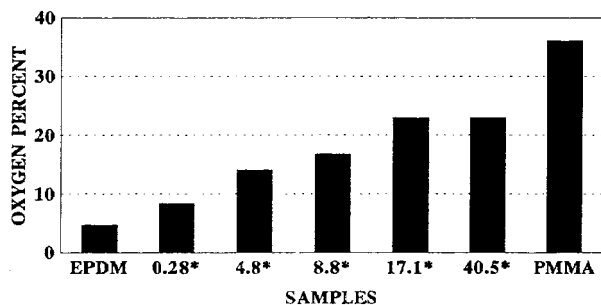


Figure 3 Percentage of oxygen on the surface of modified EPDM vulcanizates versus MMA graft degree (the asterisk indicates MMA graft degree in wt %).

24 h to remove unreacted monomer and external homopolymers. The extracted samples were then dried in vacuum to constant weight. The graft degree was determined gravimetrically using the following equation:

$$\text{Graft Degree (Wt \%)} = \frac{W_g - W_i}{W_i} \times 100$$

where W_i and W_g are the weight of the dried unmodified and extracted modified samples, respectively.

Characterization of the Grafted Samples

The grafted samples were analyzed by the following techniques.

1. Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) with a TLBr₃ prism and an incident angle of 45°. The absorption band within the range of 1730–1720 cm⁻¹ attributed to the $\text{C}=\text{O}$ group of the grafted polymethyl methacrylate was measured. In this range, no absorption was observed in the FTIR spectrum of the unmodified EPDM.
2. Scanning electron microscopy (SEM) was performed on the surface of the gold-coated samples to study the surface morphology. For this purpose, a cambridge STEREOSCAN 360 SEM operating at 10 KV was employed.
3. Energy dispersive X-ray analysis (EDXA) was used for the determination of the oxygen content on the treated surfaces.
4. The depth of the graft layer was studied by the use of optical microscopy (OM). For this purpose, the grafted surfaces were stained in a 3% solution of eosin as a staining agent in an acetone–ethanol (50/50 by volume) solution. The stained samples were washed with

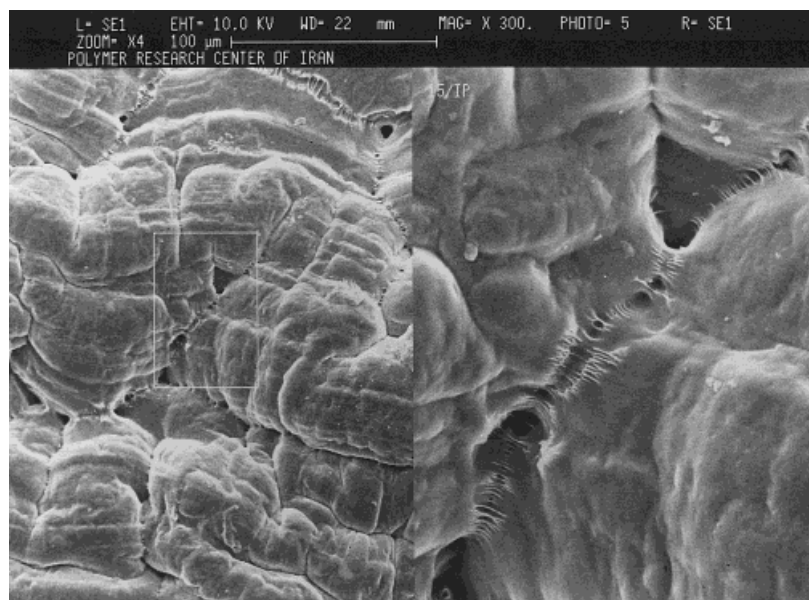


Figure 4 SEM photomicrograph of the surface of EPDM vulcanizate modified with MMA (graft degree = 21 wt %).

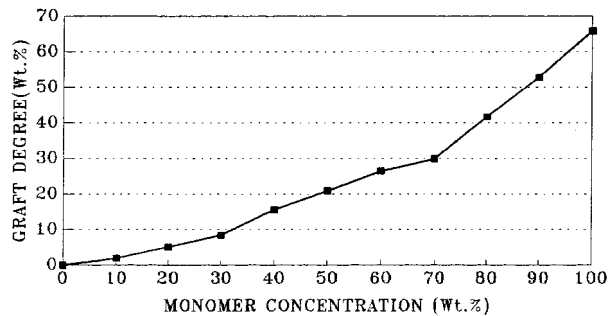


Figure 5 Variation of the graft degree of MMA onto EPDM versus the monomer concentration.

warm distilled water and then dried for the microscopic examination.

Mechanical Properties and Oil Absorptivity Measurement

Hardness

Hardness of the samples was measured at room temperature, using a Wallace microhardness tester.

Tensile Properties

Tensile properties of the samples with the dimensions in accord with ASTM-D412 were measured using an 6025 instron tensometer with the extension rate of 100 mm/min at room temperature.

Fatigue-to-Failure Test

Flex resistance of the modified samples was measured and compared with that of ungrafted ones using a Monsanto fatigue-to-failure tester with the extension of 1.61 ± 0.04 and 104 cycle per min.

The percentage of oil absorbance of the samples was determined at room temperature using the following equation:

$$\text{wt \% oil absorbed} = \frac{w_{ab} - w_i}{w_i} \times 100$$

where w_{ab} and w_i are the weights of the swelled and initial dried samples, respectively.

RESULTS AND DISCUSSION

Figure 1 illustrates the ATR-IR spectrum of a MMA-grafted EPDM vulcanizate with a graft de-

gree of 5.0 wt %. The absorption peak at 1726 cm^{-1} is attributed to the poly(MMA) (PMMA) grafted onto the EPDM surface, while this peak is absent in the spectrum of the unmodified EPDM vulcanizate (Fig. 2). This is inconsistent with the EDXA data, which shows a higher oxygen percentage on the surface of the modified EPDM samples compared with that of unmodified sample (Fig. 3). A typical SEM photomicrograph of a PMMA-grafted EPDM sample is shown in Figure 4. The formation of a dense microlayer on top of the extracted modified samples and different surface morphology compared with that of unmodified surface evidently shows that PMMA has been grafted onto the EPDM surface. The effect of the MMA concentration upon the graft yield is also demonstrated in Figure 5. It is clearly seen that increasing the monomer concentration leads to the increase in the yield of graft copolymerization of MMA. However, at a low monomer concentration, the yield of grafting is not significant, although the bulk mechanical properties (hardness, extensibility) of the samples are almost retained. Above a monomer concentration of 30 wt %, which is associated with the graft degree of 12 wt %, the surface roughness of the samples increases and the rubbery behavior is lowered, which could be explained to be due to higher monomer penetration into the bulk of the samples.

To increase the efficiency and, therefore, the yield of graft copolymerization at low monomer concentration, and also keeping the reaction mainly on the surface, TMPTMA was employed into the reaction system. The graft level for 10% MMA concentration was enhanced by the addition of this triacrylate monomer, as shown in Figure 6. The effectiveness of TMPTMA in the radiation

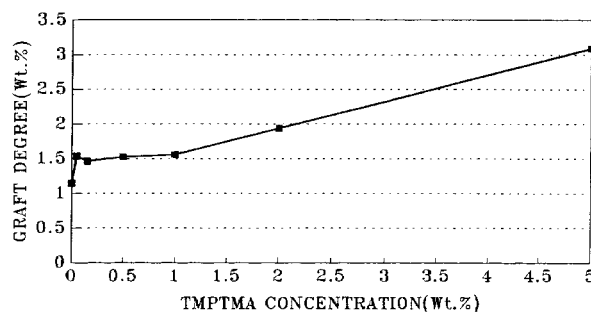


Figure 6 Variation of the graft degree of MMA onto EPDM vulcanizate versus TMPTMA concentration as a multifunctional monomer (monomer concentration in methanol = 10 wt %).

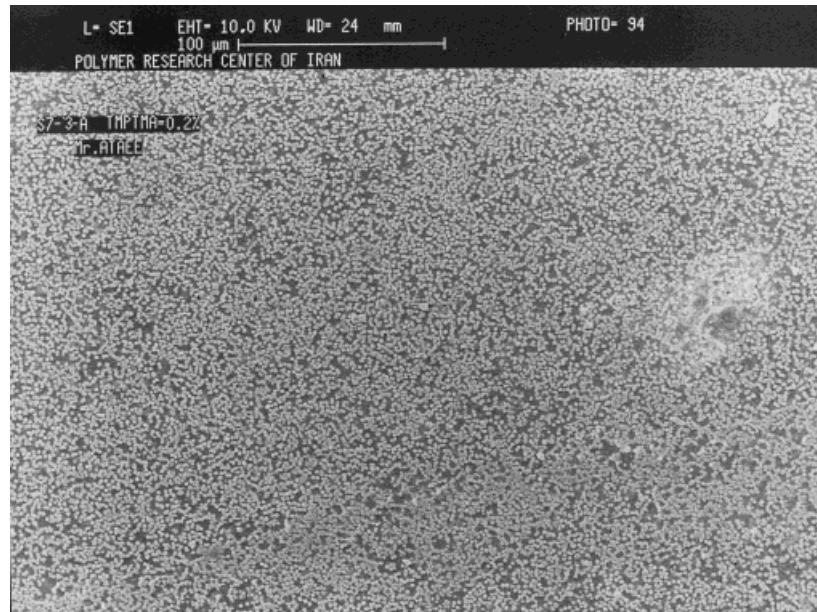


Figure 7 SEM photomicrograph of the EPDM vulcanizate modified with MMA in the presence of 0.2 wt % of TMPTMA (graft degree = 7.9 wt %; monomer concentration in methanol = 20 wt %).

grafting of vinyl monomers onto various polymeric substrates has also been reported (Katbab et al.⁹ and Dworjany and Garnett¹²). As the

grafting reactions, which are initiated by high-energy radiation, are radical in nature, it is believed that TMPTMA through its acrylic func-

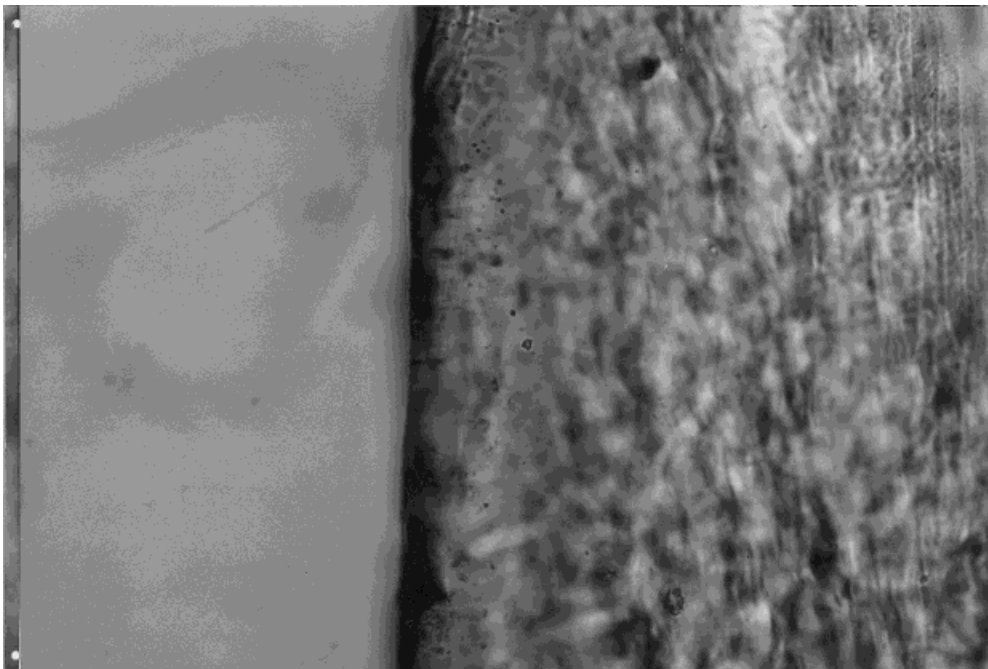


Figure 8 OM photomicrograph of the cross section of an eosin-stained MMA-modified EPDM vulcanizate (magnification = $\times 200$).

Table II Variation of the Grafted Layer Thickness Versus the Graft Degree of MMA Onto EPDM Vulcanizates

Graft Degree (wt %)	Graft Thickness (μm)
7.25	20–30
10.9	50–65
14.4	95–100
19.0	125–135
25.0	175–185
30.1	200–205
36.0	200–215
39.4	210–225
48.0	>220
59.4	>220

tional groups increases the sites of monomer consumption and leads to the formation of a three-dimensional graft network on the surface of the substrate. The uniformity of the sites of grafting on the surface of EPDM in the presence of TMPTMA is clearly seen in SEM photomicrograph shown in Figure 7.

In order to measure the depth of grafting, cross sections of the modified samples were stained by eosin solution, which could stain the grafted sites on the modified surfaces. In Figure 8, a typical OM photomicrograph of a stained cross section of a sample with 10.9 wt % graft level is given. The red region with the depth of 65 μm clearly shows the extent of graft penetration. Table II does also show the increase in graft penetration with an increase in graft degree (monomer concentration).

The effects of the graft copolymerization of MMA onto the EPDM vulcanizates upon the mechanical properties have been demonstrated in Figures 9–11. It is obvious that above the graft

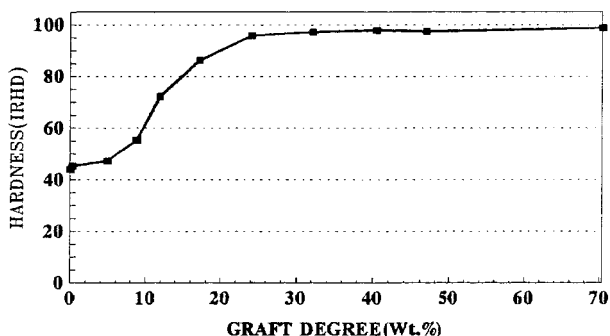


Figure 9 Hardness variation of the MMA-modified EPDM samples versus graft degree.

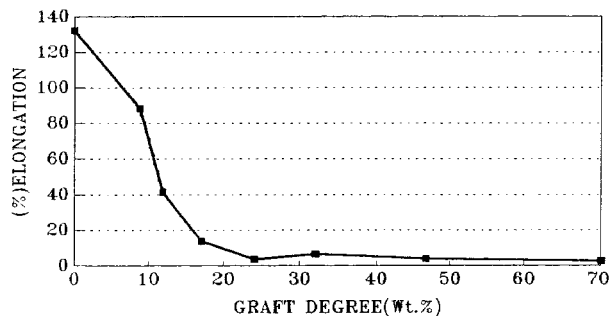


Figure 10 Variation of the percentage of elongation at break of modified EPDM vulcanizates versus the MMA graft degree (tensile rate = 100 mm/min; room temperature).

level of approximately 10 wt %, the hardness of the sample increases and the rubbery behavior decreases. This is attributed to the higher penetration of grafting into the bulk of the vulcanizates (Table II), which leads to the increase of stiffness and, therefore, less extensibility of the samples.

The effect of the MMA grafting onto the surface of EPDM vulcanizate upon the oil resistivity of this nonpolar rubber is also shown in Figure 12. It is clearly seen that the modified samples show more resistance towards the hydraulic oil compared with that of ungrafted ones, which indicates the increase in the surface polarity of this polymer. These results leads to the conclusion that by this technique, it would be possible to prepare oil-resistant samples from EPDM rubber with high resistance towards ozone degradation compared with that of acrylonitrile butadiene rubber (NBR), which is easily attacked by the molecules of the atmospheric ozone.

CONCLUSION

The results obtained in this work show that MMA monomer can be grafted onto the surface of the

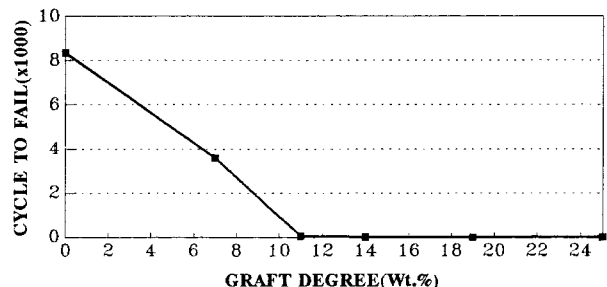


Figure 11 Fatigue life of MMA-modified EPDM vulcanizates versus the graft degree.

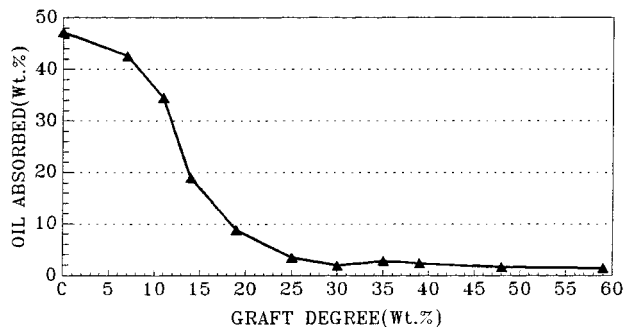


Figure 12 Oil absorbance of EPDM vulcanizates modified with MMA versus the graft degree (tested in hydraulic oil with aniline point of 91°C for 48 h). Oil absorbance of NBR (33% ACN) vulcanizate \cong 3.6%.

EPDM vulcanizate using ^{60}Co - γ -ray as excitation source. The graft yield is substantially enhanced in the presence of multifunctional monomers, such as TMPTMA. The oil resistance of EPDM rubber towards the hydraulic oils is significantly increased by this method.

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REFERENCES

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley, New York, 1962.
2. B. D. Ratner and A. S. Hoffman, *J. Appl. Polym. Sci.*, **18**, 3183 (1974).
3. P. A. Dworjanyan, B. Fields, and J. L. Garnett, *ACS Symp. Series*, 381, 1989.
4. P. A. Dworjanyan and J. L. Garnett, *Radiat. Phys. Chem.*, **33**, 429 (1989).
5. C. H. Ang, J. L. Garnett, R. Lovert, and M. S. Long, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 257 (1983).
6. J. L. Garnett and N. T. Yen, *ACS Symp. Ser.*, **2**, (1980).
7. A. K. Mukherjee and B. D. Gupta, *J. Appl. Polym. Sci.*, **30**, 2643 (1985).
8. N. M. Claramma, N. M. Mathew, and E. V. Thomas, *Radiat. Phys. Chem.*, **33**, 87 (1989).
9. A. A. Katbab, R. P. Burford, and J. L. Garnett, *Radiat. Phys. Chem.*, **39**, 293 (1992).
10. H. Mirzadeh, A. A. Katbab, and R. P. Burford, *Radiat. Phys. Chem.*, **41**, 507 (1993).
11. H. Mirzadeh, A. A. Katbab, and R. P. Burford, *J. Die Angewadte, Macromol. Chem.*, **218**, 23 (1994).
12. P. A. Dworjanyan and J. L. Garnett, *Proceedings of the International Meeting in Grafting Processes on Polymer Films and Surfaces: Scientific and Technical Aspects*, No. 5, I. R. Bellobon, Ed., Universita Deglistudi di Milano, Italy, 1990, p. 61.