

# Evidence of Irradiation-Induced Crosslinking in Miscible Blends of Poly(vinyl chloride)/Epoxidized Natural Rubber in Presence of Trimethylolpropane Triacrylate

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**ABSTRACT:** Electron-beam initiated crosslinking of a poly(vinyl chloride)/epoxidized natural rubber blend (PVC/ENR), which contained trimethylolpropane triacrylate (TMPTA), was carried out over a range of irradiation doses (20–200 kGy) and concentrations of TMPTA (1–5 phr). The gelation dose was determined by a method proposed by Charlesby. It was evident from the gelation dose, resilience, hysteresis, glass-transition temperature ( $T_g$ ), IR spectroscopy, and scanning electron microscopy studies that the miscible PVC/ENR blend underwent crosslinking by electron-beam irradiation. The acceleration of crosslinking by the TMPTA was further confirmed in this study. Agreement of the results with a theory relating the  $T_g$  with the distance between crosslinks provided further evidence of irradiation-induced crosslinking. The possible mechanism of crosslinking induced by the irradiation between PVC and ENR is also proposed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1914–1925, 2001

**Key words:** poly(vinyl chloride)/epoxidized natural rubber blend; irradiation; irradiation induced crosslinking; trimethylolpropane triacrylate

## INTRODUCTION

Blending generically different existing polymers has developed into a technologically important area, because it can offer new materials with enhanced specific properties or a better combination of properties. In this respect, poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) have attracted the attention of many researchers.<sup>1–9</sup> ENR forms miscible blends with PVC<sup>3,5,9</sup> in which PVC is expected to impart high tensile strength and good chemical resistance whereas ENR acts as a permanent plasticizer to PVC, induces good

tear strength, and enhances resistance against hydrocarbon oils. It was reported that PVC and ENR form self-crosslinkable blends.<sup>10,11</sup> Mousa et al.<sup>12,13</sup> studied various properties of dynamically vulcanized PVC/ENR blends.

Modification of polymers in the presence of irradiation is a potential method for the development of new polymers and composites. Since the 1950s rubbery polymers<sup>14</sup> and PVC<sup>15</sup> have been made crosslinkable by exposing them to high energy irradiation. The use of polyfunctional polymers in irradiation crosslinking formulations was found to be very effective in decreasing the dose level to achieve optimum properties without much deterioration in the base polymers.<sup>15–17</sup> Irradiation crosslinking has many advantages such as being fast and energy saving and creating no

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pollution.<sup>18</sup> Hence, in recent years irradiation modification of blends has generated interest among the researchers in the field. Spenandel<sup>19</sup> reported on the irradiation crosslinking of polymer blends of ethylene propylene copolymer and polyethylene. Akhtar et al.<sup>20</sup> studied the tensile failure of  $\gamma$ -ray irradiated blends of high density polyethylene and natural rubber. Ivehenko et al.<sup>21</sup> studied the irradiation modification of blends of polyethylene and certain elastomers such as chlorosulfonated polyethylene, butyl rubber, cross-linked polyethylene, and polyisobutylene. With regard to the PVC/ENR blend, we highlighted the potential for modification of the blends by electron-beam irradiation.<sup>22–25</sup> The acceleration of crosslinking by the addition of polyfunctional monomers was also reported.<sup>26</sup> In this article an attempt to further consolidate the irradiation-induced crosslinking of PVC and ENR is presented. The acceleration of crosslinking by the addition of a crosslinking agent is examined with several theories. Evidence from Fourier transform IR (FTIR) techniques and scanning electron microscopy (SEM) are also employed. The prime objective here is to provide more evidence on the irradiation-induced crosslinking that was not reported previously.

## EXPERIMENTAL

### Materials

The ENR (Epoxyprene 50) with a 50% epoxidation level was supplied by Guthrie Polymer Ltd. as a free sample. The PVC ( $K = 66$ ,  $M_n = 66,000$ ; grade MH66, 6519) was purchased from Industrial Resin (M) Ltd.

The tribasic lead sulfate (TS-100M) used as the PVC stabilizer was purchased from Lonover Scientific Suppliers Ltd. (London). Trimethylolpropane triacrylate (TMPTA) was a product of UCB Asia Pacific. These compounds were used as received.

### Formulations

The 50/50 PVC/ENR blends were prepared by mixing 50 parts of PVC with 50 parts of ENR50. The recipes are given in Table I.

### Blend Preparations

The PVC, stabilizer and the TMPTA were pre-mixed at room temperature in a tabletop high-speed mixer at 1200 rpm for 10 min. Melt blend-

**Table I Recipes of 50/50 PVC/ENR Blend**

Material	Formulation (phr)
PVC	50
ENR	50
Tribasic lead sulfate	2
TMPTA	0–5

ing was carried out at 150°C with a 50 rpm rotor speed in a Brabender Plasticorder (model PL 2000) with a mixing cam attachment. When the desired temperature was reached, ENR was charged into the mixing chamber and mixed for 1 min. The PVC compound was then added, and the blending was continued for a further 9 min.

The blends obtained from the Brabender Plasticorder were then compression molded into 1 mm thick sheets under a pressure of 14.7 MPa at 150°C for 3 min. The sheets were immediately cooled between two plates of a cold press at 25°C. Dumbbell-shaped test pieces were cut from these sheets in accordance with BS6746.

### Irradiation

The molded sheets and dumbbell test pieces were irradiated using a 3-MeV electron-beam accelerator at a dose range of 0–200 kGy. The acceleration energy, beam current, and dose rate were 2 MeV, 2 mA, and 10 kGy/pass, respectively.

### Gel Fraction

The gel fraction was determined by extraction in tetrahydrofuran (THF) at  $50 \pm 2^\circ\text{C}$ . The blends were solvent extracted with THF for 24 h, and the extracted samples were dried to constant weight. The gel fraction was calculated as

$$W/W_0 \quad (1)$$

and the soluble fraction ( $s$ ) as

$$s = 1 - \text{gel fraction}$$

where  $W$  and  $W_0$  are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively.

### Resilience

The resilience test was carried out using a Dunlop Pendulum according to BS903 (Part A8), and the rebound resilience ( $R$ ) was calculated as follows:

$$R = \frac{1 - \cos(\text{angle of rebound})}{1 - \cos(\text{angle of fall})} \times 100 \quad (2)$$

The energy not recovered is the hysteresis and it appears as heat (hysteresis = 100 - resilience).

### Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed using a Perkin-Elmer DMA-7e in the temperature-time scan mode with a parallel plate attachment. The measurements were carried out at a heating rate of 10°C/min over a temperature range of -50 to 120°C and a frequency of 1 Hz.

### FTIR Spectroscopy

The FTIR spectra were obtained using a Perkin-Elmer Spectrum 2000 FTIR and the Diamond attenuated total reflectance technique. The spectrometer was operated with a resolution of 4 cm<sup>-1</sup> and the scanning range was 4400-600 cm<sup>-1</sup>.

For selected samples the spectral changes as a consequence of irradiation were obtained by subtraction of the spectra:

$$\begin{aligned} \text{difference spectrum} &= k_o(\text{irradiated spectrum}) \\ &- k_u(\text{unirradiated spectrum}) \end{aligned}$$

where  $k_o$  and  $k_u$  are variables, which can be used to compensate for variations in the film thickness. The  $k_o$  and  $k_u$  were kept constant in this experiment by scanning an identical spot of the same film for both tests, so that  $k_o/k_u = 1$ . Absorption above the baseline indicated the formation of new species or an increment in concentration of existing ones, while those below indicated a decrease in existing species.

### SEM Examination

Selected samples were manually fractured at liquid-nitrogen temperature. The fractured surfaces were then sputter coated with gold and examined using a Philip 515 scanning electron microscope. The SEM observations were also made on unfractured sample surfaces by a similar procedure.

## RESULTS AND DISCUSSION

### Gelation Dose

The theory of irradiation crosslinking of polymers was elaborated on the basis of a probabilistic ap-

proach.<sup>27</sup> In general, radiation crosslinking of polymers was treated with the Charlesby-Pinner<sup>27</sup> relationship:

$$(S + S^{1/2}) = p_o/q_o + 1/q_o U_1 R \quad (3)$$

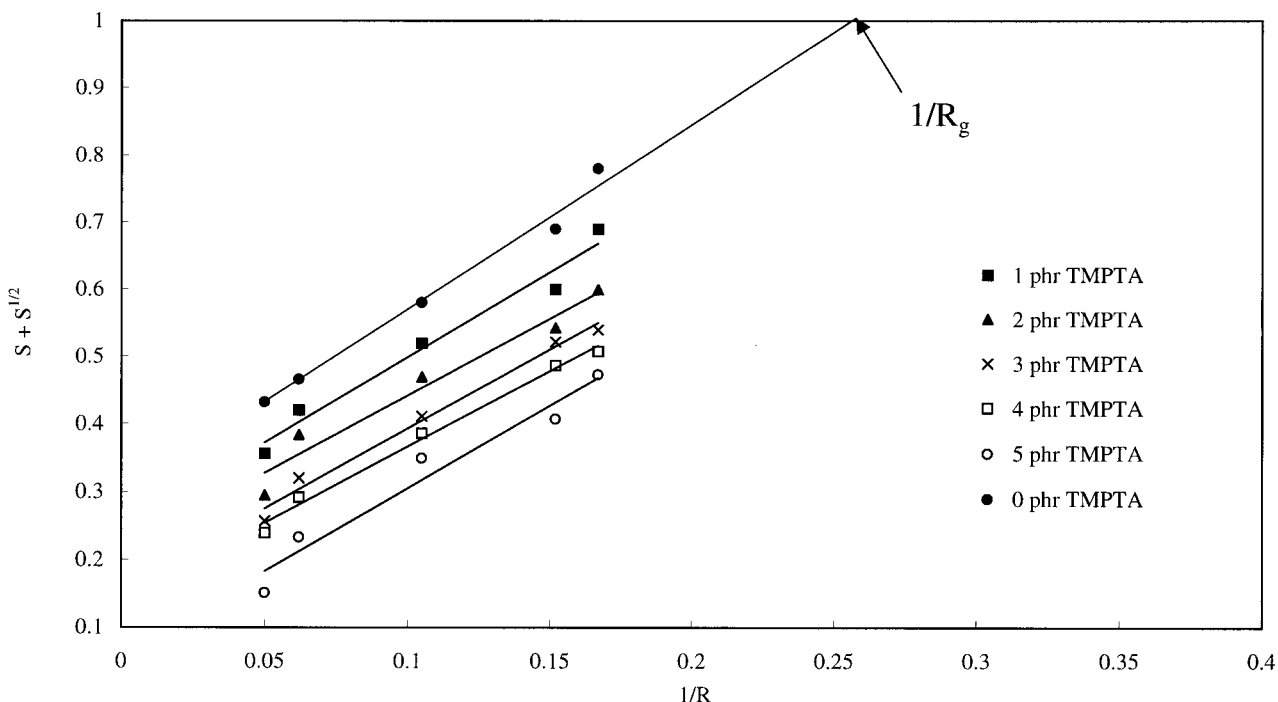
where  $S$  is the sol fraction;  $R$  is the radiation dose;  $p_o$  is the fracture density, which is the density of main chain scission per unit dose;  $q_o$  is the crosslink density for the portion of units crosslinked per unit dose; and  $U_1$  is the initial number-average degree of polymerization.

The point at which an insoluble network (when there is an average of one crosslink unit per weight network) first begins to form is termed the gel point, and the corresponding irradiation dose is the gelation dose ( $R_g$ ). It is determined by the relation

$$R_g = 1/2q_o U_1 \quad (4)$$

Charlesby and Pineer found that the  $R_g$  can be determined by an extrapolation of the linear dependence of  $S + S^{1/2}$  on  $R^{-1}$ .<sup>27</sup> In Figure 1 the dependencies of  $S + S^{1/2}$  on  $R^{-1}$  are shown at various TMPTA levels. The values of  $R_g$  obtained from this figure are summarized in Table II. It is apparent from Figure 1 and Table II that the  $R_g$  decreases with increasing TMPTA content, indicating acceleration of the irradiation-induced crosslinking by the TMPTA.

The exposure of PVC to ionizing irradiation results in an effect similar to the thermal degradation of PVC in inducing a free-radical chain reaction accompanied by the formation of allylic labile chlorine groups and the evolution of hydrogen chloride.<sup>28,29</sup> The studies of epoxy stabilization of PVC by Anderson and McKenzie,<sup>30</sup> which were based on low molecular weight models, revealed that the stabilization of PVC by the epoxy plasticizers is not based on the acid (HCl) accepting property of the oxirane function to form the corresponding chlorohydrin. Rather, the epoxide rings are opened to form ether links. A similar mechanism is believed to occur during irradiation of PVC in the presence of ENR. The reaction scheme could be represented as shown in Scheme 1. Ramesh and De<sup>10</sup> also arrived at a similar reaction as a plausible mechanism of crosslinking between PVC and ENR in their work on self-crosslinkable plastic-rubber systems based on PVC/ENR blends.



**Figure 1** The dependence of  $(S + S^{1/2})$  on  $1/R$  for the 50/50 PVC/ENR blend at various TMPTA levels;  $S$ , the sol fraction;  $R$ , the dose (Mrad).

Dworjany et al. provided a good description of the acceleration of irradiation-induced crosslinking by multifunctional additives such as TMPTA.<sup>31</sup> The addition of TMPTA is expected to accelerate the above reaction (Scheme 1) by forming crosslink bridges between the PVC and ENR, thus accounting for the lower gelation dose observed. This aspect is further demonstrated along with the FTIR results discussed later in this report.

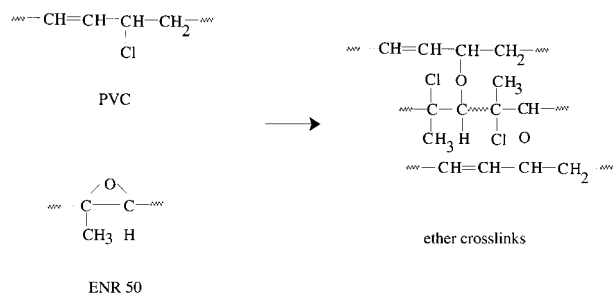
### Resilience

Figure 2 shows the effect of TMPTA on the resilience of the PVC/ENR blend upon electron-beam irradiation. The resilience was found to increase

with the irradiation dose. A further enhancement in the resilience with the addition of TMPTA was also observed. This could reflect the occurrence of irradiation-induced crosslinking and an increase in the extent of crosslinking with the addition of TMPTA. Such observations may indicate that the molecular retractability of the network upon deformation had been increased; that is, the elastic behavior of the blend became more pronounced upon irradiation. A similar trend was also reported by several researchers for the general effects of vulcanization on the resilience properties of elastomers and elastomer blends.<sup>13,32</sup> However, the irradiation of the PVC/ENR blend above 60 kGy in the presence of 5 phr TMPTA resulted in

**Table II** Gelation Dose ( $R_g$ ) of 50/50 PVC/ENR Blend at Various TMPTA Levels

TMPTA Level (phr)	$R_g$ (kGy)
0	39.37
1	33.6
2	29.08
3	27.91
4	26.17
5	25.97



**Scheme 1**

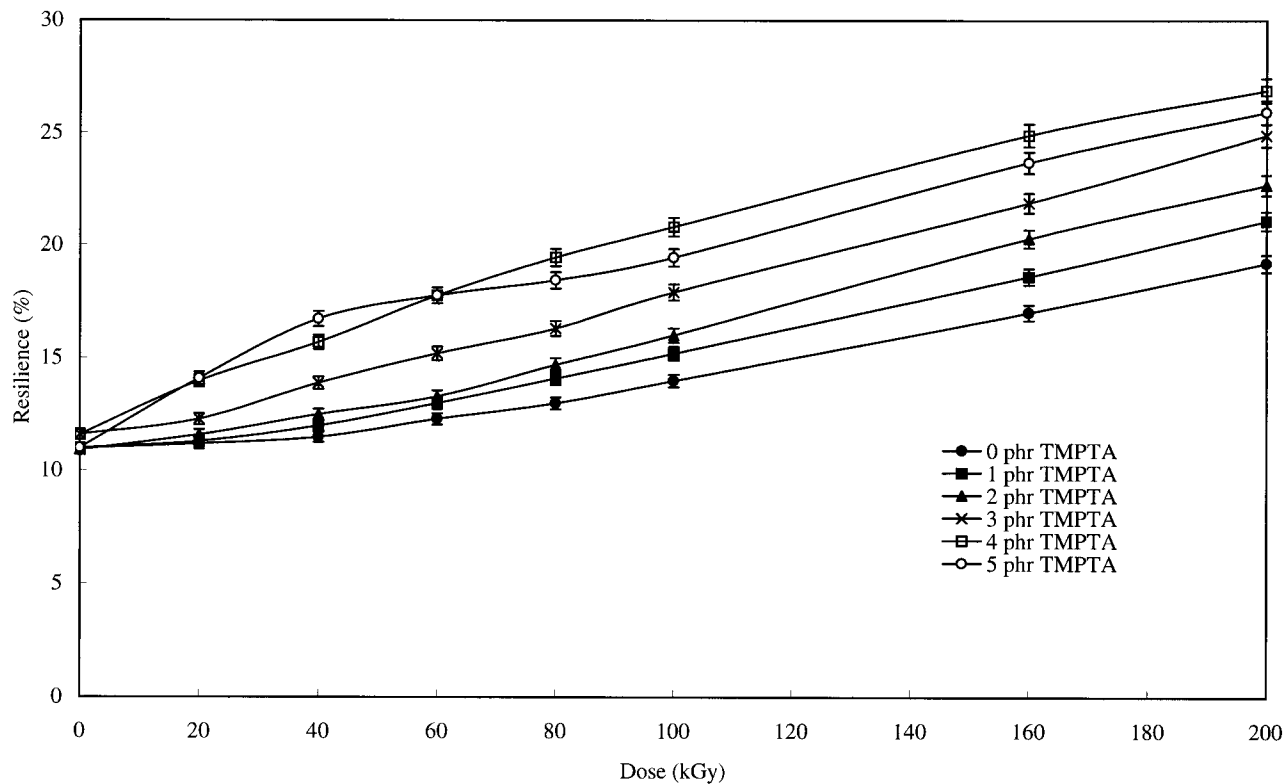


Figure 2 The effect of TMPTA on the resilience of the 50/50 PVC/ENR blend.

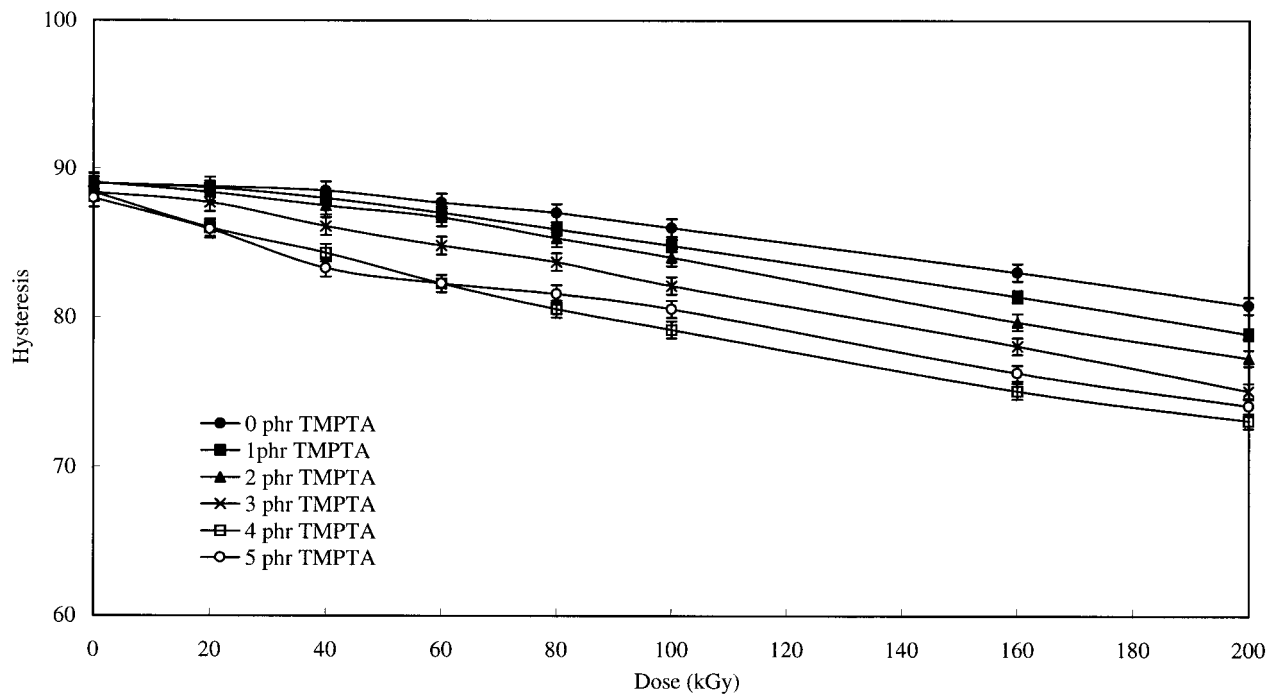
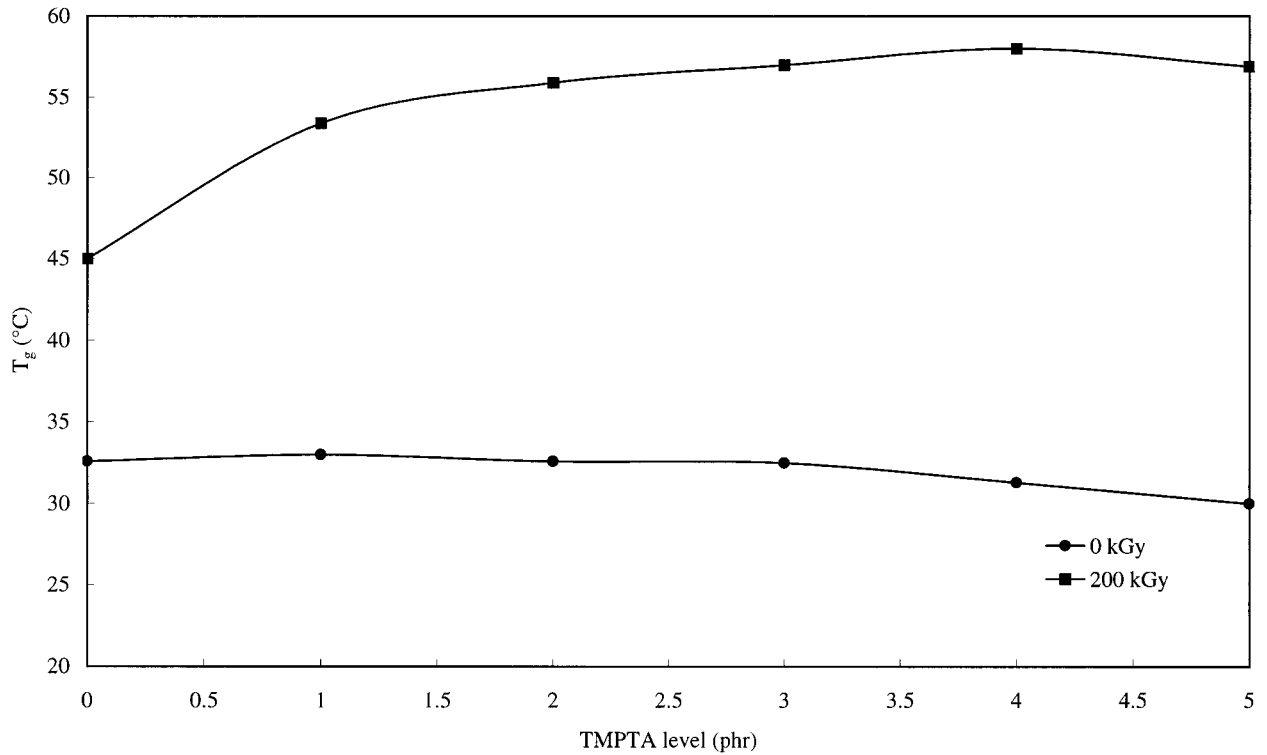


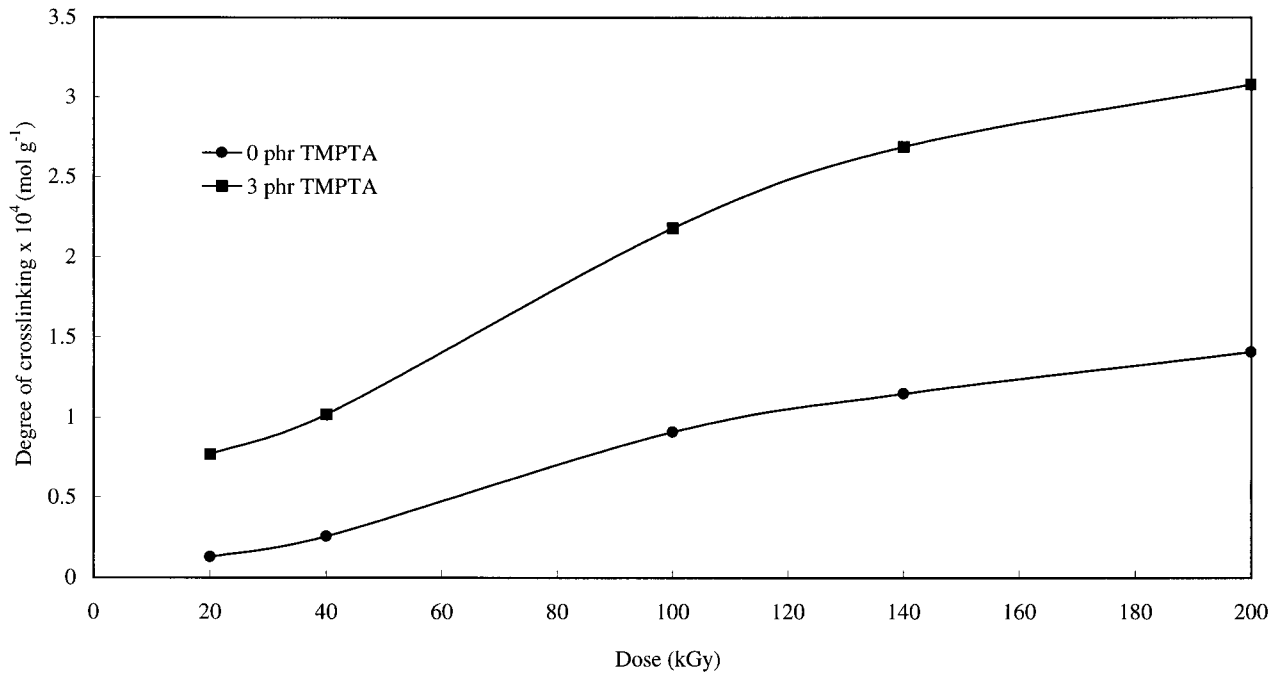
Figure 3 The effect of TMPTA on the hysteresis of the 50/50 PVC/ENR blend.



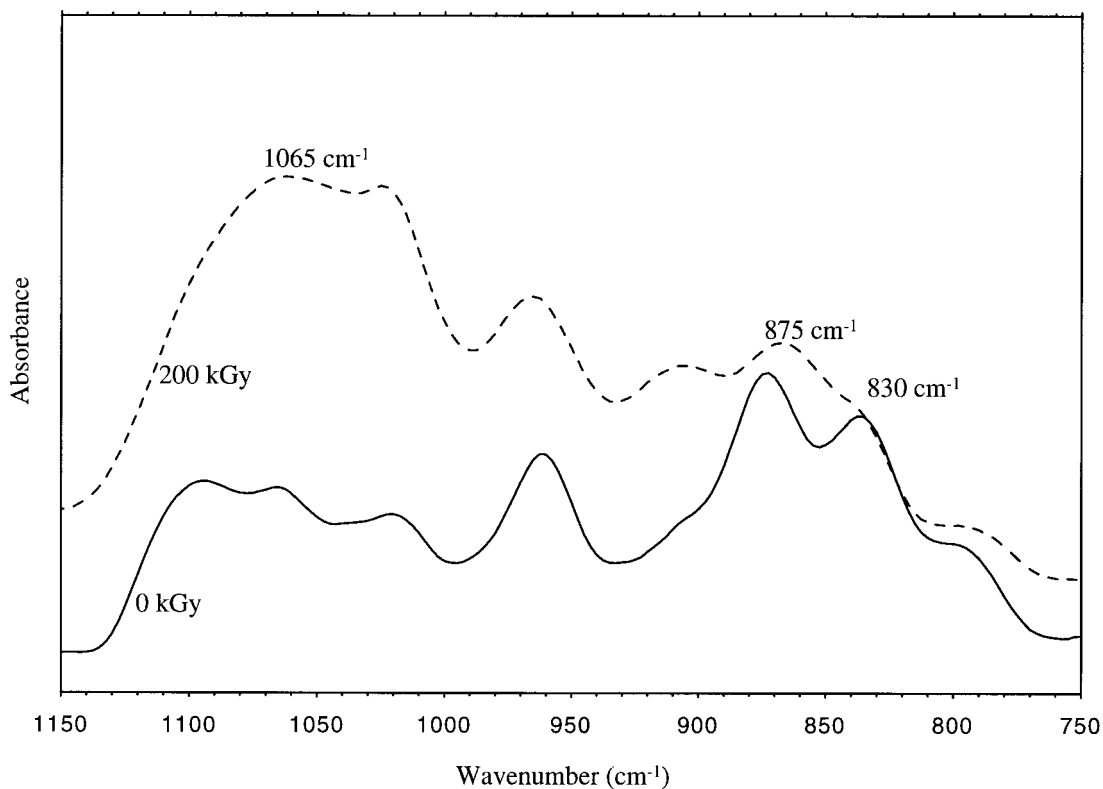
**Figure 4** The effect of TMPTA on the  $T_g$  of the 50/50 PVC/ENR blend.

lower resilience than the blend with 4 phr TMPTA. This implied that the influence of excessive TMPTA in changing the type of network

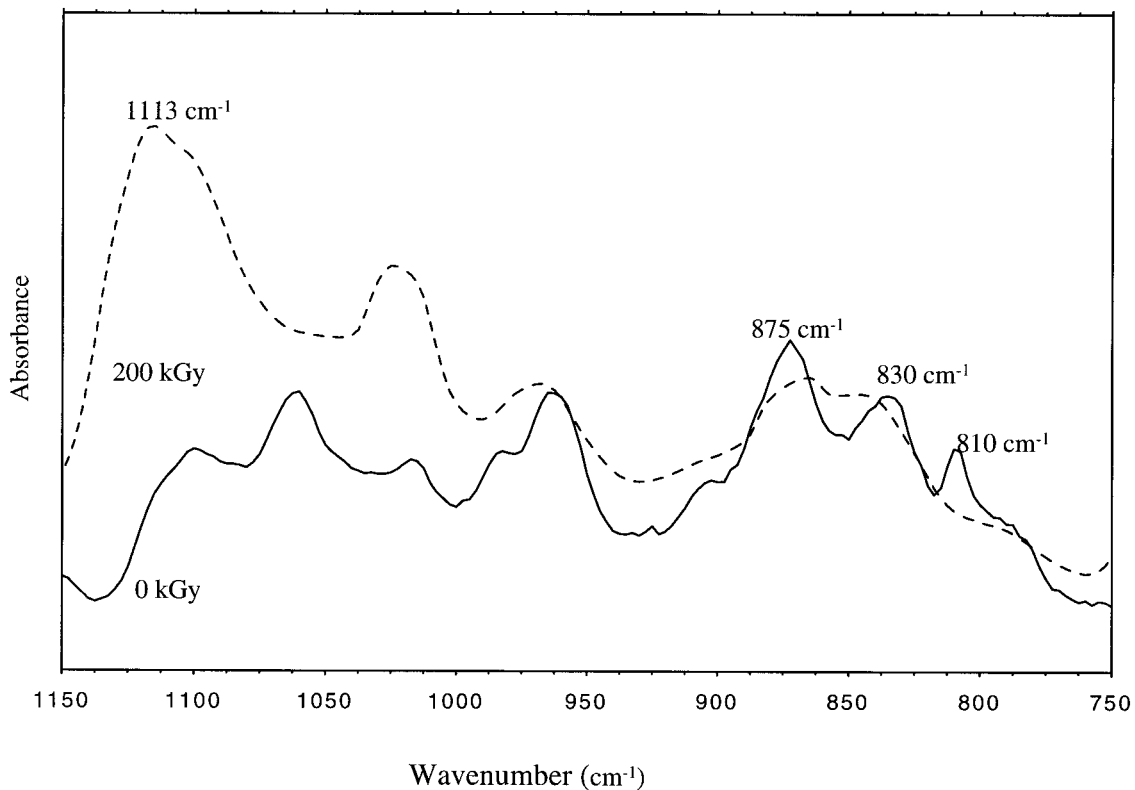
formed is breaking down the network to form a smaller network. This observation is believed to be associated with the presence of a large number



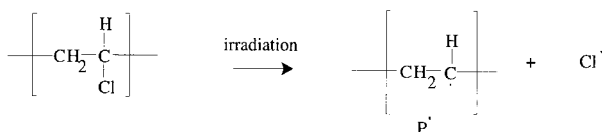
**Figure 5** The effect of irradiation on the degree of crosslinking of the 50/50 PVC/ENR blend.



**Figure 6** FTIR spectra of the 50/50 PVC/ENR blend with 0 phr TMPTA in the 1150–750  $\text{cm}^{-1}$  region.



**Figure 7** FTIR spectra of the 50/50 PVC/ENR blend with 3 phr TMPTA in the 1150–750  $\text{cm}^{-1}$  region.



Scheme 2

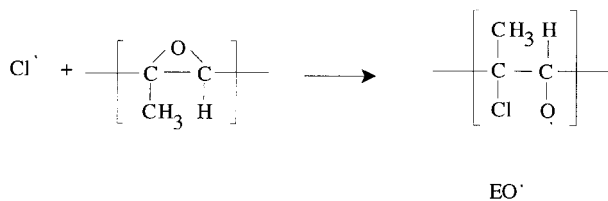
of free radicals formed during irradiation with the addition of an excessive amount of TMPTA (above 4 phr). Greater availability of free radicals could promote the breakdown of the network structure along with the formation of crosslinks. Such an effect of acrylates on ethylene vinyl acetate was also reported by Sujit et al.<sup>33</sup>

### Hysteresis

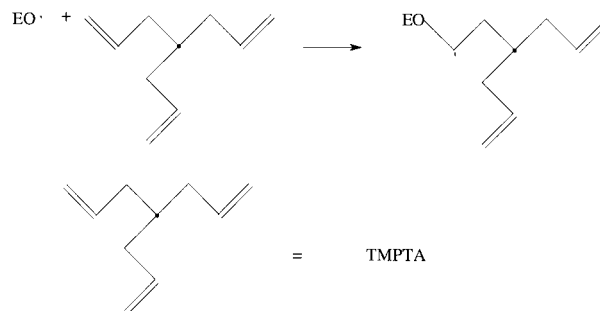
Hysteresis is a measure of energy loss when elastomeric materials are subjected to dynamic deformation. The energy loss that causes heat build-up and subsequent chain scission eventually reduces the mechanical properties. Figure 3 shows the influence of TMPTA on the hysteresis of the PVC/ENR blend upon irradiation. Clearly, there was a gradual decline in the hysteresis of the blend with the irradiation dose. A further drop was also noted when the blend was irradiated in the presence of TMPTA. This indicated that irradiation resulted in a less hysteretic PVC/ENR blend with increased rebound resilience and reduced heat build-up. From this observation it can be inferred that irradiation caused the blend to be less sensitive toward changes in dynamic deformation. The increase in crosslink density is believed to be responsible for the increase in the resistance of the blend to dynamic stress. Mousa et al.<sup>13</sup> also reported a similar observation while working on dynamic vulcanization of PVC/ENR thermoplastic elastomers, and they arrived at the same conclusion.

### Glass-Transition Temperature

Figure 4 depicts the effect of TMPTA on the  $T_g$  of a 50/50 PVC/ENR blend at 0 and 200 kGy irradiation.



Scheme 3



Scheme 4

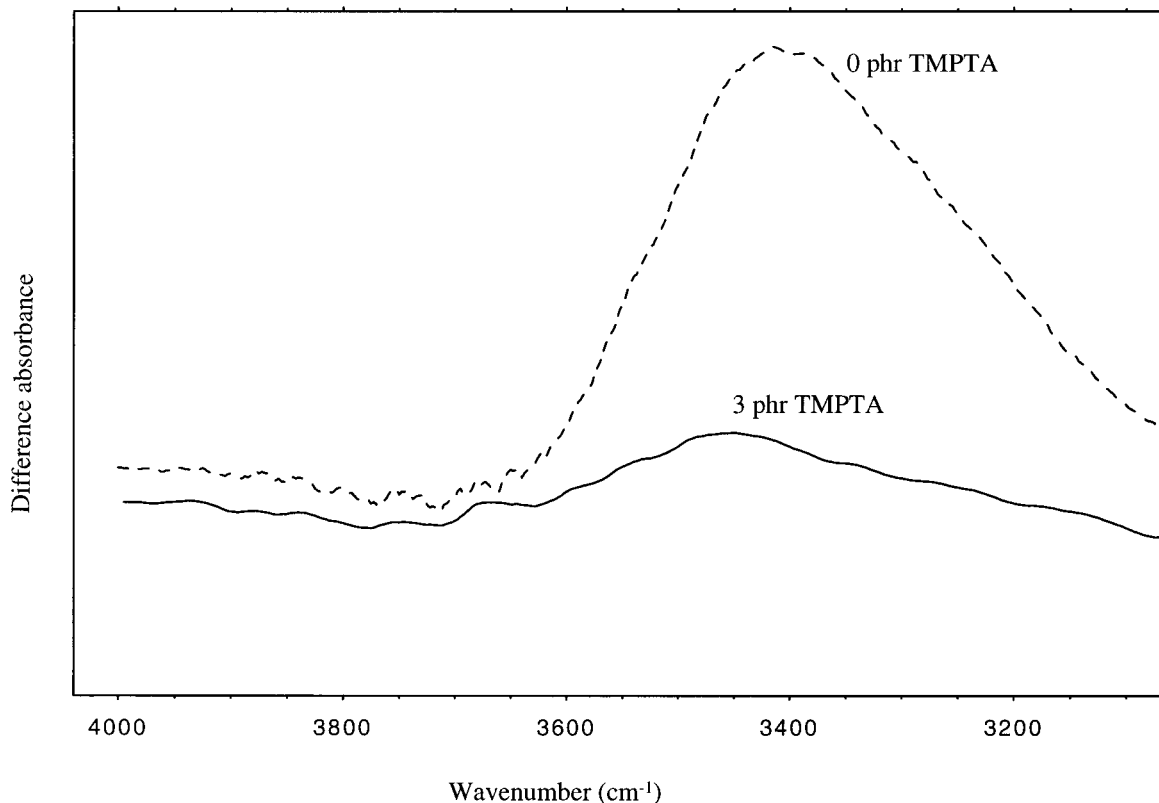
ation. Prior to irradiation the  $T_g$  showed a slight decrease with an increasing amount of TMPTA. Such a decline reflected the plasticizing effect of the TMPTA. In contrast, upon irradiation the  $T_g$  increased with the increase in TMPTA level up to 4 phr. The observed enhancement in  $T_g$  was believed to be due to the radiation-induced crosslinking of the blend through the ring opening of the ENR. A similar shift in the  $T_g$  to a higher temperature with the increasing crosslinks of the epoxy compound (Epon 828) was reported previously.<sup>34</sup> This observation was also in perfect agreement with Mukhopadhyay and De<sup>35</sup> who attributed the increase in the  $T_g$  of a 60/40 ENR50/Hypalon blend to a greater extent of crosslinking being achieved. The decline in the  $T_g$  observed with the addition of 5 phr TMPTA at 200 kGy irradiation further supported our previous assumption in which the incorporation of 5 phr TMPTA resulted in a breakdown of the network.

A correlation between the distance between crosslinks and the shift in  $T_g$  can be found in a number of studies.<sup>34,36-39</sup> Therefore, to gain a better picture of the irradiation crosslinking of the blend, the degree of crosslinking was estimated using the following  $T_g$  and the distance between crosslinks ( $M_c$ ) relation<sup>34</sup>:

$$M_c = \frac{3.9 \times 10^4}{T_g - T_{g0}} \quad (5)$$

where  $T_{g0}$  and  $T_g$  are the transition temperatures for the uncrosslinked and crosslinked polymers, respectively. For our estimation the glass-transition temperature before irradiation was taken as  $T_{g0}$  whereas  $T_g$  was taken as the glass-transition temperature at the corresponding doses. The results obtained for 0 and 3 phr TMPTA are plotted in Figure 5. It is evident from Figure 5 that the degree of crosslinking increased with the irradiation.





**Figure 8** Difference spectra of the irradiated 50/50 PVC/ENR blend in the 4050–3150  $\text{cm}^{-1}$  region.

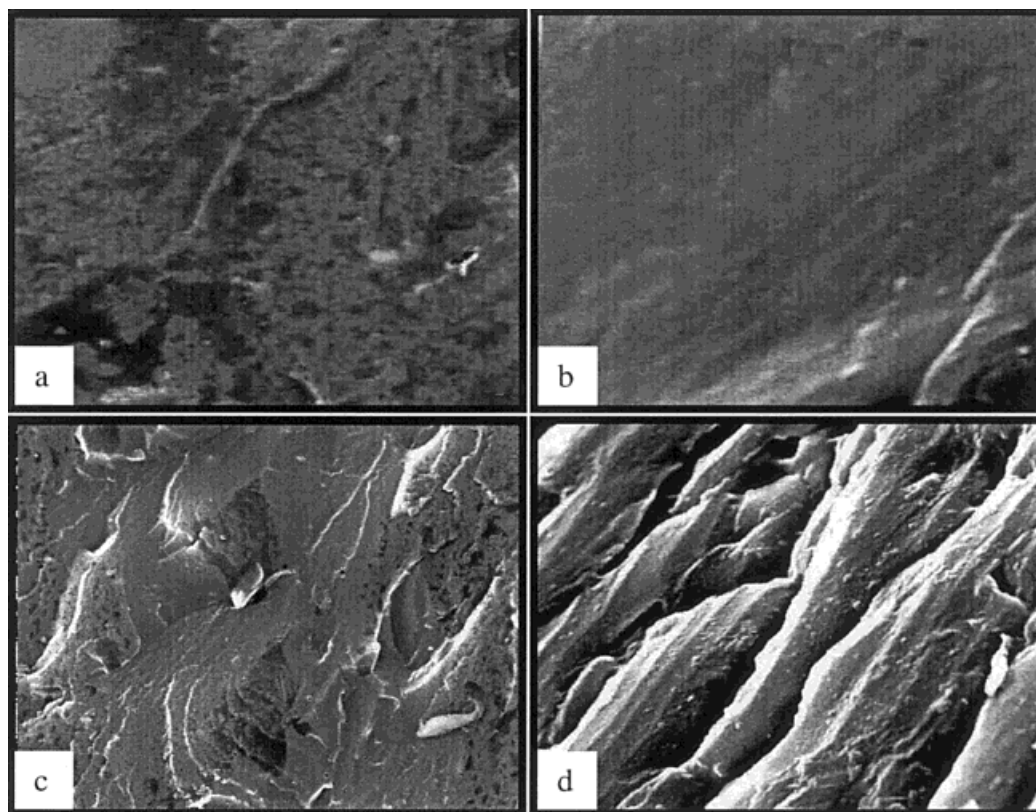
tion dose. The higher degree of crosslinking obtained with the addition of 3 phr TMPTA confirmed the acceleration of the irradiation-induced crosslinking by the TMPTA. According to Murayama and Bell,<sup>34</sup> the  $M_c$  values calculated from the shifting in the  $T_g$  using the above equation are consistent with the stoichiometry.

#### FTIR Analysis

Figures 6 and 7 illustrate the effect of irradiation on the FTIR spectra of the PVC/ENR blend at 0 and 3 phr TMPTA, respectively. These figures show a close-up of the fingerprint region of the FTIR spectrum, which permits one to follow both the disappearance of the epoxy group at  $875\text{ cm}^{-1}$  and the formation of the ether group at around  $1150\text{--}1060\text{ cm}^{-1}$ .<sup>41</sup> The remarkable increase in the  $1065\text{ cm}^{-1}$  region upon irradiation of the PVC/ENR blend in Figure 6 could also be associated with the formation of an ether bond that can be part of an aliphatic and/or a cyclic structure, like THF.<sup>42</sup> The absence of five-membered cyclic ether stretching at  $1065\text{ cm}^{-1}$  upon irradiation of the blend in the presence of TMPTA (Fig. 7) sug-

gested that the addition of TMPTA favored formation of aliphatic ether crosslinks. The reduction in the  $\text{CH}_2=\text{CH}$  twisting vibration of the acrylate group<sup>43</sup> in Figure 7 indicates the involvement of the TMPTA in the irradiation-induced reactions through unsaturation. It is also evident from Figures 6 and 7 that the peak at  $830\text{ cm}^{-1}$ , which signifies the C—H out of plane bending vibration of the *cis*-1,4-isoprene unit,<sup>40,44</sup> is reduced upon irradiation. This observation suggested that, although the epoxy group formed ether crosslinks through the ring-opening reaction, the residual unsaturation may provide an alternative site for irradiation-induced crosslinking to occur. The participation of unsaturated groups of elastomers in the formation of irradiation-induced crosslinking was well illustrated by George.<sup>45</sup>

It is well known that the radiolytic degradation of PVC is through elimination of HCl.<sup>28,29</sup> Thus, the presence of the absorbance peak at  $1065\text{ cm}^{-1}$  in Figure 6 could also be associated with the formation of THF through the acid catalyzed ring opening of the ENR through a similar mechanism



**Figure 9** SEM photomicrographs of the 50/50 PVC/ENR blend irradiated at 60 kGy and extracted with THF; original magnification  $\times 2000$ . (a) 0 phr TMPTA, extracted surface; (b) 3 phr TMPTA, extracted surface; (c) 0 phr TMPTA, extracted and cryogenically fractured surface; and (d) 3 phr TMPTA, extracted and cryogenically fractured surface.

reported elsewhere.<sup>46</sup> The carbon–chlorine bond scission resulting from the irradiation of PVC produces polymeric free radicals ( $P\cdot$ ) and chlorine atoms ( $Cl\cdot$ ) as shown in Scheme 2.<sup>28</sup> The added TMPTA can suppress the chain dehydrochlorination by reacting with the propagating radicals.<sup>28,29</sup> In this case radicals initiated graft polymerization of the TMPTA to produce graft crosslinks. The chlorine atom may also react with the epoxy group of ENR to form epoxy radicals ( $EO\cdot$ ) as shown in Scheme 3. The epoxy stabilization mechanism of PVC proposed by Anderson and McKenzie<sup>30</sup> tends to support the reaction (Scheme 3). Thus, the acceleration of crosslinks by the TMPTA could be associated with the scavenging reaction of the PVC radical at one end and grafting to ENR through an ether bond as shown in Scheme 4 at the other unsaturated end. The increase in the C—O—C (ether) stretching peak at  $1113\text{ cm}^{-1}$  and the reduction in the  $CH_2=CH$  twisting vibration of the acrylate group (Fig. 7) at

$810\text{ cm}^{-1}$  further supported this notion. These findings were in good agreement with several reports in which polyfunctional monomers, including multifunctional acrylates, were found to accelerate irradiation-induced grafting of styrene onto polyethylene, polypropylene, and cellulose substrates.<sup>31</sup>

Figure 8 shows the different spectra of the blend in the region of  $4050\text{--}3350\text{ cm}^{-1}$ . These spectra were obtained by subtracting the spectrum of the unirradiated sample from that of the irradiated one at 200 kGy. The increased hydroxyl bond intensity is often associated with the degradation product of PVC,<sup>47</sup> as well as a ring-opened product of ENR, such as THF.<sup>48</sup> From Figure 8 it is clear that the blend containing 3 phr TMPTA showed a relatively lower increase in hydrogen bond peak intensity compared to the blend without the TMPTA. This observation further agreed with our initial assumption that with the incorporation of TMPTA the blend showed an in-

creased tendency for aliphatic ether crosslinking rather than furanation. The lowering of the hydrogen bond peak intensity of the blend could also be attributed to the reduced degradation of the PVC as a consequence of increased crosslinking, as well as grafting, through the double bond of the TMPTA.

### SEM Study

Figure 9 shows the SEM micrograph of the PVC/ENR blend irradiated at 60 kGy and extracted with THF. Figure 9(a,b) shows the surfaces of the blend without and with the presence of 3 phr TMPTA, respectively. Accordingly, Figure 9(c,d) shows the cryogenically fractured surfaces of the above samples. On comparing Figure 9(a,b) it is clear that the presence of TMPTA provided more resistance to the solvent attack than the blend without TMPTA. The blend containing TMPTA thus retained a more uniform surface, which is believed to be attributed to the higher extent of crosslinking. The fractured surface of the blend in the absence of TMPTA [Fig. 9(c)] was found to be rather smooth with a few fracture paths confined to the surface. On the contrary, Figure 9(d) shows extensive matrix tearing that penetrates deeply into the bulk of the sample. This was because irradiation of the blend in the presence of TMPTA resulted in a higher extent of crosslinking; hence, the resistance offered by the blend toward crack propagation increased. Therefore, the SEM studies further confirmed the occurrence of irradiation-induced crosslinking in the blend.

### CONCLUSIONS

It was observed that irradiation-induced crosslinking occurred in the PVC/ENR blend. Addition of TMPTA significantly enhanced the irradiation-induced crosslinking in the blend. It was evident from the FTIR spectra that the irradiation-induced reaction in the PVC/ENR blend was associated with the ring opening of the epoxy group to form ether crosslinks. The results revealed that the blend network may consist of crosslinked PVC with ENR along with the crosslinked homopolymers. The possible mechanism of crosslinking between PVC and ENR upon irradiation was discussed. The blends were still found to be miscible in the crosslinked condition. In future articles we hope to address further aspects of the enhancement of the miscibility of

the blend through the irradiation-induced crosslinking between the PVC/ENR.

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