

Electron-Beam-Induced Crosslinking of Natural Rubber/Acrylonitrile–Butadiene Rubber Latex Blends in the Presence of Ethoxylated Pentaerythritol Tetraacrylate Used as a Crosslinking Promoter

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Received 24 January 2006; accepted 12 June 2006

DOI 10.1002/app.25383

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A natural rubber latex, an acrylonitrile–butadiene rubber latex, and their 50 : 50 blends were exposed to an electron beam in air. A polyfunctional monomer, ethoxylated pentaerythritol tetraacrylate, was used as a crosslinking promoter. Cast films from the irradiated systems were characterized for their gel contents, swelling properties, and tensile strength. An increase in the radiation dose from 0 to 500 kGy resulted in increased crosslink-

ing, as measured by an increase in the gel content and better swelling resistance. The effect of the polyfunctional monomer, ethoxylated pentaerythritol tetraacrylate, as a crosslinking promoter was studied with infrared spectroscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1206–1214, 2007

Key words: blends; crosslinking; electron beam curing

INTRODUCTION

The radiation vulcanization of natural rubber (NR) latex has been extensively studied. This vulcanization technology, when applied to NR latex, provides certain advantages over conventional sulfur-based methods in terms of the absence of *N*-nitrosoamines, lower cytotoxicity, lesser protein allergy response, and better transparency and softness.¹ However, a high vulcanization dose (250 kGy) is required for the effective curing of NR latex in terms of achieving the maximum tensile strength with high-energy radiation. Crosslinking promoters such as polyfunctional monomers (PFMs) are frequently used to promote radiation crosslinking. Thus, an equivalent degree of cure is obtained in the latex as measured by increasing gel contents at a radiation dose much lower than the dose of 250 kGy required otherwise. Trimethylol propane trimethacrylate (TMPTMA) has been used to cure NR latexes.² Studies based on other polyfunctional acrylates³ and monofunctional acrylates such 2-ethyl hexyl acrylate⁴ and *n*-butyl acrylate^{5,6}, have shown the effectiveness of these monomers in reducing the radiation dose for blending with NR latexes. Blends of NR with acrylonitrile–butadiene rubber (NBR) have attracted interest in the past.^{7,8} These blends have superior

chemical resistance in comparison with NR. However, in the solid state, the compounding and blending of NBR with NR are difficult because of their incompatibility, so phase segregation is common, leading to less than impressive physical properties. NBR is also responsive to high-energy radiation. Yasin et al.⁹ reported on electron-beam-induced crosslinking of NBR in the presence of various PFMs. Increases in the tensile strength, hardness, and gel fraction were reported as the concentration of the PFMs was increased from 1 w to 5 wt % in the NBR samples, whereas the elongation percentage decreased in a steady manner. Similar observations were made by Bhowmick and Vijayabaskar¹⁰ in their study on the electron-beam modification of NBR in the presence of PFMs. They reported increases in the tensile strength and modulus of NBR with increases in the PFM level. However, the NBR samples for which the tetraacrylate PFM tetramethylolmethane tetraacrylate was used exhibited better crosslinking efficiency than the samples for which trifunctional TMPTMA or the difunctional monomer tripropylene glycol diarylate was used as the crosslinking agent. In this study, the electron-beam-induced vulcanization of an NR latex, an NBR latex, and their 50 : 50 blends was carried out in the presence of the multifunctional monomer ethoxylated pentaerythritol tetraacrylate (EPTA) as an alternative method for the development of NR/NBR blends, and the role of crosslinking promoter EPTA in the radiation vulcanization of these blends was evaluated. Under the influence of an electron beam, both the NR and NBR phases were expected to undergo

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Journal of Applied Polymer Science, Vol. 103, 1206–1214 (2007)
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predominantly crosslinking reactions, more so in the presence of the PFM EPTA, which was used as a crosslinking promoter. The inclusion of NBR in the NR latex was expected to impart improved chemical resistance to the blend, though at the cost of reduced physical properties in comparison with those expected from irradiated NR latex.

EXPERIMENTAL

Materials

The NR latex was supplied by the Rubber Board of India (Kottayam, India). The NBR latex (Aparene NL 248) was generously donated by Apar Industries, Ltd. (Mumbai, India). The specifications of the NR and NBR latexes are given in Table I. The crosslinking promoter EPTA was imported from Sartomer, Inc. (Exton, PA).

Experimental procedure

Film preparation

The NR and Aparene NL 248 NBR latexes were mixed in equal proportions along with EPTA, stirred for 4 h at room temperature, and stored overnight. Similar control samples were prepared for the NR latex and NBR latex. The latex samples, containing 0, 2, or 4 parts by weight of EPTA with respect to the solid content of the latexes, were subjected to electron-beam irradiation (20, 50, 100, 200, and 500 kGy) in air at a 20 kGy/min dose rate at the Bhabha Atomic Research Centre (Mumbai, India); the electron energy was 2 MeV. Thin latex layers (2 mm) in watch glasses were irradiated. The films were cast from the irradiated latexes by being poured from the watch glasses into 6-in. \times 6-in. glass molds and were left to dry at room temperature to constant weights. A schematic representation of the film formation is provided in Figure 1. The dried films were leached for 2 h in boiling water to ensure the removal of the adsorbed components and enhanced the fusion of the latex particles, leading to greater entanglements among the rubber molecular chains.¹

TABLE I
Specifications for the NR and NBR Latexes

NR latex	
Rubber hydrocarbon	60.00%
Water	38.30%
Protein	1.20%
Lipids	0.80%
Sugars	0.20%
Ash	0.20%
NBR latex (Aparene NL 248)	
Total solid content	50.00%
pH	10
Acrylonitrile content	35.00%

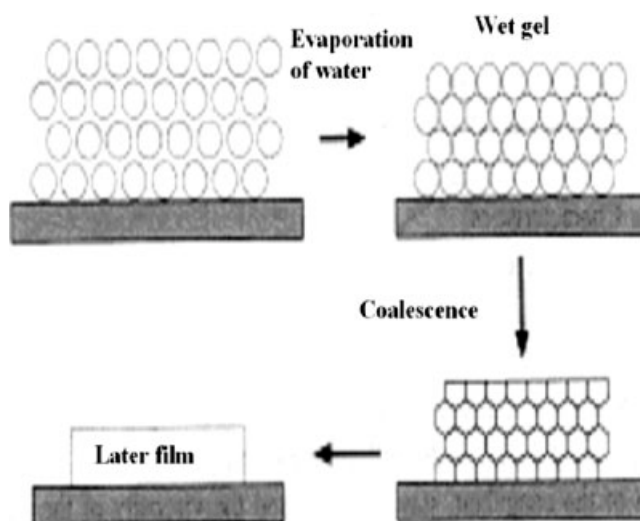


Figure 1 Film formation from irradiated latex.

The leached films were subsequently dried for 3 h at 70°C before further characterization.

Measurements

Horizontal attenuated total reflection (HATR) spectroscopy. IR-HATR spectra of the films were taken with a PerkinElmer (Shelton, CT) Paragon 1000 model spectrophotometer in the HATR mode.

Swelling studies and gel content. The swelling behavior of the film samples was investigated through the equilibrium swelling of known weights of the film samples in toluene for 24 h at room temperature.

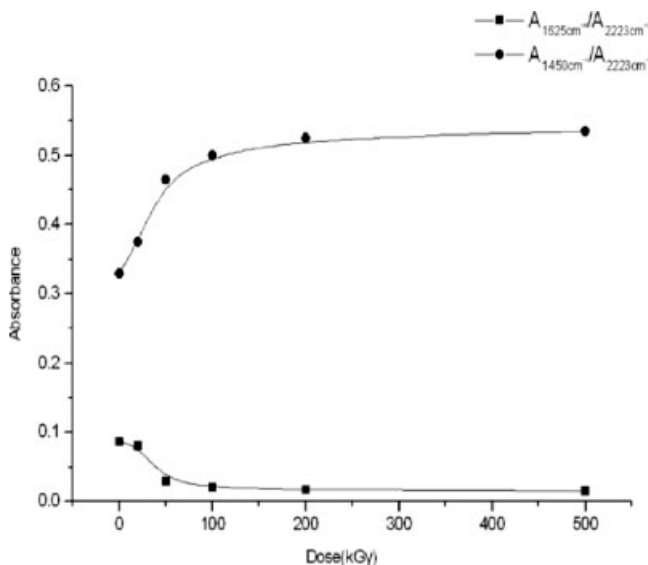
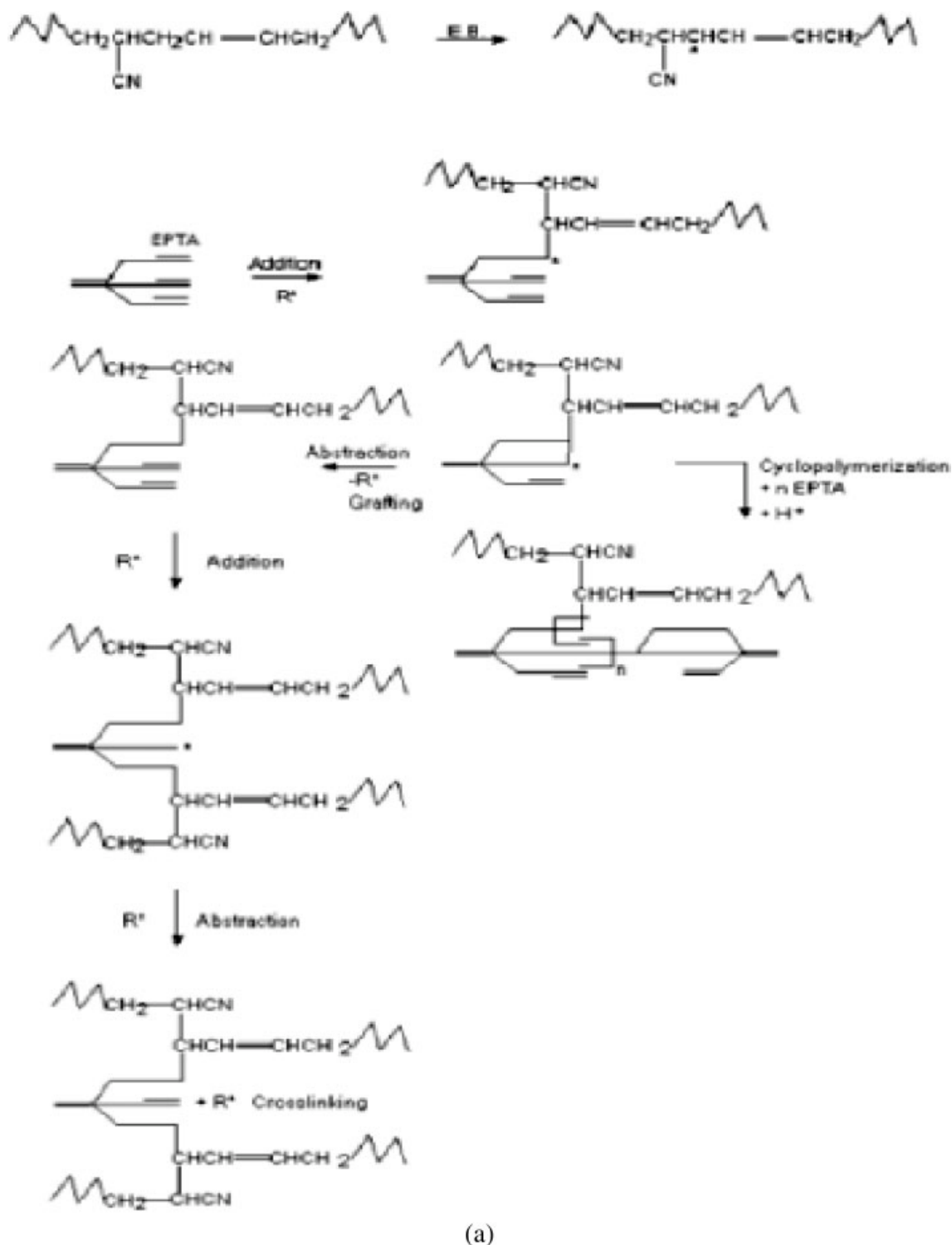


Figure 2 Variation of the normalized absorbances at 1625 (vinylene C=C) and 1450 cm^{-1} ($-\text{CH}_2-$ scissor) against the absorbance at 2223 cm^{-1} ($-\text{CN}$ stretch) with the radiation dose (0–500 kGy).



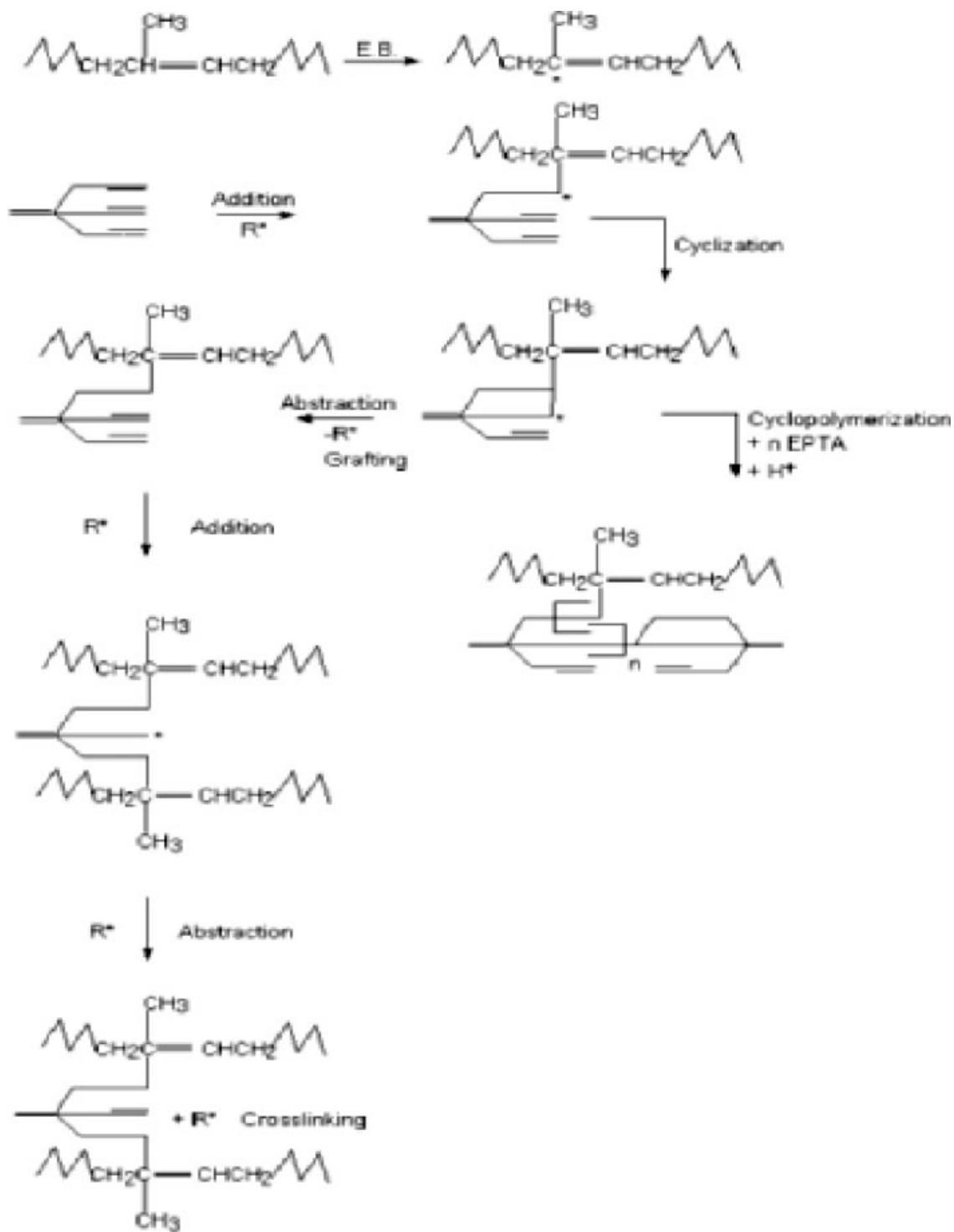
Scheme 1 Plausible mechanism of EPTA-promoted crosslinking of (a) NBR and (b) NR.

The swollen films were dried *in vacuo* to constant weights. The gel and sol fractions were subsequently calculated with relations furnished elsewhere.¹¹ The correlation between the radiation dose and gel formation (i.e., a measure of the relative crosslinking efficiencies) for the irradiated samples was studied with the Charlesby–Pinner equation:¹²

$$S + S^{0.5} = p_0/q_0 + 1/\alpha P_n D$$

$$CE = p_0/q_0 = G(S)/2G(X)$$

where S is the sol fraction, P_n is the number-average degree of polymerization, D is the radiation dose, p_0 and q_0 are the fractions of the ruptured and cross-



(b)

Scheme 1 (Continued from the previous page).

linked main-chain units per unit of radiation, CE (p_0/q_0 , i.e., the intercept of the Charlesby–Pinner plots) is the crosslinking efficiency, $G(S)$ is the sol yield, and $G(X)$ is the yield of the crosslinks.

Mechanical properties. The tensile strengths of the film samples were measured at a straining rate of

500 mm/min with dumbbells punched out of the films. Five replicate dumbbells were used for each formulation, and the averages are reported.

Differential scanning calorimetry. The glass-transition temperatures of the 50 : 50 NR/NBR latex blend films were determined with a TA Instruments (New Castle,

DE) Q10 differential scanning calorimeter in a temperature range of -100 to 0°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ with a liquid-nitrogen-cooling system under inert, dynamic helium.

RESULTS AND DISCUSSION

IR-HATR spectra

The IR-HATR spectra were taken of dried films of NR-NBR latex blends containing 4 parts by weight of EPTA. Figure 2 shows the normalized peak absorbances of the specimens with 4 parts by weight of EPTA irradiated with 0-, 20-, 50-, 100-, 200-, and 500-kGy doses. The absorbance at 1625 cm^{-1} due to the C=C stretching vibration, normalized against the unaffected absorbance at 2223 cm^{-1} due to $-\text{CN}$ stretching, dropped sharply up to 100 kGy, probably because of depletion of the C=C bonds during grafting and crosslink formation involving the PFM (Scheme 1) and partly because of self-crosslinking of the polymers during irradiation.¹⁰ However, above 100 kGy, the changes in the absorbance values were marginal. The $1450\text{-cm}^{-1}/2223\text{-cm}^{-1}$ absorbance ratio, with the absorbance at 1450 cm^{-1} due to the $-\text{CH}_2-$ scissor vibration,¹⁰ increased sharply up to 100 kGy, probably because of enhanced grafting and crosslinking reactions in both NR and NBR in the latex blend promoted by EPTA; this was manifested by the increase in the gel contents and decrease in the swelling ratios with irradiation (Table II).

Swelling and gel development

Table II shows the swelling properties and changes in the gel content of the latex-based films at various radiation doses. For all types of the latexes, the swelling ratios decreased with the radiation dose. This was due to increased crosslinking and the consequent development of gelling in the irradiated samples. As expected, the NBR-based films had higher swelling resistance than the NR-based ones. The 50 : 50 NR-NBR latex blend films gave intermediate swelling values. The difference in the swelling behavior, however, decreased with the radiation dose because the crosslink densities improved, resulting in lower swelling in the samples. With the inclusion of the PFM, EPTA, in the latex feed stock, the swelling resistances for all the samples at a given radiation dose increased because of crosslinking promotion by the multifunctional monomer, which resulted in higher crosslink densities, as observed by the corresponding increase in the gel contents. The Charlesby-Pinner plots for all the latex systems were plotted and are given in Figure 3. The p_0/q_0 intercepts of the plots are indicative of the relative crosslinking efficiencies of the irradiated samples against high-energy radiation. Lower intercepts (p_0/q_0) in the Charlesby-Pinner plots for the

TABLE II
Gel Contents and Swelling Ratios for the Irradiated Samples

Sample	Gel content	Swelling ratio
NR _{0/20}	0.9391	14.36
NR _{0/50}	0.9560	8.79
NR _{0/100}	0.9700	6.90
NR _{0/200}	0.9800	5.85
NR _{0/500}	0.9880	4.01
NR _{2/20}	0.9547	12.67
NR _{2/50}	0.9624	8.33
NR _{2/100}	0.9748	6.77
NR _{2/200}	0.9825	5.52
NR _{2/500}	0.9930	3.93
NR _{4/20}	0.9562	10.84
NR _{4/50}	0.9662	8.14
NR _{4/100}	0.9777	6.01
NR _{4/200}	0.9890	4.75
NR _{4/500}	0.9934	3.71
NR-NBR _{0/20}	0.9010	10.32
NR-NBR _{0/50}	0.9490	6.27
NR-NBR _{0/100}	0.9716	4.74
NR-NBR _{0/200}	0.9835	3.70
NR-NBR _{0/500}	0.9904	2.87
NR-NBR _{2/20}	0.9101	9.79
NR-NBR _{2/50}	0.9596	6.21
NR-NBR _{2/100}	0.9746	4.73
NR-NBR _{2/200}	0.9862	3.67
NR-NBR _{2/500}	0.9912	2.56
NR-NBR _{4/20}	0.9214	9.14
NR-NBR _{4/50}	0.9660	6.14
NR-NBR _{4/100}	0.9761	3.99
NR-NBR _{4/200}	0.9872	3.58
NR-NBR _{4/500}	0.9917	2.44
NBR _{0/20}	0.8990	5.19
NBR _{0/50}	0.9670	3.53
NBR _{0/100}	0.9800	3.00
NBR _{0/200}	0.9850	2.32
NBR _{0/500}	0.9890	1.73
NBR _{2/20}	0.9107	4.97
NBR _{2/50}	0.9788	3.50
NBR _{2/100}	0.9884	2.94
NBR _{2/200}	0.9910	2.31
NBR _{2/500}	0.9970	1.70
NBR _{4/20}	0.9210	4.82
NBR _{4/50}	0.9820	3.43
NBR _{4/100}	0.9891	2.85
NBR _{4/200}	0.9927	2.22
NBR _{4/500}	0.9981	1.66

The subscripts indicate the multifunctional monomer levels (wt %) and the radiation doses (kGy).

NBR samples at a given irradiation dose were indicative of higher gel contents in comparison with those in the NR and NR-NBR blend. Although there was less gel in the NBR latex at lower doses compared with those in NR or the NR-NBR latex blend, the former increased rapidly at higher doses. The trend was in accordance with the increases in the tensile strength for the irradiated samples with the radiation dose, as shown in Figure 4, in which the NBR latex films exhibit a faster improvement in the tensile strength with an increased dose in comparison with the other latex

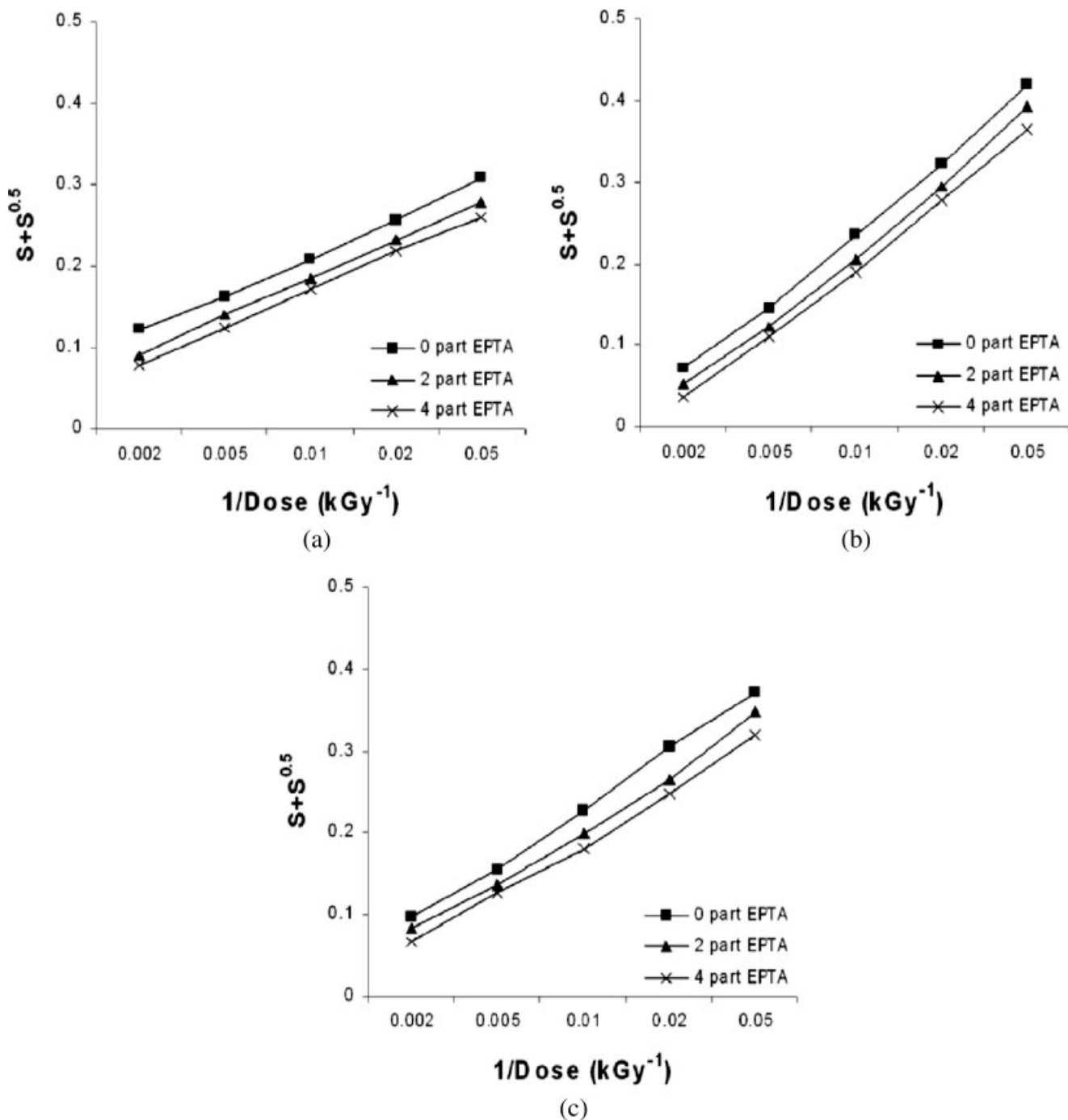


Figure 3 Charlesby–Pinner plots for the irradiated latexes: (a) the NR latex, (b) the NBR latex, and (c) the NR–NBR latex blend.

systems. This can be seen as a result of the better response to radiation for NBR in comparison with NR. The NR–NBR latex blends exhibited intermediate sensitivity toward radiation, as manifested by the slopes of their Charlesby–Pinner plots [Fig. 3(c)].

Effect on the mechanical properties

Figure 4 shows the changes in the tensile strength for the irradiated samples. For the NR latex, in the ab-

sence of the crosslinking promoter, the required vulcanization dose was about 225 kGy [Fig. 4(a)]. This was in agreement with earlier reported values.¹ However, in the presence of EPTA, the same decreased with 4 parts of PFM. Jayasuriya et al.² reported on a similar vulcanization dose for NR latex in the presence of trimethylol propane trimethylacrylate (TMPTMA). One reason for the low crosslinking efficiency of PFM is probably the reduced solubility of the crosslinking promoter EPTA in NR on account of

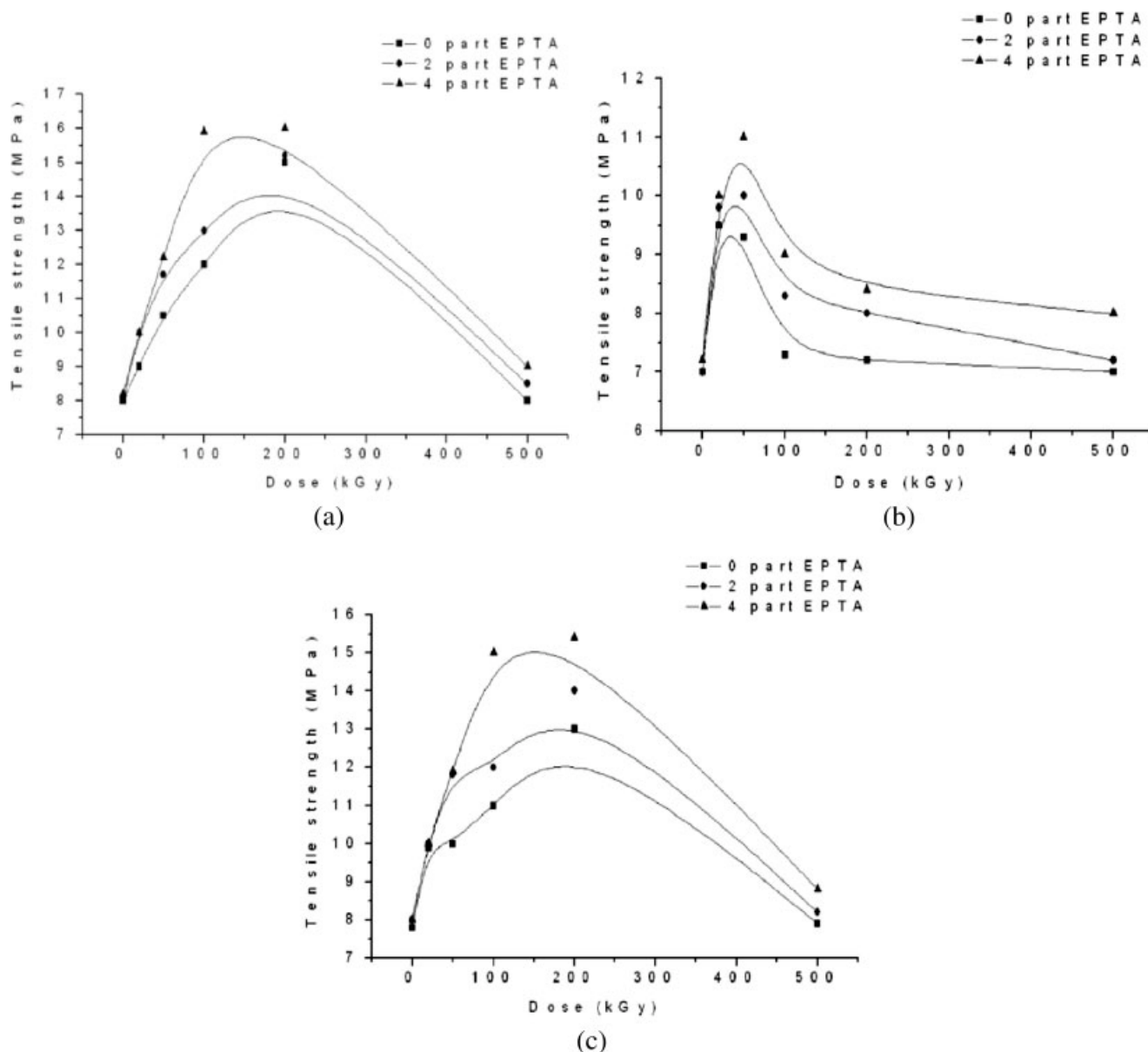


Figure 4 Variation of the tensile strength for the irradiated samples with the radiation dose (0–500 kGy) and the concentration of EPTA (0–4 parts): (a) the NR latex, (b) the NBR latex, and (c) the NR–NBR latex blend.

the greater polarity of the tetraacrylate monomer.¹ In the absence of the PFM, a tensile strength of 13 MPa was obtained in NR, which improved to 16 MPa with the inclusion of 4 parts of EPTA in the latex, probably on account of crosslinking promotion from the PFM. With the NBR latex, the polymer seemed to have greater responsiveness toward high-energy radiation; at a lower vulcanization dose of 50 kGy, a tensile strength of about 9.5 MPa was achieved even without EPTA. However, with the inclusion of 4 parts of PFM, the optimum tensile strength increased and reached 11 MPa at 50 kGy [Fig. 4(b)]. Yasin et al.⁹ reported a similar improvement in the tensile strength in an NBR latex with various types of PFMs. However, no signifi-

cant reduction of the vulcanization dose could be achieved with EPTA. Figure 4(c) shows the variation in the tensile strength with the dose for the 50 : 50 NR–NBR latex blends. The radiation response in terms of the change in the strength properties for the blends seemed to be similar to that of the NR latex. The vulcanization dose of 100 kGy decreased with the inclusion of 4 parts of the PFM in the latex feed stock. The optimum tensile strength increased from 11.5 (0 parts of EPTA) to 15.5 MPa (4 parts of EPTA). At higher doses, however, the tensile strength decreased for all the samples, probably because of the generation of excessive crosslinks, as measured by their respective gel fractions, which approached unity at high doses.

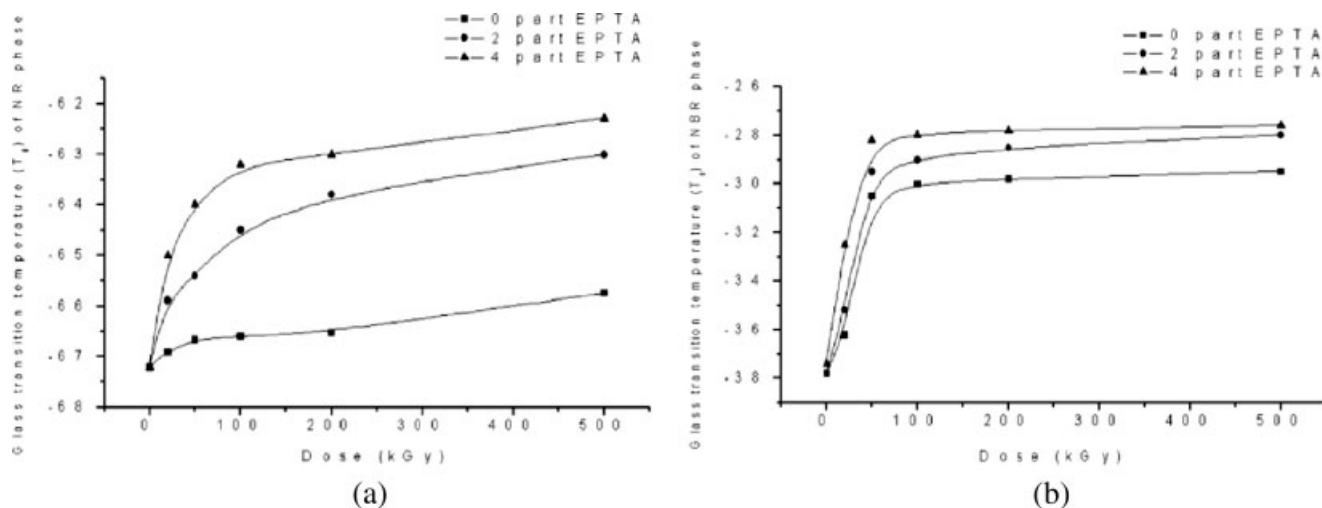


Figure 5 Changes in the glass-transition temperatures of (a) the NR component and (b) the NBR component in the NR–NBR latex blend with the radiation dose (0–500 kGy).

Differential scanning calorimetry

The determination of the glass-transition temperatures of the NR–NBR latex films was carried out to determine the progress of radiation-induced crosslinking in the NR and NBR components in the latex blend. Figure 5 shows the changes in the glass-transition temperatures for the two components. The same for NBR increased from -38 to -28°C [Fig. 5(b)] versus an increase from -67.5 to -62.5°C for NR with radiation [Fig. 5(a)] in the presence of 4 parts of EPTA in the feed stock. Up to 50 kGy, the glass-transition temperature for the NBR component increased rapidly with the radiation dose, and this was followed by marginal improvements with more radiation. For NR, the glass transition continued a slow, upward trend beyond 100 kGy. Thus, for NBR, the generation of crosslinks seemed to occur easily in comparison with that in the NR phase, as manifested by a sharper increase in the glass-transition temperature of the former. The higher crosslink generation in NBR at lower doses greatly restricted the segmental mobility of the polymeric chains, thereby increasing the glass-transition temperature. The result of the same was evident in the development of the gel and in the variation of the tensile strength with the radiation dose.

CONCLUSIONS

The PFM EPTA promoted crosslinking in the irradiated latex samples by grafting onto the polymeric chains by opening up its vinyl $\text{C}=\text{C}$ bonds and linking across the polymeric chains through the $-\text{CH}_2-$ bridges into a three-dimensional network structure. The decrease in the unsaturation was monitored by reduced peak absorbances at 1625 cm^{-1} , which was

attributed to the $\text{C}=\text{C}$ stretching vibration. The development of the crosslinked structure promoted by EPTA was evident from the increased peak absorbance at 1430 cm^{-1} for the $-\text{CH}_2-$ scissor vibration, which was attributed to the increased concentration of the $-\text{CH}_2-$ bridges in the resulting crosslinked network promoted by EPTA. A higher concentration of the PFM resulted in a higher crosslink density, which resulted in increased gel contents and higher swelling resistances. As expected, on account of their greater polarity, NBR samples provided greater swelling resistance than NR, whereas the NR–NBR blend showed intermediate resistance. The variation of the tensile strength suggested that at lower doses, the crosslinking for NR was probably lower than that of NBR, and this was further supported by the higher p_0/q_0 intercepts in their Charlesby–Pinner plots. Thus, the increased crosslinking of NBR at low doses could be attributed to the chemical lability of its molecular structure to high-energy radiation, as it tended to crosslink faster than NR. This seemed to be substantiated further by the faster increase in the glass-transition temperature for the NBR component in the irradiated NR–NBR latex blend.

Comparing the properties of the film samples of the NR latex and the NR–NBR latex blend with 4 parts of EPTA incorporated into their respective feed stocks and with exposure to 100 kGy, we observed that a significant improvement of about 34% in the swelling resistance was achieved with a marginal drop of about 7% in the tensile strength on account of a 50% replacement of NR by the NBR latex in the NR–NBR feed stock. This assumed greater significance as the latex blend could be considered to be a chemically resistant variant of the NR latex. The inclusion of the PFM as a crosslinking promoter enhanced gel formation and

reduced swelling because of the higher crosslink densities achieved in the irradiated latexes.

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