Polymer Vol. 37 No. 1, pp. 45–55, 1996
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

Electron beam initiated modification of ethylene vinyl acetate using trimethylolpropane trimethacrylate

Sujit K. Datta, A. K. Bhowmick and T. K. Chaki*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

and A. B. Majali and R. S. Despande
Radiation Processing Section, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India
(Received 22 July 1994; revised 23 February 1995)

Electron beam initiated crosslinking of ethylene vinyl acetate (EVA), containing 12% vinyl acetate with trimethylolpropane trimethacrylate (TMPTMA), has been carried out over a range of radiation doses (2–20 Mrad) and concentrations of TMPTMA (0.5 to 5 parts by weight). The residual concentration of carbonyl groups due to oxidation and incorporation of TMPTMA into the crosslinked EVA, as determined from i.r. difference spectra increases with the radiation dose and with the TMPTMA level in the initial stages. The gel content increases with the radiation dose, though the increase is marginal with the TMPTMA level. X-ray studies indicate that there are two peaks at 10.8–10.9° and 11.8–11.9° and that the corresponding interplanar distances are 4.07 Å and 3.73 Å. With an increase in the radiation dose or TMPTMA level, the crystallinity increases in the initial stage and then decreases. The interplanar and interchain distances of the modified polymer do not change. Differential scanning calorimetry (d.s.c.) studies also support the X-ray results. Tensile properties increase with the radiation dose and the TMPTMA level up to 5 Mrad at 1 part TMPTMA level, and 1 part at a 5 Mrad dose, because of the formation of a large network structure. Beyond a 5 Mrad radiation dose and 1 part TMPTMA level, the tensile properties decrease due to a breakdown of the network structure.

(Keywords: ethylene vinyl acetate; trimethylolpropane trimethacrylate; irradiation)

INTRODUCTION

Modification of polymers in the presence of radiation is a potential method for the development of new polymers and composites. Use of some polyfunctional monomers in such reactions is very effective in decreasing the dose level to achieve optimum properties, without much deterioration of the base polymers. These polyfunctional monomers form a three dimensional network structure with the base polymer. The polymer can therefore be modified and crosslinked simultaneously without many processing difficulties.

Radiation crosslinking thus endows the polymers with special properties. Such irradiated polymers are non-melting and exhibit elasticity above their crystalline melting point. These properties are used for making heat shrinkable materials, which have applications in wire and cable industries, particularly in nuclear power station control cables, rubber tyre components, etc.

Polyethylene[1–3] and its blends, and PVC[4,5] have been modified using methylmethacrylate, triallylcyanurate, trimethylolpropane trimethacrylate by electron beam radiation.

EVA is a copolymer of ethylene and vinyl acetate. It is a good insulating material for high voltage cables. Migunova *et al.*[6] modified EVA by using gamma rays. Sumitomo Electric Industries Ltd (Japan)[7] developed a non-halogen, fire resistant, polyolefin composition based on blends of EVA and ethylene–ethylacrylate, by using an electron beam. There is no attempt however, to modify EVA in the presence of polyfunctional monomers using high energy electron beam radiation. In this article, electron beam initiated modification of EVA in the presence of trimethylolpropane trimethacrylate (TMPTMA) has been investigated. The influence of the level of TMPTMA and the dose of EB radiation on the structure, crosslinking, tensile and thermal properties of ethylene vinyl acetate copolymer, containing 12% vinyl acetate, is described.

EXPERIMENTAL

Materials

Ethylene vinyl acetate copolymer (PILENE EVA, 12% vinyl acetate content) was supplied by Polyolefin Industries Ltd, Bombay, India (density = 940 kg m^{-3}, melt index = 0.2–0.4 dg min^{-1}.

---

* To whom correspondence should be addressed

Table 1 Formulations of samples

Sample code	EVA (weight by parts)	TMPTMA (weight by parts)	Radiation dose (Mrad)
ETM-12/0/0	100	0	0
ETM-12/0/5	100	0	5
ETM-12/0.5/5	100	0.5	5
ETM-12/1.0/5	100	1.0	5
ETM-12/1.5/5	100	1.5	5
ETM-12/2.0/5	100	2.0	5
ETM-12/2.5/5	100	2.5	5
ETM-12/3.0/5	100	3.0	5
ETM-12/5.0/5	100	5.0	5
ETM-12/1.0/2	100	1.0	2
ETM-12/1.0/10	100	1.0	10
ETM-12/1.0/15	100	1.0	15
ETM-12/1.0/20	100	1.0	20
ETM-12/5/2	100	5.0	2

Trimethylolpropane trimethacrylate, [CH_3–CH_2–C (CH_2–O–CO–CH = CH_2)$_3$] was obtained from ANCOMER Ltd, UK.

Preparation of samples

EVA was mixed with TMPTMA in a Brabender Plasticorder PLE-651 at 120°C and 60 rev min^{-1}. EVA was first allowed to melt for 2 min, followed by TMPTMA for another 2 min. The mixes so obtained were sheeted out under hot conditions through the open mill set at a 2 mm nip gap.

The sheets were compression moulded between aluminium foils for 2 min at 120°C, at a pressure of 13 MPa in an electrically heated press. Aluminium foils were used to reduce the shrink marks on the moulding surface. The mouldings were cooled under compression to maintain the overall dimensional stability of the moulded articles.

Radiation

The moulded EVA samples in the form of rectangular sheets were irradiated by an electron beam accelerator (model ILU-6) at Bhabha Atomic Research Centre, Bombay.

Irradiation doses of 2, 5, 10, 15 and 20 Mrad were used. The formulations of the samples are given in *Table 1*, and specifications of the electron beam accelerator in *Table 2*.

Characterization of samples

I.r. study. I.r. spectra were taken on thin films ($\approx$100 μm) using Perkin-Elmer (model 837) spectrophotometer. Difference spectra of various modified samples were also taken by subtracting the spectra of the unmodified sample from those of the modified ones.

Gel fraction. Gel fraction was measured gravimetrically by immersing the samples in xylene at 80°C for 72 h. The amount of gel (i.e. insoluble material) was expressed as a percentage of the theoretical maximum, the latter being the total amount of material which could form a gel, i.e. the weight of all components which could be involved in gel formation[1–4].

Table 2 Specifications of the electron beam accelerator

Energy range	0.5–2.0 MeV
Beam power through the whole energy range	20 kW
Beam energy spread	±10%
Average current (E-1.5 MeV)	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration	400–700 μs
Repetition rate	2–50 Hz
Pulse current: Maximum	900 mA
Minimum	400 mA
Power supply voltage	3 × 380/220 V
P.S. voltage frequency	50 Hz
Consumption of power (total)	150 kW

X-ray diffraction analysis. X-ray diffraction patterns of the samples were recorded with a Philips X-ray diffractometer (Type PW-1840) using Ni-filtered CuKα radiation in the angular range 5–35° (2θ) at an operating voltage of 40 kV and a current of 20 mA.

The area under the crystalline and amorphous portions was determined in arbitrary units; the degree of crystallinity X_c and the amorphous content (X_a) were measured, using the relationships:

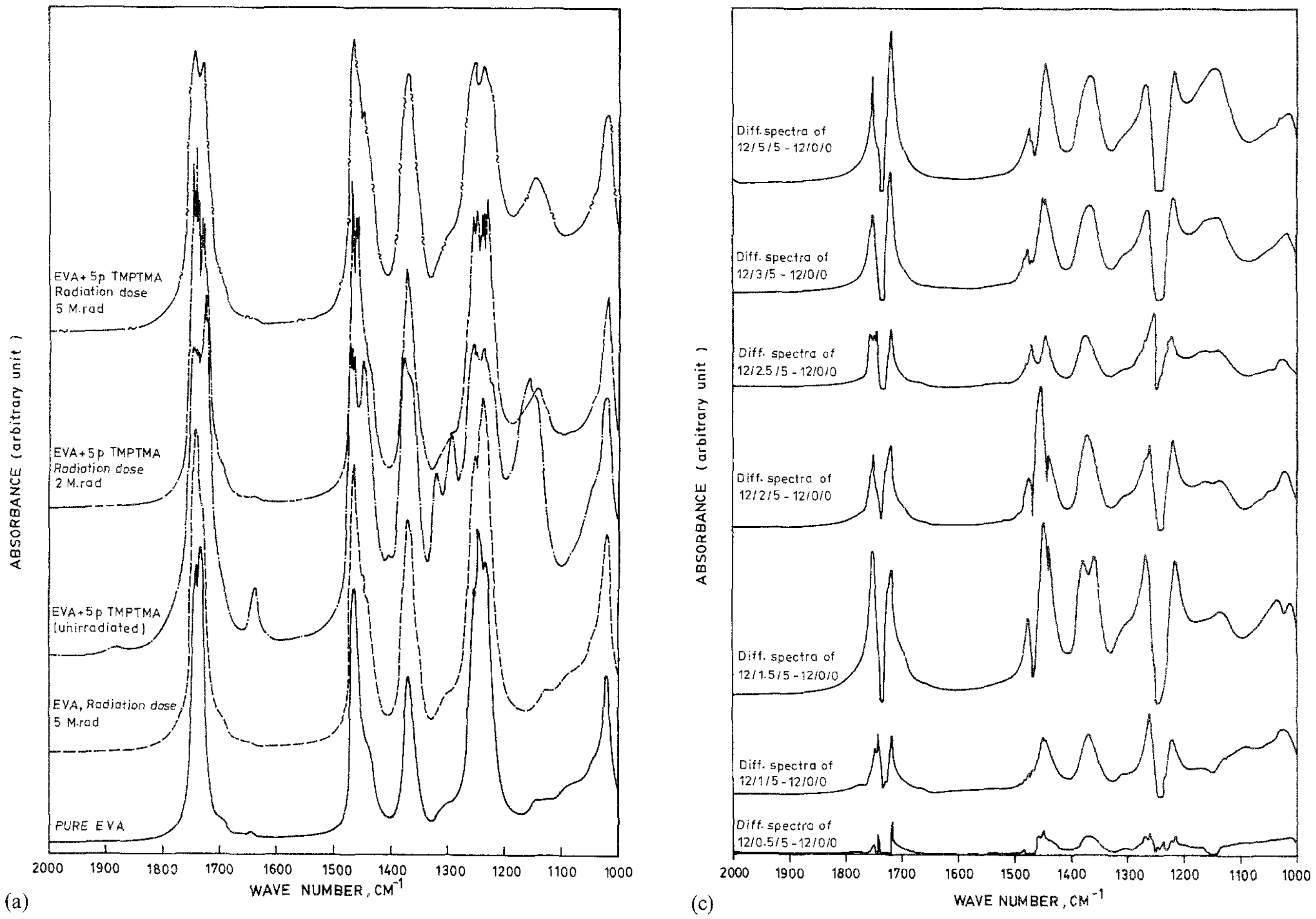
$$X_c = \frac{I_c}{I_a + I_c}; \; X_a = \frac{I_a}{I_a + I_c}$$

where I_c and I_a are the integrated intensities corresponding to crystalline and amorphous hallow respectively.

Peak half width (β), crystallite size (P), interchain distance (r) and interplanar distance (d) were calculated as follows[8]:

$$\beta = \frac{\text{Area of peak}}{\text{Height of peak}} \times \frac{1}{5}$$

$$P = \frac{78.62}{\beta \cos \theta}$$



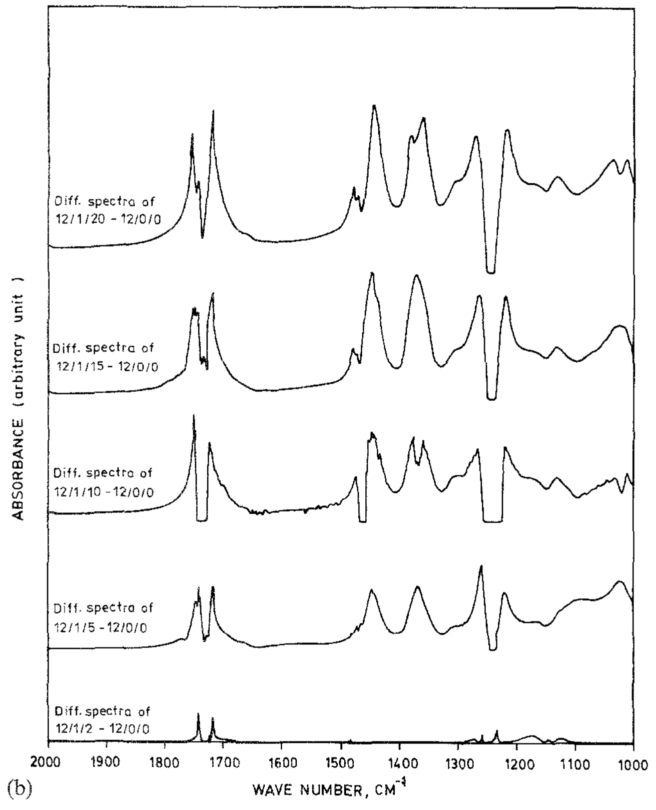


Figure 1 (a) I.r. spectra of (i) pure EVA (control), (ii) EVA irradiated with a 5 Mrad dose, (iii) unirradiated EVA containing 5 parts by weight of TMPTMA, (iv) irradiated EVA containing 5 parts by weight of TMPTMA with a 2 Mrad dose and (v) irradiated EVA containing 5 parts by weight of TMPTMA with a 5 Mrad dose; (b) i.r. difference spectra of irradiated samples of EVA containing 1 part by weight of TMPTMA irradiated with (i) 2 Mrad, (ii) 5 Mrad, (iii) 10 Mrad, (iv) 15 Mrad and (v) 20 Mrad doses and control sample; (c) i.r. difference spectra of irradiated samples of EVA with a 5 Mrad dose containing (i) 0.5, (ii) 1.0, (iii) 1.5, (iv) 2.0, (v) 2.5, (vi) 3.0 and (vii) 5 parts by weight of TMPTMA and control sample

$$r = \frac{5}{8} \cdot \frac{\lambda}{\sin \theta}$$

$$d = \frac{1.5418}{2 \sin \theta} \quad (\lambda = 1.5418\,\text{Å}).$$

The results reported here were based on three samples. The errors in peak angle, percentage crystallinity, crystallite size, interplanar distance and interchain distance were ±0.1, ±2%, ±0.02 Å, ±0.02 Å and ±0.001 Å respectively.

Differential scanning calorimetry. D.s.c. studies were carried out using a Stanton Redcroft STA-625 thermal analyser at a heating rate of 20°C min^{-1} in nitrogen in the temperature range of room temperature to 150°C. The peak maximum from the melting thermogram was considered as the melting point (T_m).

Crystallinity was calculated from the heat of fusion i.e. the area of the melting peak using the relation:

$$\text{Percent crystallinity} = \frac{\Delta H_m}{\Delta H_c} \times 100$$

ΔH_m = melting enthalpy of the sample

ΔH_c = melting enthalpy of perfectly crystalline sample = 68.499 mcal mg^{-1} (ref. 9).

The results reported here were the average of three samples. T_m and ΔH were reproducible within ±1°C and 5% respectively.

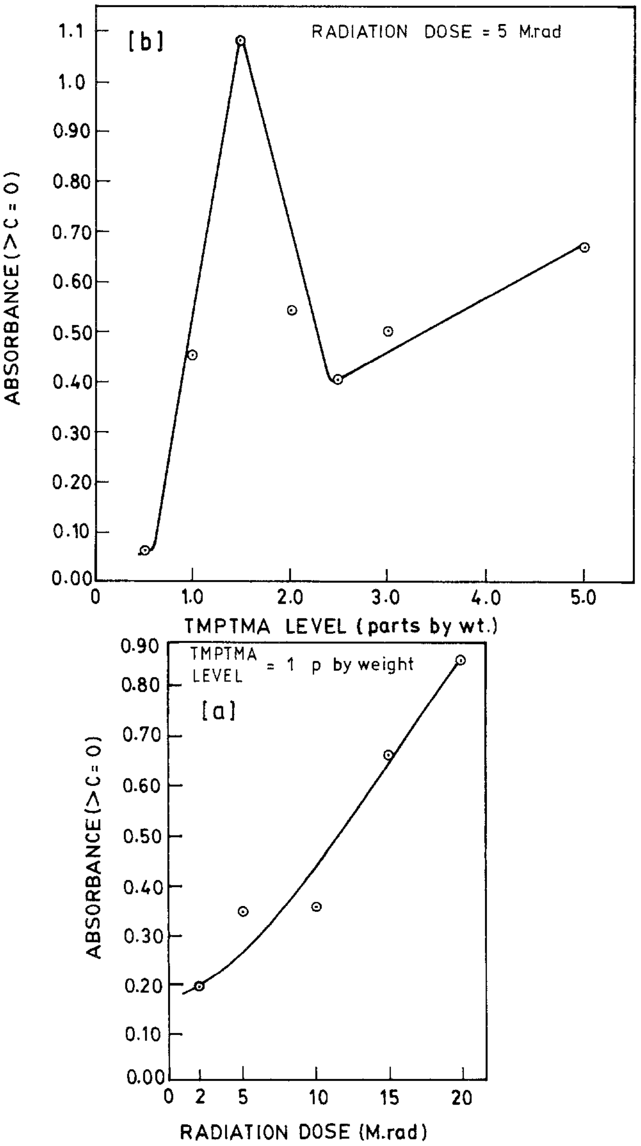


Figure 2 Plot of carbonyl (>C = O) absorbance of different irradiated samples: (a) with variation of radiation dose at a constant level of TMPTMA; (b) with variation in TMPTMA level at a constant irradiation dose

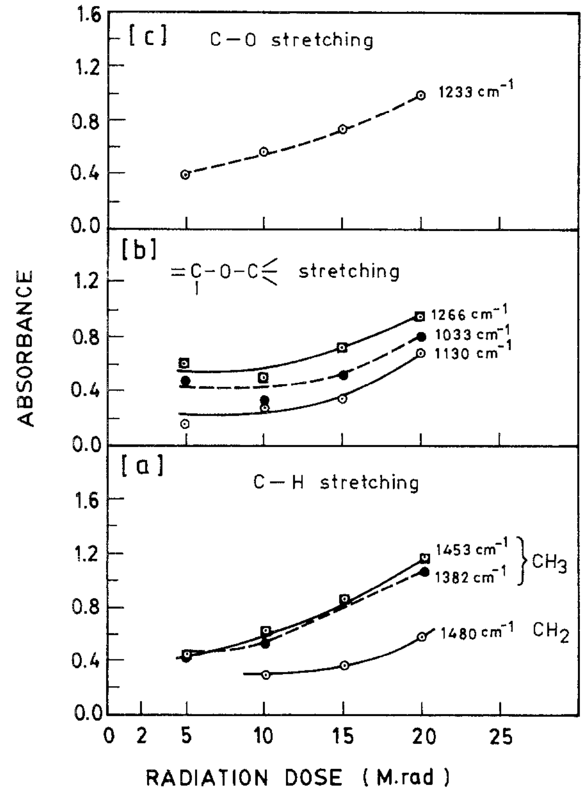


Figure 3 Plot of absorbance of (a) C–H stretching vibration of CH_2 and CH_3 groups; (b) C–O–C stretching vibration; (c) C–O stretching vibration at different frequencies with radiation dose

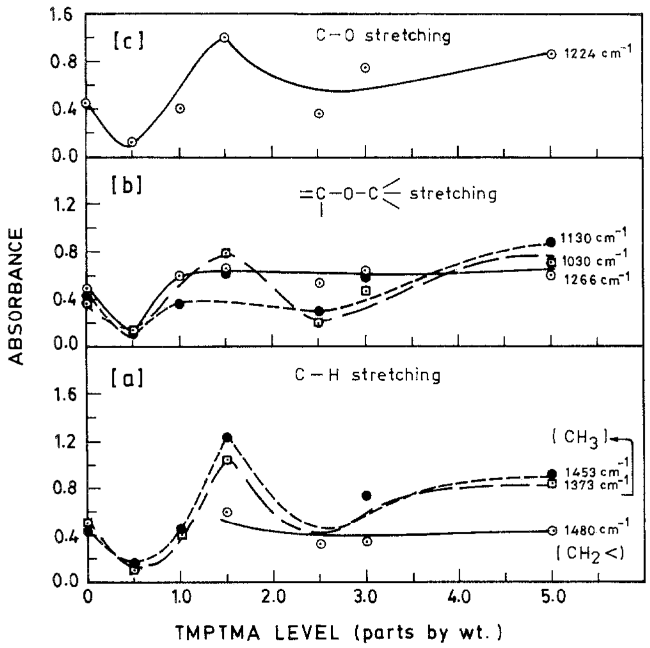


Figure 4 Plot of absorbance (at different frequencies) with varying TMPTMA for: (a) C–H stretching vibration of CH_3 groups; (b) C–O–C stretching vibration; (c) C–O stretching vibration

Tensile properties. Tensile strength, elongation at break, 100%, modulus and energy at break were measured on dumb-bell specimens according to ASTM D412 in a Zwick-1445 Universal Testing machine, at a strain rate of 500 mm min^{-1} at 27 ± 2°C. The average was taken on three samples and the experimental error was ± 5%.

RESULTS AND DISCUSSION

I.r. study

Figure 1a shows the i.r. spectra in the region of 2000 cm^{-1}–1000 cm^{-1} of pure EVA, EVA irradiated with a 5 Mrad dose, unirradiated EVA containing 5 parts TMPTMA and irradiated EVA containing 5 parts TMPTMA having 2 and 5 Mrad irradiation doses respectively.

The infrared spectra of pure EVA shows an absorption peak at 1740 cm^{-1} due to carbonyl stretching ($>$C = O) for an ester group, 1480 cm^{-1} due to C–H bending of $-CH_2$, 1370 cm^{-1} due to C–H bending of $-CH_3$, 1260 cm^{-1} due to C–O stretching and at 1030 cm^{-1} due to ether linkage (-C–O–C-). These peaks are in good agreement with the literature values[10].

There is no significant difference in spectra when EVA is irradiated. Sultan and Sorvik[11] reported that unlike LDPE, the formation of vinyl end groups in EVA is suppressed at high temperatures due to the addition of macroradicals to the π electrons, and cyclization. The spectra of unirradiated blend of EVA and TMPTMA shows a sharp peak at around 1640 cm^{-1} mainly resulting from $>$C = C$<$ stretching of *trans*-vinylene which are present in TMPTMA. When the blands are irradiated with 2 and 5 Mrad doses, the peak at

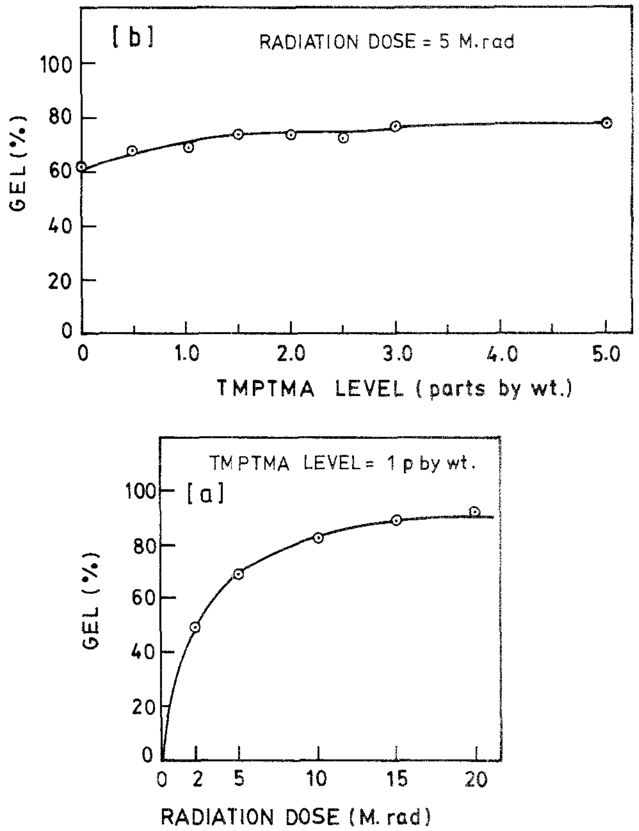
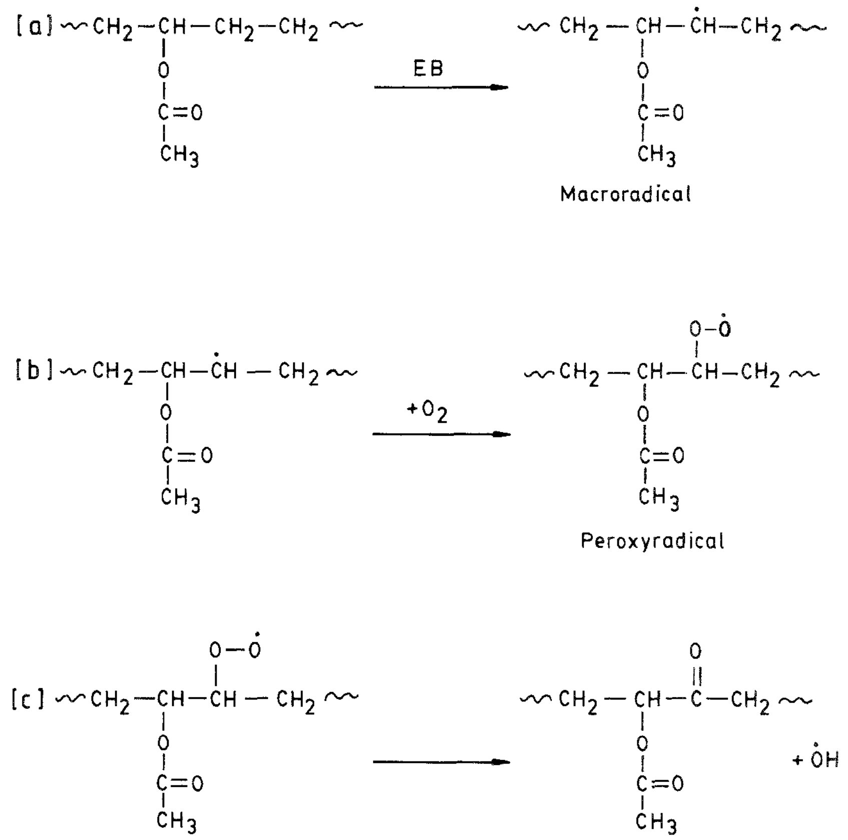


Figure 5 Variation of percent gel content (a) with the change of radiation dose at a constant level of TMPTMA; (b) with changes in the TMPTMA level at a constant irradiation dose



Scheme 1

1640 cm^{-1} due to >C = C< stretching disappears. This is probably because of grafting or crosslinking of TMPTMA with EVA through unsaturation.

Figures 1b and *c* show the difference spectra in the 2000–1000 cm^{-1} region of samples with varying radiation doses at a constant TMPTMA level of 1 part by weight and with varying TMPTMA levels at a constant radiation dose of 5 Mrad.

The peak at 1640 cm^{-1} due to *trans*-vinylenes which is the characteristic peak of TMPTMA disappears, when the samples are irradiated with a 2 Mrad radiation dose at various levels of TMPTMA. No characteristic peak of TMPTMA was found in ether extract of the samples. It can be concluded that all TMPTMA added in various samples are used for grafting and crosslinking at a 2 Mrad radiation dose. Nethsinghe and Gilbert[4,5] also reported that there was no such peak at 1640 cm^{-1} for PVC modified by TMPTMA and arrived at the same conclusion.

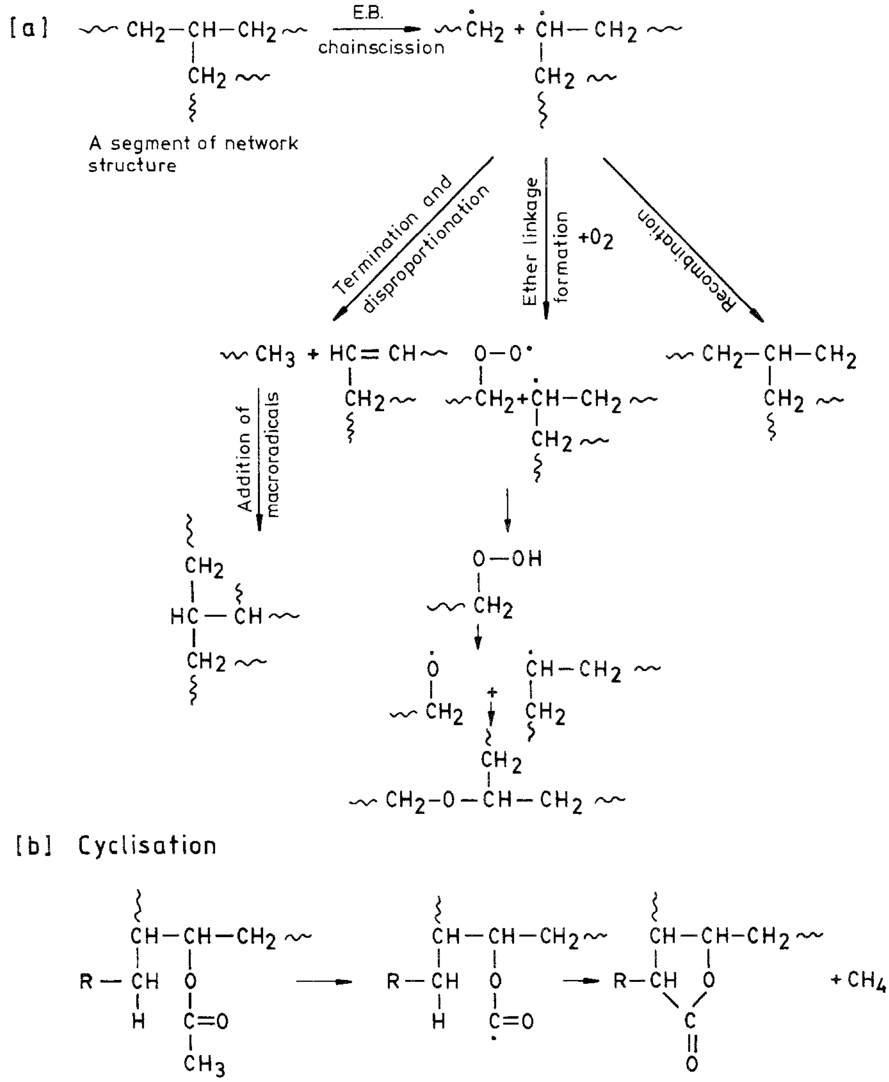
Figures 2a and *b* show the variation of absorbance at 1740 cm^{-1} due to >C = O stretching vibration with variation of irradiation dose and TMPTMA level. >C = O stretching absorbance increases sharply with radiation dose, whereas with increasing TMPTMA level there is a maximum at 1.5 parts TMPTMA level.

The increase of carbonyl (>C = O) group concentration in the backbone chain of EVA is due to aerial oxidation of the samples during irradiation under normal atmosphere (*Scheme 1*).

Variation of >C = O absorbance with TMPTMA level is rather irregular. Probably the grafting, crosslinking and oxidation reactions predominate up to 1.5 parts of TMPTMA, when the >C = O concentration increases. Beyond 1.5 parts, chain scission and breakdown of the network structure, because of the availability of a large number of free radicals, take place (*Scheme 2*). Ultimately, oxidation predominates and absorbance of >C = O stretching vibration increases.

In *Figure 3a* absorbance values at 1480 cm^{-1}, 1453 cm^{-1} and 1382 cm^{-1} from the difference spectra are plotted against the irradiation dose. Absorbance due to >CH_2 scissor vibration at 1480 cm^{-1} remains almost constant with the increase of irradiation dose up to 15 Mrad. Then its absorbance increases marginally up to 20 Mrad.

Up to a 15 Mrad dose, probably there is a balance between various reactions i.e. aerial oxidation, crosslinking of EVA with TMPTMA or itself, and chain scission or disproportionation (*Schemes 1, 2* and *3*) followed by the addition of macroradicals to π electrons



Scheme 2

and cyclization. After 15 Mrad, chain scission and disproportionation or cyclization reactions probably predominate[3] (*Scheme 2*).

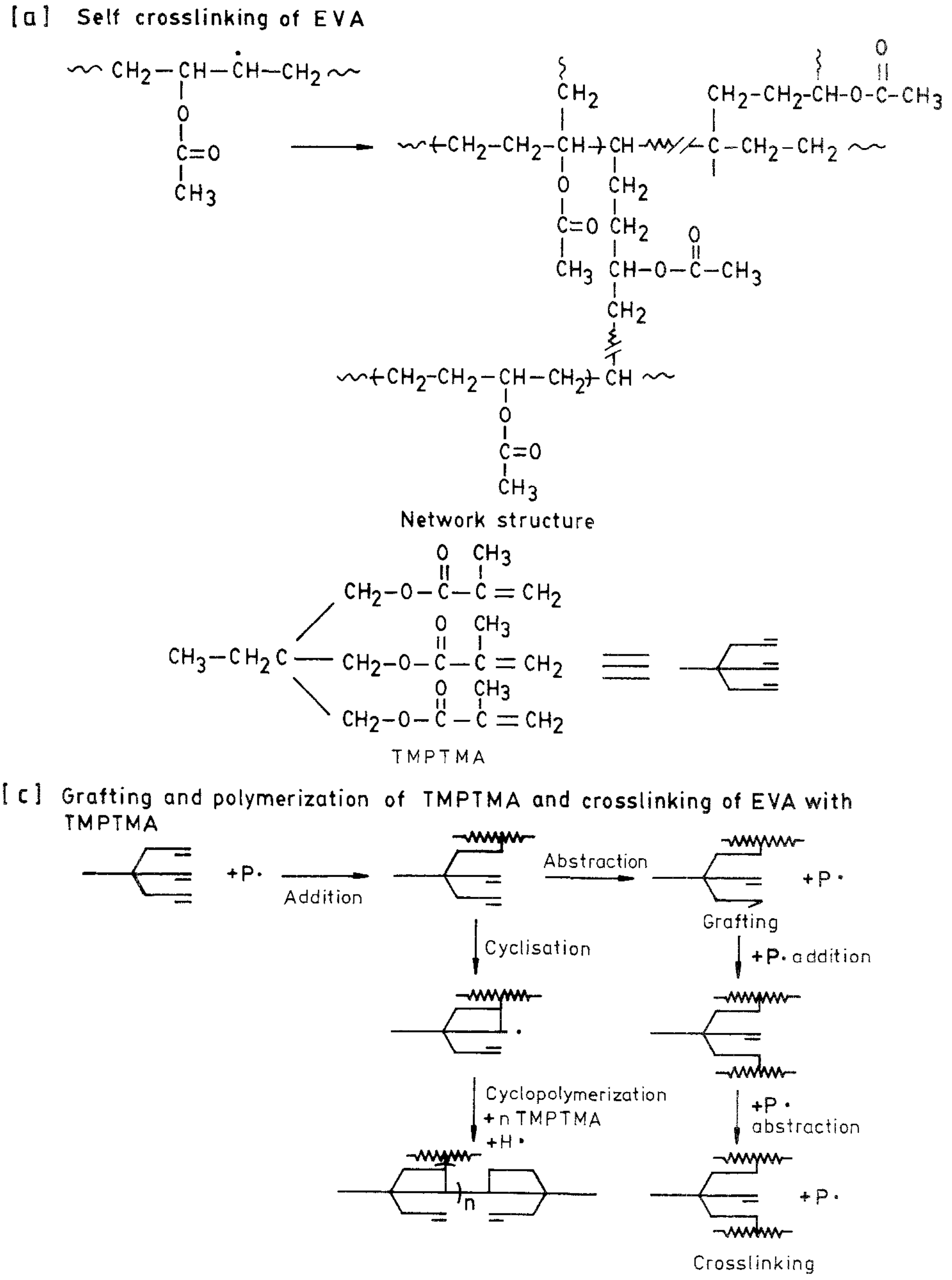
Absorbances at 1453 cm^{-1} and 1382 cm^{-1} due to C–H bending vibration of $-CH_3$ increase with increasing irradiation dose. This may be due to the tendency of chain scission to predominate termination of chains by disproportionation and cyclization reactions (*Scheme 2*) at a higher dosage.

Variations of absorbance at 1266 cm^{-1}, 1033 cm^{-1}, 1130 cm^{-1} and 1233 cm^{-1} (*Figures 3b* and *c*) with irradiation dose are due to -C–O–C- stretching and C–O stretching of ether linkage. These show a similar trend to that in *Figure 3a*. The ether linkage is formed due to chain scission and oxidation by a free radical mechanism.

Figure 4a shows the effect of TMPTMA levels on the absorbance at 1480 cm^{-1} due to $>CH_2$ scissor vibration and at 1373 cm^{-1} and 1453 cm^{-1} due to C–H bending vibration of CH_3.

Absorbance due to $>CH_2$ scissor vibration remains almost constant over the whole range of TMPTMA levels. This is probably because of a balance between different factors i.e. addition of TMPTMA, chain scission, oxidation of the backbone of EVA and disproportionation or cyclization reactions (*Schemes 1, 2* and *3*).

Absorbances at 1373 cm^{-1} and 1453 cm^{-1} due to C–H bending at $-CH_3$ increase with increasing TMPTMA level up to 1.5 parts and then decrease before a final increase beyond 2.5 parts. Initial increase of absorbance may be due to greater availability of CH_3 from TMPTMA (*Schemes 2b* and *c*). After 1.5 parts, the absorbance decreases probably due to predominating tendency of crosslinking and cyclization, chain scission (*Schemes 2a, 3a* and *3b*). Finally it increases because of



Scheme 3

further oxidation and chain scission resulting from the presence of a large number of free radicals (*Schemes 1a, b, c* and *3*).

In *Figures 4b* and *c*, the absorbance at 1266, 1030, 1130 and 1224 cm^{-1} due to ether linkage and C–O stretching of ether are plotted against TMPTMA level. All these plots have the same trend as in *Figure 4a*. The values pass through a maximum at 1.5 parts and then decrease followed by a final increase beyond 2.5 parts.

From these plots, it may be concluded that some ether linkages due to oxidation and chain scission in the presence of free radicals are generated, which increase with TMPTMA level up to 1.5 parts. After that, reaction between free radicals and the matrix takes place predominantly. Finally, oxidation predominates due to the presence of a large number of free radicals as the TMPTMA level increases.

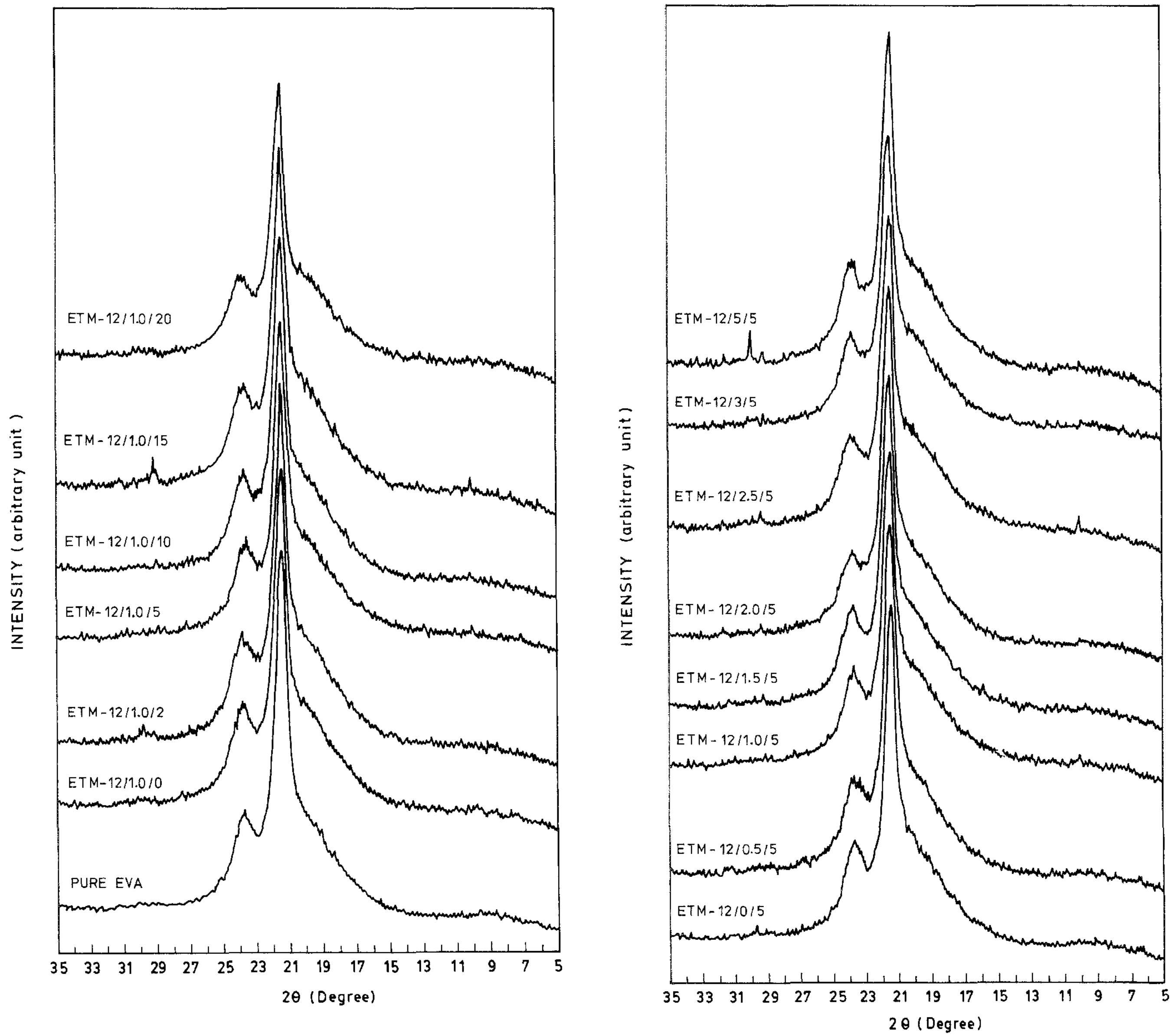
Gel content

The gel content is plotted against irradiation dose (*Figure 5a*) and TMPTMA level (*Figure 5b*). The gel content increases sharply with irradiation dose up to 10 Mrad. The increase is marginal after this. The higher values of the gel content at higher irradiation doses indicate the formation of a three dimensional network structure.

At a constant irradiation dose of 5 Mrad, the gel content marginally increases with the TMPTMA level. The values are much lower than those expected from higher levels of TMPTMA. This is probably due to the breakdown of the network structure. At higher TMPTMA levels more radicals are formed during irradiation which promotes this breakdown of the structures along with the formation of microgels.

X-ray study

X-ray diffraction patterns of pure EVA and EVA modified by 1 part TMPTMA at different doses of electron beam irradiation, and at different TMPTMA



(a) (b)

Figure 6 (a) X-ray diffraction pattern of pure EVA and samples having different doses of radiation; (b) X-ray diffraction pattern of irradiated samples containing different levels of TMPTMA

Table 3 Parameters evaluated from X-ray diffraction studies

Sample code	Peak angle θ		Percent crystallinity		Crystallite size (Å)		Interplanar distance (Å)		Interchain distance (Å)	
ETM	Low angle	High angle	Low angle	High angle	Low angle	High angle	Low angle	High angle	Low angle	High angle
12/0/0	10.9	11.9	32	4	78.8	96.8	4.07	3.38	5.09	4.67
12/0/5	10.9	11.9	30	4	77.3	97.8	4.07	3.73	5.09	4.67
12/0.5/5	10.8	11.9	31	4	76.0	81.9	4.09	3.73	5.11	4.67
12/1/5	10.9	11.9	31	4	75.7	80.3	4.07	3.73	5.09	4.67
12/1.5/5	10.8	11.9	27	4	86.1	97.5	4.11	3.75	5.14	4.69
12/2/5	10.8	11.8	34	4	88.5	102.7	4.09	3.75	5.12	4.69
12/2.5/5	10.9	11.9	25	4	84.6	97.7	4.07	3.72	5.09	4.65
12/3/5	10.8	11.9	28	4	81.0	95.3	4.11	3.73	5.14	4.67
12/5/5	10.9	11.9	25	3	81.4	96.8	4.05	3.73	5.07	4.67
12/1/0	10.9	11.9	29	5	80.0	88.9	4.07	3.72	5.09	4.65
12/1/2	10.9	11.9	28	4	82.9	90.9	4.07	3.72	5.09	4.65
12/1/5	10.9	11.9	31	4	75.7	80.3	4.07	3.73	5.09	4.67
12/1/10	10.8	11.8	35	4	82.3	87.3	4.09	3.75	5.12	4.69
12/1/15	10.9	11.9	27	4	84.9	89.6	4.07	3.73	5.09	4.66
12/1/20	10.8	12.0	29	4	83.9	88	4.09	3.70	5.11	4.63

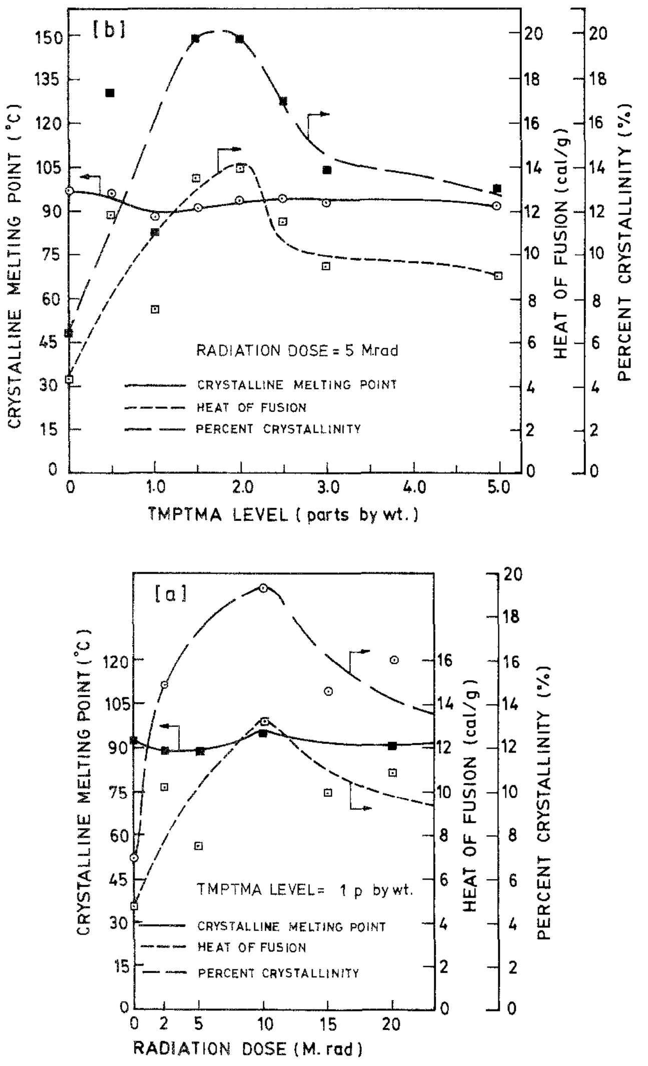


Figure 7 Plots of crystalline melting point, heat of fusion and percent crystallinity of samples *versus* (a) radiation dose; (b) TMPTMA level from d.s.c. studies

levels at a constant irradiation dose of 5 Mrad are displayed in *Figures 6a* and *b*. The results of percentage crystallinity, crystallite size, interplanar distance (*d*-value), and interchain distance of various samples are tabulated in *Table 3*.

There are mainly two peaks in the diffraction pattern—one at 10.8–10.9° and another at 11.8–11.9°. The percent crystallinity shows a maximum and then decreases for both variations of irradiation dose and TMPTMA level. The maximum is observed at a level of 2 parts TMPTMA when the TMPTMA level is varied at a constant dose of 5 Mrad irradiation whereas with the variation of irradiation dose, the percentage crystallinity shows a maximum at 10 Mrad, at a constant level of 1 part TMPTMA. The crystallite size follows almost a similar trend.

At higher irradiation doses and TMPTMA levels, more polar groups ($>C=O$) are formed, which is confirmed by i.r. studies. Higher intermolecular interactions are developed due to the presence of an increased number of polar groups, leading to the increase of percentage crystallinity. After attaining a maximum, it decreases because of the breakdown of the structure.

The interplanar distances (*d*) corresponding to the values 10.8–10.9° and 11.8–11.9° are 4.07 Å and 3.73 Å respectively. The (*h*, *k*, *l*) planes have also been calculated, assuming EVA to be orthorombic and using[8,12]

$$d = \left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{-1/2}$$

4.07 Å and 3.73 Å correspond to 110 and 200 planes respectively. On modification of EVA, either by TMPTMA or irradiation dose, the *d* values do not change (*Table 3*). The interchain distance remains almost constant for all the systems.

D.s.c. study

D.s.c. results also support the increase of crystallinity in the initial stage with increase of radiation dose (*Figure 7a*). With a further increase in radiation dose, the crystallinity decreases. Heat of fusion increases sharply with radiation dose, showing a maximum at 10 Mrad, followed by a decreasing trend. The crystalline melting point remains constant.

In *Figure 7b*, the percentage crystallinity, the heat of fusion and the crystalline melting point are plotted against TMPTMA level. These parameters excepting crystalline melting point increase with TMPTMA level up to 2 parts TMPTMA and then decrease.

The above results also support the strong intermolecular interactions up to 10 Mrad and 2 part TMPTMA level, and the breakdown of structure and chain slippage at higher radiation dose and TMPTMA level. These results are very similar to the results obtained from X-ray studies although the value of percentage crystallinity is slightly higher. It is well known that the crystallinity depends very much on the method of preparation of samples and the technique of measurement[2].

Tensile properties

Tensile strength, elongation at break and 100% modulus are plotted against irradiation dose at a constant TMPTMA level of 1 part (*Figure 8a*) and TMPTMA levels at a constant irradiation dose of 5 Mrad (*Figure 8b*).

The tensile strength and elongation at break initially increase sharply with increasing radiation dose, reaching a maximum at a radiation dose of 5 Mrad and then decrease. On the other hand, 100% modulus increases marginally.

The initial increase in strength may be due to the formation of a network structure and a slight increase in crystallinity. At higher irradiation doses, the large network structure begins to break down into a small network structure (microgel). Chain slippage takes place and as a result the strength falls.

Tensile strength and elongation at break increase with increasing TMPTMA levels reaching a maximum at 1 part and then decrease. This is also due to the combined effect of more crosslinking and crystallinity. Beyond 1 part the network structure breaks to a smaller network; molecular imperfection also plays an important role. For this reason, the tensile strength and elongation at break decrease with higher TMPTMA levels.

The increase in tensile strength is also evident from the trend in values of energy at break shown in *Figures 8c* and *d*. These values show a maximum at 5 Mrad at a constant TMPTMA level of 1 part, and at 1 part at a constant irradiation dose of 5 Mrad.

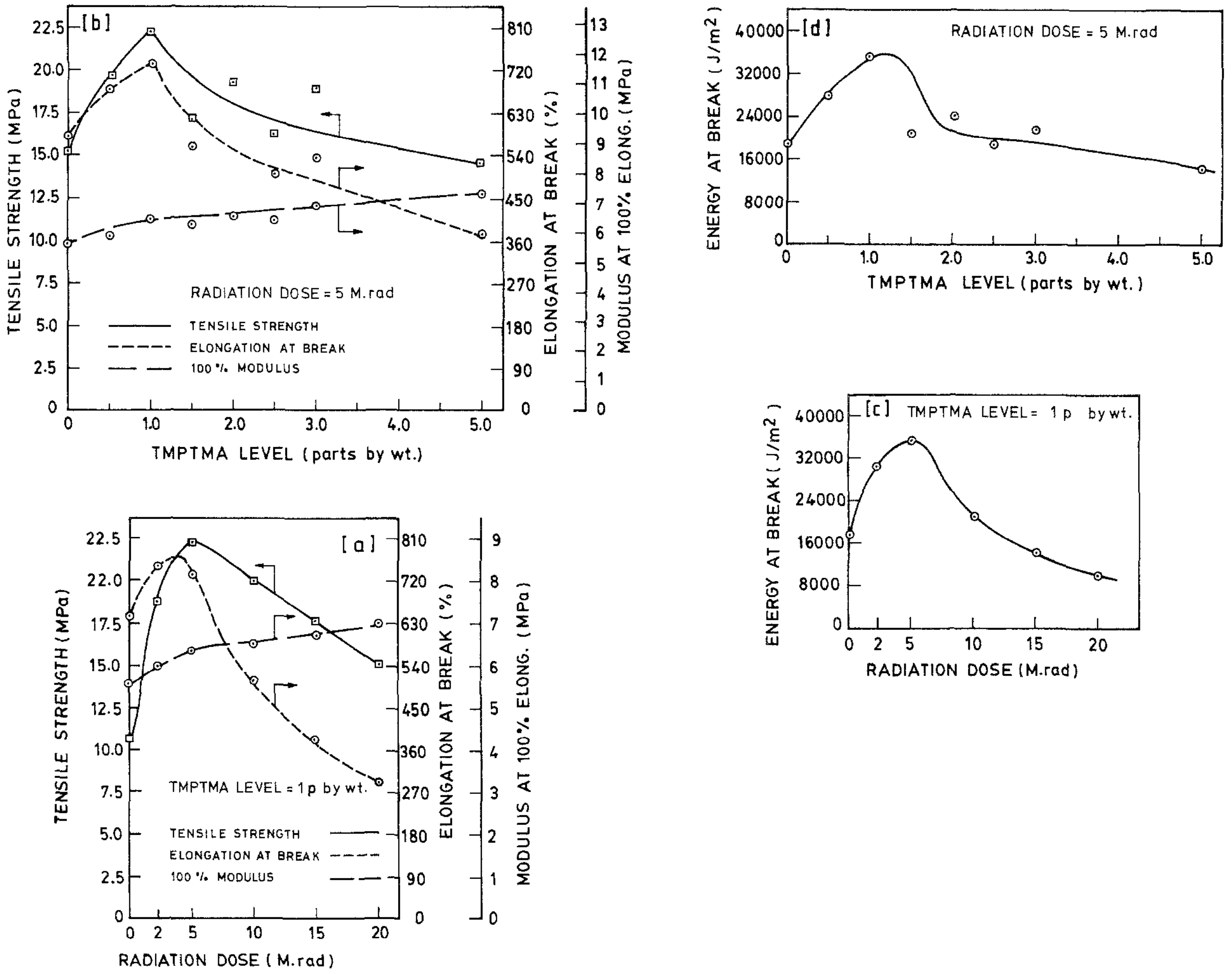


Figure 8 Plots of tensile strength, elongation at break and modulus at 100% elongation of irradiated samples *versus* (a) radiation dose; (b) TMPTMA level; (c) plot of energy at break of irradiated samples with radiation dose; (d) plots of energy at break of irradiated samples with TMPTMA level

CONCLUSIONS

Crosslinking of EVA (12% vinyl acetate content) by TMPTMA in the presence of an electron beam has been investigated and the results may be concluded as follows:

(1) The concentrations of the carbonyl group, ether linkage, methyl group and methylene group increases with radiation dose at 1 part TMPTMA level, whereas the formation of these groups reaches a maximum at a TMPTMA level of 1.5 parts, at a dose of 5 Mrad. All the monomers are consumed at a very early stage of irradiation (2 Mrad).

(2) Gel fraction increases with irradiation dose, whereas it increases marginally with an increase of TMPTMA level.

(3) X-ray and d.s.c. analyses show that the percentage crystallinity and melting enthalpy increase up to 10 Mrad and then decrease. These values increase up to 2 parts TMPTMA at a 5 Mrad irradiation dose, and then decrease.

(4) Ultimate tensile strength, elongation at break, 100% modulus and energy at break increase with irradiation dose up to 5 Mrad, and then decrease. These values also increase up to a TMPTMA level of 1 part at a 5 Mrad radiation dose.

From the above points, it seems that an irradiation dose of 5 Mrad is particularly suitable for these systems. Similarly, a TMPTMA level of 1 part is the optimum level of monomer beyond which the properties begin to deteriorate.

REFERENCES

1 Chaki, T. K., Despande, R. S., Majali, A. B., Tikku, V. K. and Bhowmick, A. K. *Angew. Makromol. Chem.* 1994, **61,** 217

2 Chaki, T. K., Roy, S., Despande, R. S., Majali, A. B., Tikku, V. K. and Bhowmick, A. K. *J. Appl. Polym. Sci.* 1994, **141,** 53

3 Chaki, T. K., Biswas, G., Despande, R. S., Majali, A. B., Tikku, V. K. and Bhowmick, A. K. *Radiat. Phys. Chem.* 1995, **45**, 829

4 Nethsinghe, L. P. and Gilbert, M. *Polymer* 1988, **29,** 1935

5 Nethsinghe, L. P. and Gilbert, M. *Polymer* 1989, **30,** 35

6 Migunova, L. L., Panina, T. E., Kuznetsov, A. V., Abksandrov, G. N. and Ivanov, V. S. *Leninger Ventu, Fiz. Khim* 1991, **4,** 70 (in Russian)

7 Norihiro, Hosoi (Sumitomo Electric Industries Ltd, Japan), Japan Patent 04,175,352 [92,175,352] (ClC08L23/08), 23 June, 1992

8 Alexander, L. E. 'X-ray Diffraction Methods in Polymer Science', Wiley Interscience, New York, 1969

9 Kamp, G. 'Polymer Characterization', Hanser Publishers, New York, 1980

10 Socrates, G. 'Infrared Characteristic Group Frequencies', Wiley Interscience, New York, 1980

11 Sultan, B. and Sorvik, E. *J. Appl. Polym. Sci.* 1991, **43,** 1747

12 Roychowdhury, N., Chaki, T. K., Dutta, A. and Bhowmick, A. K. *Polymer* 1989, **30,** 2047