

Electron-Beam-Initiated Grafting of Triallyl Cyanurate onto Polyethylene: Structure and Properties

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SYNOPSIS

Electron-beam (EB)-initiated grafting of triallyl cyanurate (TAC) onto polyethylene (PE) has been carried out over a range of radiation doses (2–20 Mrad) and concentrations of TAC (0.5–3 parts by weight). The grafting level, as determined from IR spectroscopy, is maximum at a 10 Mrad radiation dose using 1 part TAC. With increasing TAC level at a 15 Mrad dose, the grafting level is higher only after 1.5 parts TAC. The gel content increases with radiation dose in the initial stages. X-ray studies indicate two peaks at 10.6–10.8° and 11.7–11.9° and the corresponding interplanar distances of 4.15 and 3.80 Å. With increase in radiation dose or TAC level, the crystallinity decreases in the initial stage and then increases. It shows a decreasing trend again at higher radiation dose. The interplanar distance or the interchain distance of the modified polymer does not change. However, the crystallite size increases initially and then decreases. The tensile properties are relatively insensitive to the variation of radiation dose because of the interplay of various factors. The dielectric loss, $\tan \delta$, shows a maximum at a 10 Mrad dose and minimum at 5 and 15 Mrad due to changes of polarity and the carrier mobility. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Electron-beam-initiated grafting of monomers onto polymer is a relatively new technique. It has certain advantages over conventional grafting processes such as absence of catalyst residue and complete control of temperature and in being a solvent-free system and a source of enormous amount of radicals and ions with single control and accurate reproducibility. These are the reasons for which this technique has gained commercial importance in recent years, especially in the production of heat-shrinkable materials, wire, and cable terminations. Treatment of polymers by electron beam has been reviewed recently.^{1,2} Generally, rubbers can be cross-linked using an electron beam, whereas some plastics like polypropylene and poly(vinyl chloride) have a tendency to degrade.^{3,4} Compared to the cross-linking reaction, systematic studies of grafting initiated by

an electron beam have not been widely reported. In our earlier work, we attempted to graft methyl methacrylate (MMA) onto polyethylene.⁵ However, the grafting efficiency is not very high because of the volatility of MMA, though the properties of the grafted polyethylene (PE) are encouraging. The objective of the present article was to graft triallyl cyanurate onto PE, to characterize the modified polymers by IR spectroscopy, and to study X-ray, DSC, mechanical, and electrical properties with a view to develop heat-shrinkable plastics. Triallyl cyanurate is a polyfunctional unsaturated monomer, which is very efficient in producing high yields of radicals during irradiation. As a result, this helps in achieving better graft copolymerization of the monomer into PE and enhances the cross-linking efficiency.

EXPERIMENTAL

Materials

Polyethylene (PE) (Indothene 16 MA 400) of density 0.916 g/cc and melt-flow index (MFI) of 40 g/

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10 min was obtained from IPCL, Baroda, India. Triallyl cyanurate (TAC, Nouryset 300) of density 1115 kg/m³, flash point > 142°C, and thermal decomposition temperature > 150°C was obtained from Akzo Chemie Rubber Chemical, Netherlands.

Grafting of TAC onto Polyethylene

PE samples were mixed with TAC at various doses in a Brabender Plasticorder, PLE-330, at 60 rpm at 120°C. The samples were then compression-molded in the form of rectangular sheets (150 × 150 mm) of 2.5 mm thickness, which were then subjected to electron-beam irradiation in air at 25°C at the 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 I, and the specification of the electron-beam accelerator, in Table II.

Measurement of Properties

Degree of Grafting

The degree of grafting was determined on thin films using IR spectroscopy (Perkin-Elmer, Model 837).

Gel Fraction

Gel fraction was measured gravimetrically by immersing the samples in xylene for 72 h.

DSC

DSC studies were carried out using a Stanton Redcroft STA 625 thermal analyzer at a heating rate of 20°C/min in the temperature range of room temperature to 150°C. The peak maximum from the melting thermograms was considered as the melting point (T_m), and the area, as the heat of fusion, ΔH . The results reported here were the average of three

Table I Formulations of the Samples

PE (Parts)	TAC Level (Parts)	Irradiation Dose (Mrad)	Code of Samples
100	0	0	T _{0/0}
100	1	2	T _{1/2}
100	1	5	T _{1/5}
100	1	10	T _{1/10}
100	1	15	T _{1/15}
100	1	20	T _{1/20}
100	0.5	15	T _{0.5/15}
100	1.5	15	T _{1.5/15}
100	2	15	T _{2/15}
100	3	15	T _{3/15}

Table II 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)	15 mA
Adjusting limits for current	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration	400–700 μ s
Repetition rate	2–50 Hz
Pulse current	
Maximum	900 mA
Minimum	400 mA
Power supply voltage	3 × 380/220 V
Power supply voltage frequency	50 Hz
Consumption of power (total)	150 kW

samples. T_m and ΔH were reproducible within $\pm 1^\circ\text{C}$ and 5%, respectively.

X-ray Study

X-ray diffraction patterns of two samples from each system were recorded with a Philips X-ray diffractometer (Type PW 1840) using Ni-filtered CuK α radiation in the angular range from 5° to 35° (2θ) at an operating voltage of 40 kV and current of 20 mA. The area under the crystalline and amorphous portions was determined in arbitrary units and the degree of crystallinity (x_c) and the amorphous content (x_a) were measured using the relations

$$x_c = \frac{I_c}{I_c + I_a} \quad x_a = \frac{I_a}{I_c + I_a}$$

where I_c and I_a are the integrated intensity corresponding to the crystalline and amorphous phases, respectively. The results (2θ values) could be reproduced within a $\pm 0.01^\circ$ variation.

Peak half-width (β) and crystallite size P were calculated as follows⁶:

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

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

Tensile Properties

Tensile properties of dumbbell specimens were carried out in a Zwick 1445 at a testing speed of 50 mm/min at $27 \pm 2^\circ\text{C}$. Three samples were tested and the variations were $\pm 5\%$.

Dielectric Properties

Dielectric properties of the irradiated samples were measured in a Hioki LCR-Hi-Tester, Model 3530, at a frequency of 300 Hz at room temperature. The results reported here were the average of four samples and the $\tan \delta$ values were reproducible within $\pm 2\%$.

RESULTS AND DISCUSSION

IR Study

Figures 1(a) and (b) show the IR spectra of samples with different radiation dosages and TAC levels in

the 1800–1500 cm^{-1} region. The carbonyl stretching absorption at 1730 cm^{-1} initially increases and then falls off marginally with the radiation dose. A similar trend in the initial stage is also shown by the 1670 cm^{-1} peak due to C=C stretching of mainly *trans*-vinylenes.⁷ The formation of vinylene structure and carbonyls in PE was reported earlier.⁸ Figure 2 shows the variation of absorbance ratios of these two peaks with respect to the 1470 cm^{-1} peak due to the scissor vibration of $>\text{CH}_2$ groups. The absorbance ratio passes through a maximum at a 10 Mrad dose. At high dosages of irradiation, the reduction in the absorbance ratio (A_{1670}/A_{1470}) after the maximum is quite large. Figure 3 (a) and (b) display the IR spectra of different samples in the 1200–800 cm^{-1} region.

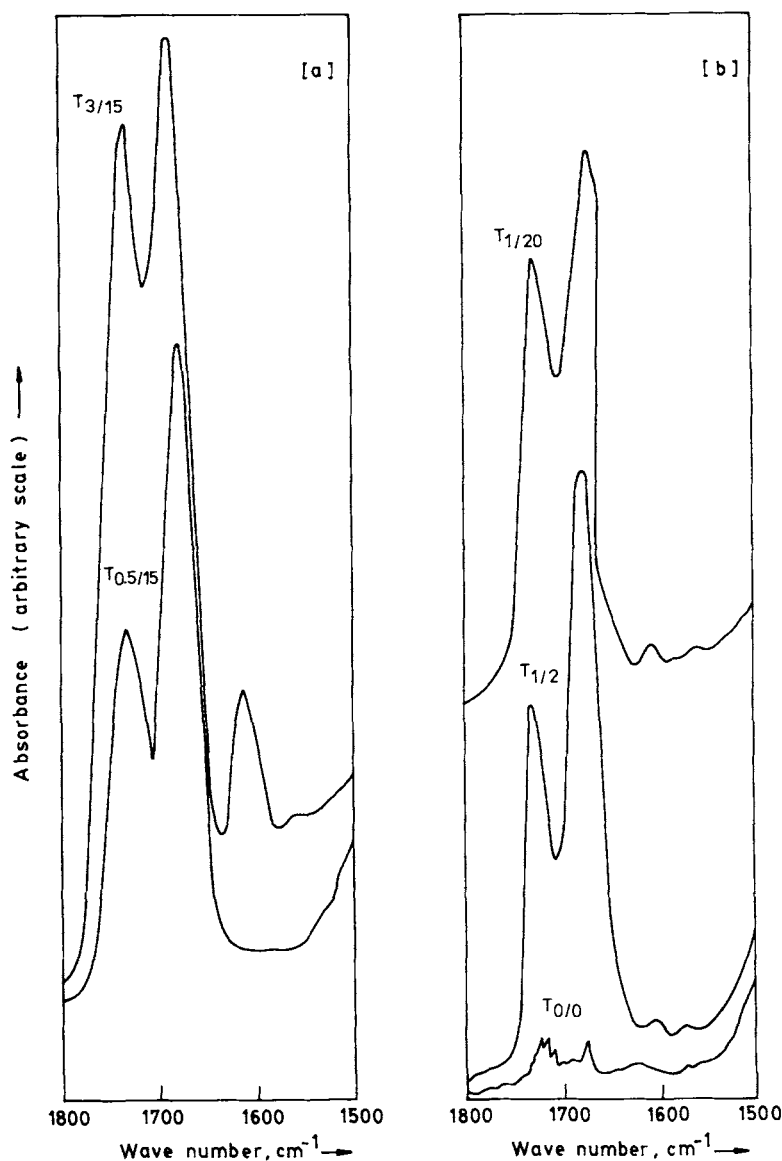


Figure 1 IR spectra of samples with different (a) TAC levels at a 15 Mrad irradiation dose and (b) radiation dosages at 1 part TAC in the range 1800–1500 cm^{-1} .

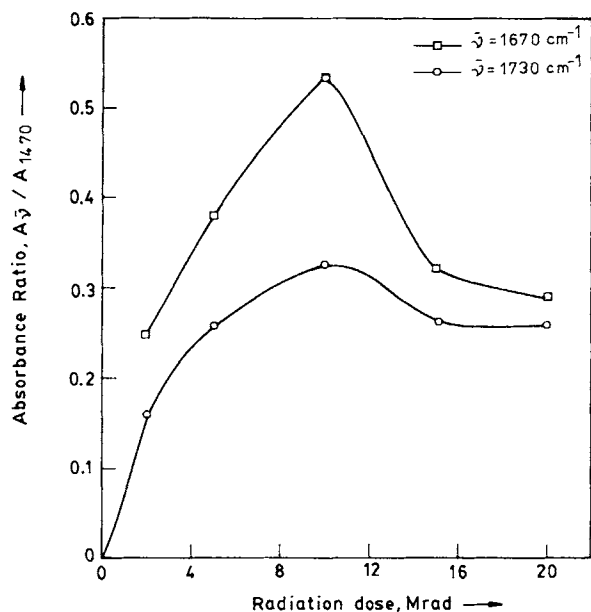


Figure 2 Variation of absorbance ratio of carbonyl and vinylene groups with radiation dose. The samples contain 1 part TAC.

The peak at 1140 cm^{-1} corresponds to the $-\text{O}-\text{CH}_2-$ stretching of TAC.⁷ From the absorbance ratio of the 1140 cm^{-1} peak with respect to that of the 1470 cm^{-1} peak, the relative grafting level is calculated. Figure 4 shows the variation of the grafting level with the radiation dose. The grafting level is maximum at a 10 Mrad radiation dose using 1 part TAC.

From the above observations, it seems that the PE matrix undergoes oxidation initially by interacting with the electron beam by formation of olefinic double bonds and carbonyl groups supported by the peaks at 1670 and 1730 cm^{-1} . Then, the grafting and cross-linking reactions take place. The cross-linking of PE as well as cyclization and cyclopolymerization of TAC result in a decrease of the peak height at 1670 cm^{-1} at a later stage. These are shown in Schemes 1a and b.

Variation of carbonyl and olefinic group content is rather irregular with the variation of TAC dose. Both the absorbance ratios of >C=C< and >C=O initially fall from 0 part by weight to 0.5 part by weight; then, the >C=C< absorbance ratio gradually increases with the increasing dose of TAC (Fig. 5). The >C=O absorbance ratio increases from 0.5 to 1.0 part, then flattens off up to 2 parts by weight and finally sharply increases. This is depicted in Figure 5. The initial decrease of the 1670 cm^{-1} peak may be due to gelling and interaction of PE with TAC through double bonds. The final increase is

due to the unreacted double bonds from the tri-functional monomer.

The variation of the grafting level with TAC dose exhibits a similar trend; up to 1.5 parts of TAC, there is marginal increase in grafting level, whereas beyond 1.5 parts by weight, the increase is very sharp (Fig. 6). The increased level of grafting due to a higher dosage of TAC is obviously due to more availability of the free TAC. It may be mentioned here that at a similar concentration of grafting material TAC has a higher grafting level than that of the MMA reported earlier.⁴

Gel Content

The gel content is plotted against the radiation dose (Fig. 4) and the level of TAC (Fig. 6). It increases with the radiation dose, passes through a maximum, and then decreases. The electron beam produces excited chemical species and free radicals. The free radicals then may undergo chain scission, cross-linking, and recombination of broken chains depending on the structure of the polymers. The increased gel fraction in the initial stage indicates a cross-linking reaction, whereas a reduction in the same at higher dosage is due to chain scission. The trend is very similar to that of the grafting level. With increase in the TAC level, the gel content increases after an initial reduction. The higher values of gel contents are due to greater cross-linking reactions.

X-ray Study

X-ray diffraction patterns of pure PE and PE modified by TAC at different doses of electron-beam irradiation are displayed in Figure 7. The results of percent crystallinity, crystallite size, interplanar distance, and interchain distance of various samples are tabulated in Table III.

There are mainly two peaks in the diffraction pattern—one at 10.6° – 10.8° and another between 11.7° and 11.9° . The crystallinity, in general, decreases in the initial stage, then increases, and, finally, shows a decreasing trend with increase in the irradiation dose. With increasing TAC level, this decreases also in the initial stage and then increases. The decrease in crystallinity in the initial stage is due to the fact that there is an increased number of imperfections in the molecular chain with the grafting of TAC onto PE or with irradiation dose. The latter increase may be ascribed to prevention of

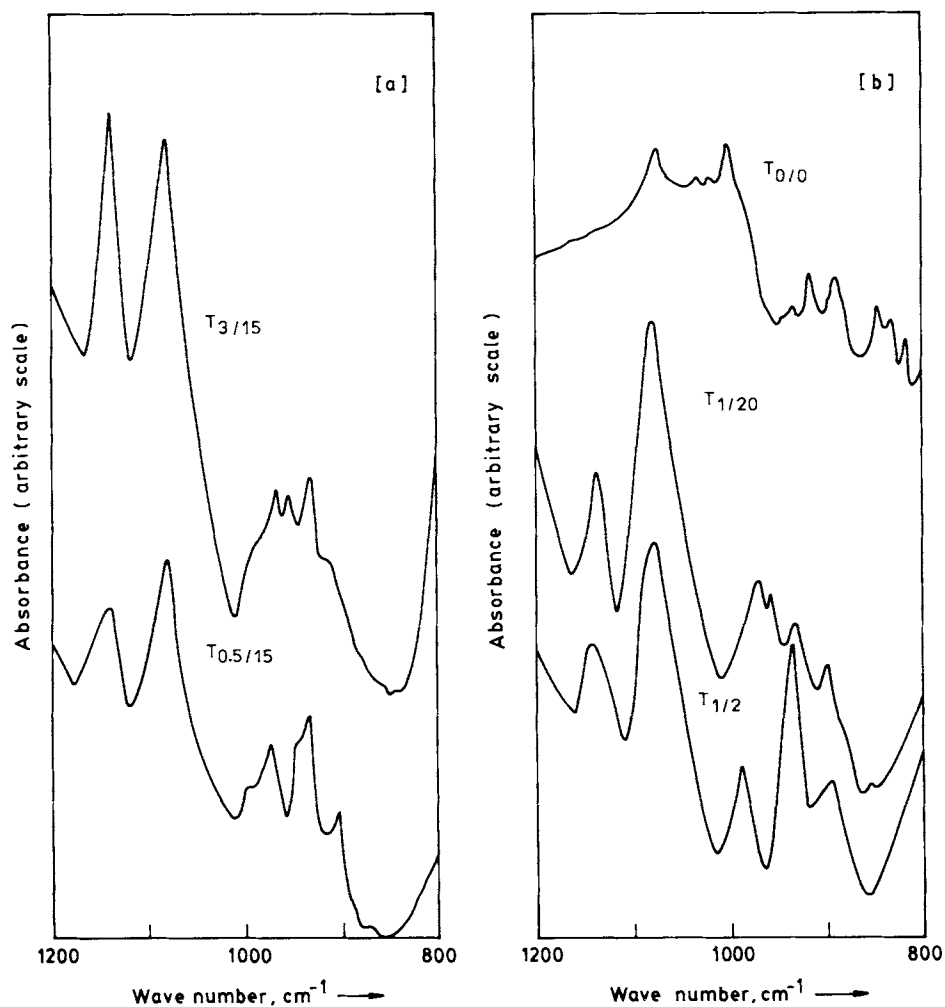


Figure 3 IR spectra of samples with different (a) TAC levels and (b) radiation dosages in the range 1200–800 cm^{-1} .

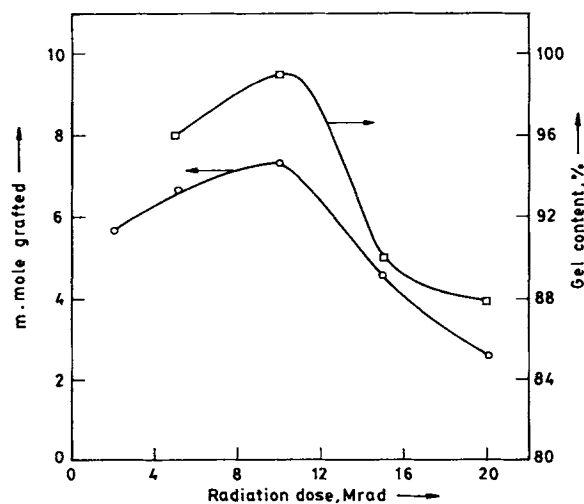


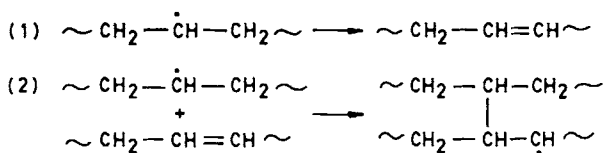
Figure 4 Variation of grafting level and gel content with radiation dose. The samples contain 1 part TAC.

chain slippage and higher intermolecular interaction. The larger number of imperfections at higher dosages causes the crystallinity to decrease.

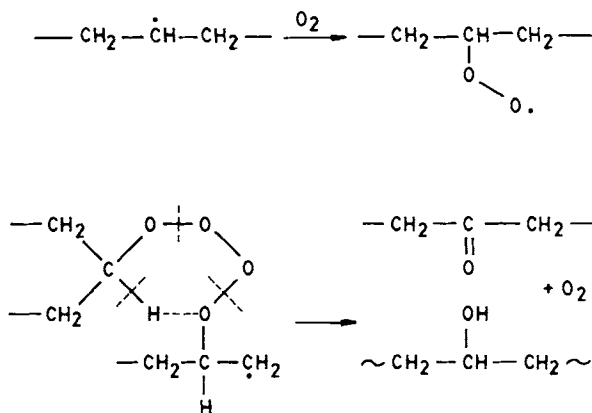
DSC results also support the decreasing trend of crystallinity in the initial stage, although the value of the percent crystallinity is slightly lower (31%) and the difference between the values is small. It is well known that the crystallinity depends very much on the method of preparation of the sample and the technique of measurement. Peak T_m in the DSC measurement also decreases from 118 to 110°C on modification by TAC or irradiation to the maximum level (Table IV).

The interplanar distances (d) corresponding to the θ values at 10.7° and 11.7° are 4.15 and 3.80 Å. These are very similar to those reported earlier.⁹ The (h, k, l) planes are also calculated assuming PE to be orthorhombic and using

Mechanism of vinylene formation and depletion :



Mechanism of formation of carbonyls :



Scheme 1a

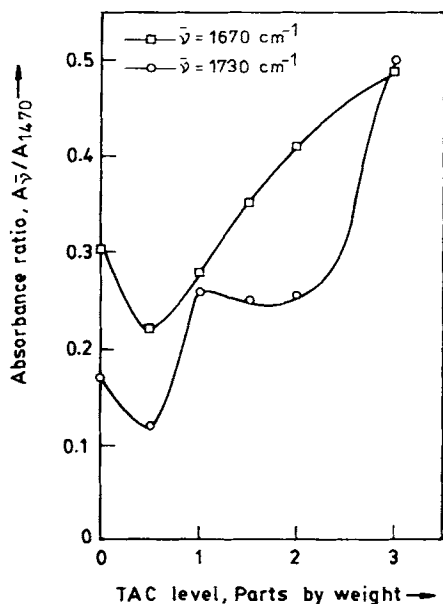


Figure 5 Variation of absorbance ratio of carbonyl and vinylene groups with TAC level. Irradiation dose = 15 Mrad.

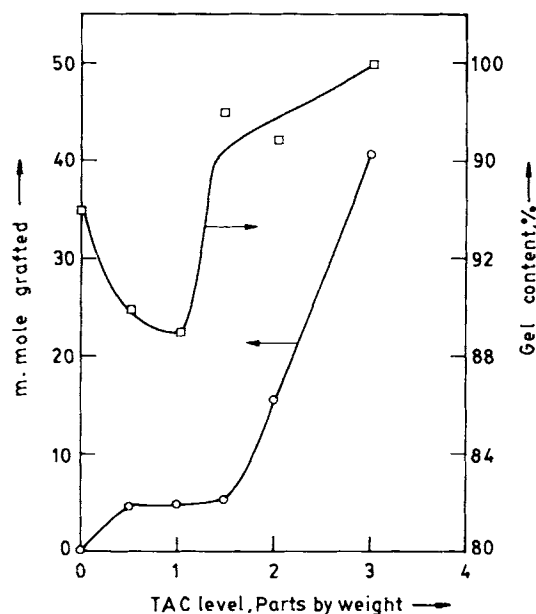


Figure 6 Variation of grafting level and gel content with TAC level. Irradiation dose = 15 Mrad.

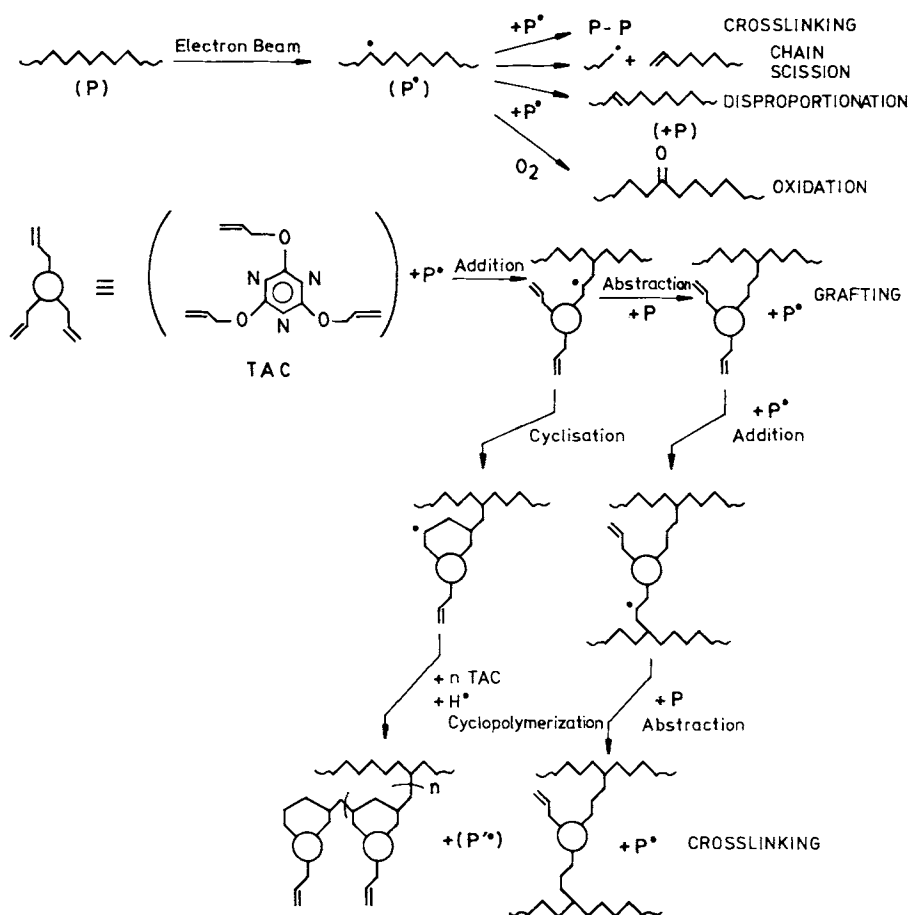
$$d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

where $a = 7.40 \text{ \AA}$, $b = 4.93 \text{ \AA}$, and $c = 2.5 \text{ \AA}$. The d values are 4.15 and 3.80 \AA , corresponding to $[110]$ and $[200]$ planes, respectively. On modification by TAC or irradiation, the d values do not change significantly (Table III). The interchain distance remains almost constant for all the systems. The crystallite size, calculated from the peak half-width, increases initially and then decreases after showing a maxima, with increase in the irradiation dose or TAC level.

Tensile Properties

The tensile strength remains almost constant with increase in the radiation dose (samples $T_{1/2}-T_{1/20}$), though there is a marginal increase at 10 Mrad radiation (Table V). Increasing TAC level decreases the strength in the initial stage. At 2.0 parts, it increases again. The elongation at break, however, constantly decreases with either increasing radiation dose or TAC level. The tensile strength is a function of crystallinity, gel content, molecular imperfection, and reduced chain length due to degradation in the present system. Whereas the increase in the first two factors would enhance the strength, the last two would contribute to its decrease. Our results indicate

Mechanism of crosslinking of PE and interaction of TAC with PE



Scheme 1b

Table III Parameters Evaluated from X-ray Diffraction Studies

Sample No.	Peak Angle, (θ) Degree		Percent Crystallinity		Crystallite Size (Å)		Interplaner Distance (Å)		Interchain Distance (Å)	
	Low	High	Low Angle	High Angle	Low Angle	High Angle	Low Angle	High Angle	Low Angle	High Angle
	T _{0/0}	10.75	11.85	44.64	5.64	80.0	80.3	4.13	3.75	5.17
T _{1/5}	10.60	11.72	39.40	4.03	112.6	118.0	4.19	3.80	5.24	4.74
T _{1/10}	10.75	11.80	42.50	4.50	97.6	104.3	4.13	3.77	5.17	4.71
T _{1/15}	10.70	11.72	43.00	3.67	108.0	121.6	4.15	3.80	5.19	4.74
T _{1/20}	10.70	11.72	41.30	2.96	106.7	100.4	4.15	3.80	5.19	4.74
T _{0.5/15}	10.65	11.70	39.30	4.30	107.2	104.3	4.17	3.80	5.21	4.75
T _{2/15}	10.70	11.80	42.00	3.86	119.4	127.5	4.15	3.77	5.19	4.71
T _{3/15}	10.80	11.90	44.40	3.72	108.2	95.6	4.11	3.74	5.14	4.67

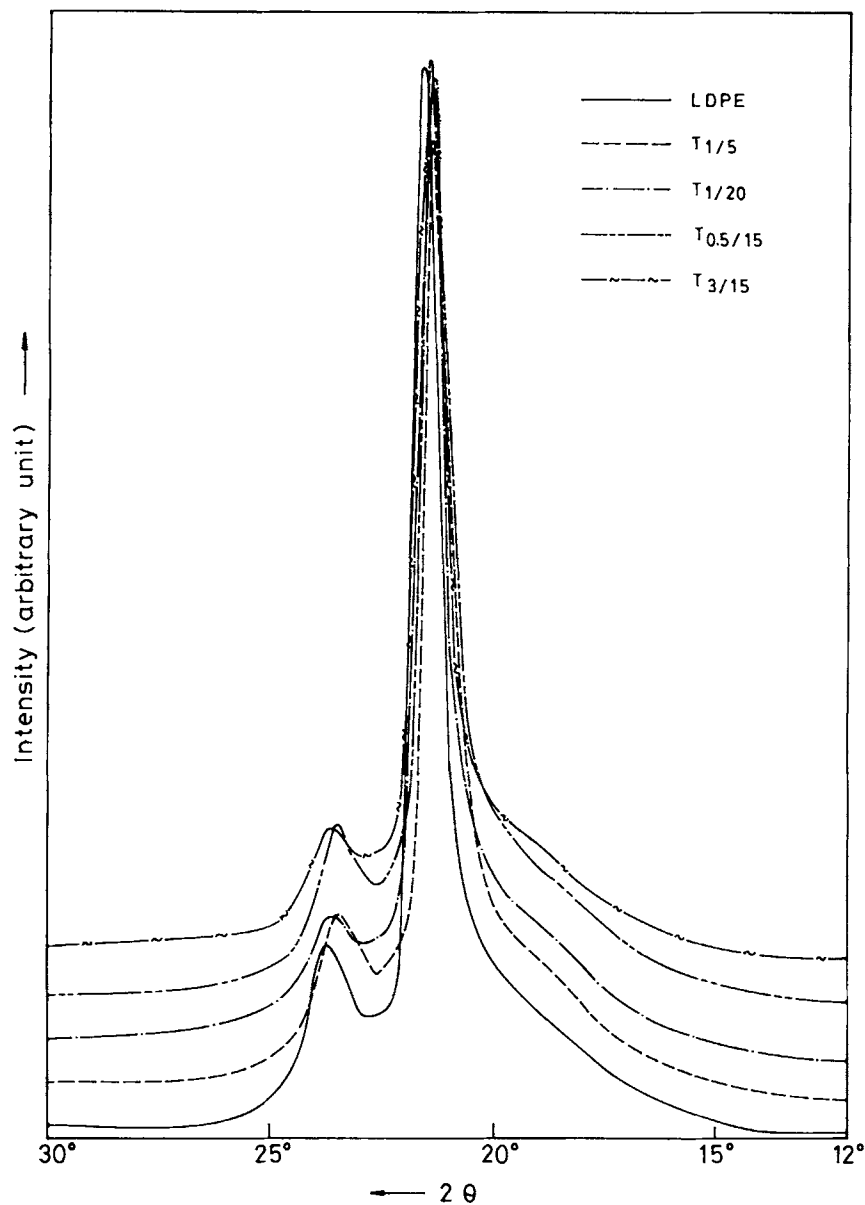


Figure 7 Variation of X-ray diffraction pattern from PE and different irradiated samples.

interplay of all the factors. The reduced elongation at break may also be ascribed to the same reasons.

Dielectric Properties

Dielectric properties were investigated at a single frequency of 300 Hz for PE samples having various doses of irradiation at a constant TAC level (1 part) and also various concentrations of TAC at constant radiation dose (15 Mrad). The dielectric loss of representative samples is plotted in Figure 8. With in-

creasing radiation dose, the loss decreases sharply in the initial stage and then increases, giving a broad peak at a 10 Mrad radiation dose and then again decreases to a minimum and, finally, increases sharply with the radiation dose. The samples containing various levels of TAC also show almost a similar trend. Here, a broad peak is obtained at 1 part by weight of the TAC level, giving a minimum $\tan \delta$ value at 1.5 parts TAC. The $\tan \delta$ value increases up to 2.0 parts by weight of the TAC level and then remains almost constant with increase in the TAC level.

Table IV Parameters Evaluated from DSC Curves

Sample No.	Crystalline Melting Point (°C)	Percent Crystallinity (%)
$T_{0/0}$	118	32
$T_{1/2}$	113	31
$T_{1/5}$	111	30
$T_{1/10}$	112	31
$T_{1/15}$	110	32
$T_{1/20}$	111	33
$T_{0/15}$	110	33
$T_{0.5/15}$	110	30
$T_{1.5/15}$	113	32
$T_{2/15}$	110	32
$T_{3/15}$	110	32

Table V Physical Properties of Electron-beam-irradiated Samples

Sample No.	Tensile Strength (MPa)	Elongation at Break (%)
$T_{0/0}$	11.30	506
$T_{1/2}$	14.61	422
$T_{1/5}$	14.94	404
$T_{1/10}$	15.63	382
$T_{1/15}$	14.55	342
$T_{1/20}$	14.50	275
$T_{0/15}$	16.75	387
$T_{0.5/15}$	14.40	343
$T_{1/15}$	14.55	342
$T_{2/15}$	16.25	387
$T_{3/15}$	10.80	310

The above observations may be explained as follows: The dielectric properties are very sensitive to local inhomogeneities¹⁰ or structure defects, especially dipole introduction into the structure. With increasing radiation dose or TAC level, $\tan \delta$ decreases due to structure heterogeneities. Gradually, the contribution from ionic conduction becomes far greater than that from relaxation loss, generating a broad peak either at a 10 Mrad dose or at a 1 part TAC level.

The numerical value of $\tan \delta$ is generally deter-

mined by both the polarity and the carrier mobility. The polarity determines the nature of the relaxation and relaxation time determines the numerical value of $\tan \delta$ at a specific temperature and frequency for that relaxation. Again, polar carbonyl groups formed in PE due to oxidation are responsible for greater dielectric loss. At low TAC level or at low irradiation dose, a low value of $\tan \delta$ may be due to a smaller number of carbonyl groups or a smaller number of short branches. Gradually, due to cross-linking of PE chains and grafting of TAC onto PE, the number

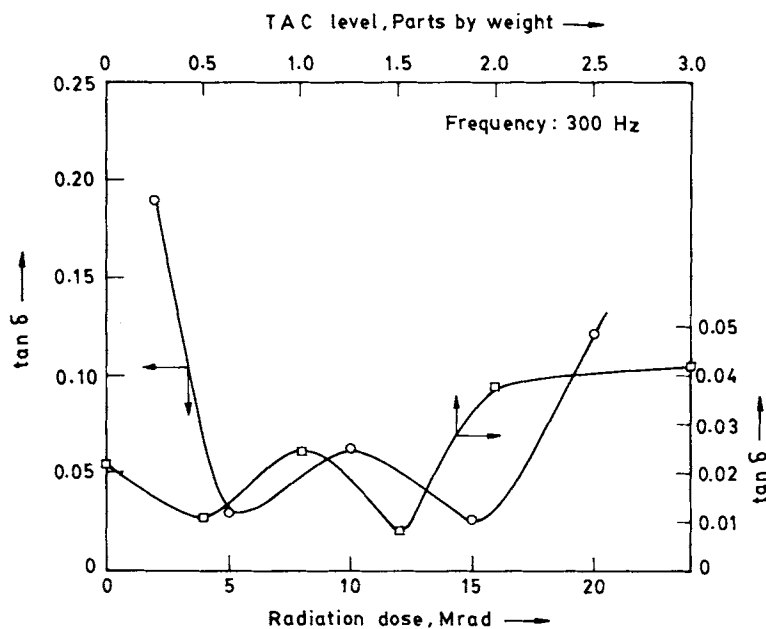


Figure 8 Effect of radiation dose at 1 part TAC level and TAC level at 15 Mrad irradiation on electrical $\tan \delta$.

of short branches increasing more and more and the higher structural heterogeneity developed results in a broad peak. Again, $\tan \delta$ decreases as the degree of cure increases with increasing radiation dose or TAC level. In general, an increase in density leads to a decrease in $\tan \delta$. Here, also, stretching of semi-crystalline PE affects the unit cell crystallization¹¹ and leads to a lower $\tan \delta$. Finally, higher irradiation dose or higher TAC level results in breaking of chains and formation of more polar carbonyl groups into the system and $\tan \delta$ starts increasing again.

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