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# 10 MeV electron beam cross-linking of plasticized PVC in presence of EHPTM and TAC additives

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**Abstract.** Irradiation of plasticized PVC (PPVC) compound containing a cross-linking monomer was carried out by a 10 MeV electron beam. This compound mainly is used as insulation in the wire and cable industry. The cross-linking monomers EHPTM and TAC at different ratio of 3, 6, and 9 phr were used. The dose range was varied from 50 to 150 kGy. The effects of monomers and radiation dose on radiation cross-linking were studied by hot-set testing and gel content measurements. In the absence of EHPTM and TAC, cross-linking did not take place by high energy electron beam at any dose and samples had very large elongation in a hot-set apparatus. But in the presence of these monomers, gel content augmented with an increase in radiation dose and EHPTM level. The highest value of approximately 76% gel content was obtained. In this case the lowest hot-set value was about 12%. Also, tensile strength, elongation at break, modulus, volume resistivity, dielectric strength, and limiting oxygen index of samples were examined. It was found that the mechanical properties of samples containing EHPTM and TAC improved significantly with increasing radiation dose. But for PPVC samples loaded with EHPTM, tensile strength values were higher than those of the loaded ones with TAC at all radiation doses. From the hot-set data it is concluded that the samples loaded with EHPTM had a low thermal expansion compared with samples loaded with TAC. The results indicated that EHPTM is a more effective cross-linking agent for PPVC compound compared with TAC.

**Key words:** plasticized PVC • electron beam • cross-linking • EHPTM • triallylcyanurate (TAC)

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## Introduction

Ionizing radiation (gamma rays, electron beam and ion beams) are used for modifying the structure and properties of polymers [3]. Plasticized polyvinylchloride (PVC) is a suitable material for insulation of wire and cable, having good physical properties. This halogenated organic compound is flame retardant with good resistance to chemicals and with ease of processing. The electron beam utilization to improve key properties of selected plastic products has been discussed [2]. Radiation cross-linked PVC has new properties and for this reason it renders itself for many applications including wire and cable insulation especially at high temperature. A unique advantage of radiation cross-linking is its capability of cross-linking at low temperature. The wire insulation is generally thin and electron beam of 10 MeV energy is a suitable source for irradiation of wire and cable insulation. The methods for irradiation of wire and cable insulation by high energy (10 MeV) electron beam have been reported earlier [1].

Cross-linking of PVC was reported with gamma radiation in the presence of unsaturated multifunctional monomers [11]. These monomers are capable to enhance radiation cross-linking of PVC [4, 7, 9, 10, 12, 13, 15, 16]. Hell *et al.* [8] have studied gamma radiation cross-linking of plasticized PVC. They have verified

**Table 1.** Ingredients of the PPVC compounds

| Sample formulation | PVC (phr) | Dioctyl phthalate (phr) | Lead sulphate (phr) | Stearic acid (phr) | Calcium carbonate (phr) | EHPTM (phr) | TAC (phr) | Antioxidant (phr) |
|---|---|---|---|---|---|---|---|---|
| PPVC-1 | 100 | 45 | 2 | 0.8 | 45 | 3 | – | 0.25 |
| PPVC-2 | 100 | 45 | 2 | 0.8 | 45 | 6 | – | 0.25 |
| PPVC-3 | 100 | 45 | 2 | 0.8 | 45 | 9 | – | 0.25 |
| PPVC-4 | 100 | 45 | 2 | 0.8 | 45 | – | 3 | 0.25 |
| PPVC-5 | 100 | 45 | 2 | 0.8 | 45 | – | 6 | 0.25 |
| PPVC-6 | 100 | 45 | 2 | 0.8 | 45 | – | 9 | 0.25 |

the efficiencies of various multifunctional monomers in radiation cross-linking of PPVC. From their gel measurements it was concluded that 2-ethyl-2-(hydroxymethyl)-propandiol-(1,3)-trimethacrylate (EHPTM) and triallylcyanurate (TAC) at small concentrations with low gamma radiation doses give high cross-linking yield. Sharma *et al.* [14] reported cross-linking of PPVC by 2 MeV electron beam radiation in the presence of TMPTMA (trimethylolpropan trimethacrylate) as a cross-linking agent. They observed an increase in tensile strength (TS), gel content and a decrease in hot-set values of irradiated PPVC samples. In this work, a 10 MeV electron beam has been used to study the influence of cross-linking monomers EHPTM, TAC and radiation doses, on cross-linking of PVC compound. We have measured the mechanical and thermal properties of various samples before and after irradiation and the results are presented.

## Experimental

### Materials

Polyvinylchloride (PVC, K value 70), S6558, supplied by Imam Petrochemical Co., Iran, di-octyl phthalate (DOP) plasticizer, lead sulphate as stabilizer, stearic acid, calcium carbonate as fillers, Irganox 1010 as antioxidant, were compounded to form a plasticized compound. To this basic mixture, two multifunctional monomers EHPTM and TAC obtained from Merck Company were added. The formulations of prepared samples and samples codes are listed in Table 1.

### Sample preparation

From the above material six types of compounds according to the formulation of Table 1 were chosen and coded. The various formulations were mixed in a Brabender Plasticorder PL2000 at 60 rpm rotor speed. The temperature of mixing was 150°C. Sheets of 2 ± 0.05 mm thickness were prepared by compression moulded between an aluminum foil at 160°C under pressure in an electrically heated press. The sheets were cut in dumbbell shapes specimens using standard die.

### Irradiation

Samples were irradiated at atmospheric pressure and at ambient temperature by a 10 MeV electron beam of RHODOTRON TT200 accelerator of the Yazd Radiation Processing Centre. Radiation dose ranged varied from 50 to 150 kGy. The specification of the electron beam accelerator can be found in Ref. [6]. Dosimetery was performed by a cellulose triacetate (CTA) film. Details of dose measurements are given in Ref. [1].

### Gel content measurements

The gel contents were determined by extraction of irradiated samples in boiling tetrahydrofuran (THF) over a period of 24 h using a Soxleht extractor. After being dried, the insoluble residue was weighed. The gel content (%) was calculated as $100 \times (m_2/m_1)$, where $m_1$ is the initial mass of the irradiated sample and $m_2$ is the mass of the insoluble residue.

### Mechanical testing

Tensile strength (TS), elongation at break (EB) and modulus at 100% elongation for PPVC samples before and after irradiation were measured on dumbbell specimens according to ASTM D-638 in a Zwick (1496) universal testing machine at a test speed of 50 mm/min. TS, EB and modulus were determined from the stress-strain curve. The results reported here are the averages of three samples measurements, and the experimental error is 5%.

### Hot-set testing

Hot-set testing was carried out at 150°C under 20 N/cm$^2$ for 15 min using a hot-set oven UT6050HS (Heraeus). Thermal expansion [%] of the samples was calculated as $(l_1 - l_o)/l_o$ [%], where $l_o$ and $l_1$ are the initial and elongated length, respectively. All measurements were carried out with the VDE standard 57472 part 602. Testing and measuring were made by the use of laser optics. The results reported here are the averages of three samples measurements and the experimental error is 3.5%.

### Volume resistivity

Volume resistivity of the samples were measured using a Teraohmmeter, 6148000 from Ceast Co., Italy and the dielectric strength was determined with Dielectric Rigidity, P/N 6135000 from Ceast Co., Italy. The results are listed in Table 2.

**Table 2.** Hot-set values as a function of radiation dose for different samples

| Sample | 50 kGy | 100 kGy | 150 kGy | 200 kGy |
|---|---|---|---|---|
| PPVC-2 | 87.0 | 51.50 | 51.95 | 48.50 |
| PPVC-3 | 26.7 | 17.35 | 11.45 | 8.65 |
| PPVC-5 | Fail | 203.00 | 45.80 | 22.50 |

### Limiting oxygen index (LOI) measurements

A candle type flammability tester from Toyofeikim Co., Japan was used for measuring limiting oxygen index (LOI) in accordance with ASTM D 2863. The specimens used for the test had dimensions of 100 × 6.5 × 2 mm.

## Results and discussions

### Gel content study

Irradiated and unirradiated PPVC samples, without multifunctional monomers (control samples) were found soluble in THF. The gel content was very low for these irradiated samples (about 2%) and did not increase significantly with increasing radiation dose. Addition of EHPTM and TAC to PPVC and irradiation of the compound with electron beam produces a gel as a result of network formation in the compound system. Figure 1 represents the variation of gel content as a function of radiation dose obtained for four different samples. It can be seen that even with lower concentration of EHPTM and TAC monomers (6%), the gel content is quite significant and increases with monomer level. However, the samples containing 9% TAC display a lower gel content compared with similar samples containing 9% EHPTM.

### Mechanical properties

PPVC usually shows poor mechanical resistance. Cross-linking of PVC occurs by high energy electron beam after the addition of unsaturated multifunctional monomers such as TAC or EHPTM. The unirradiated samples containing EHPTM and TAC have a low tensile strength and modulus. However, these samples obtain

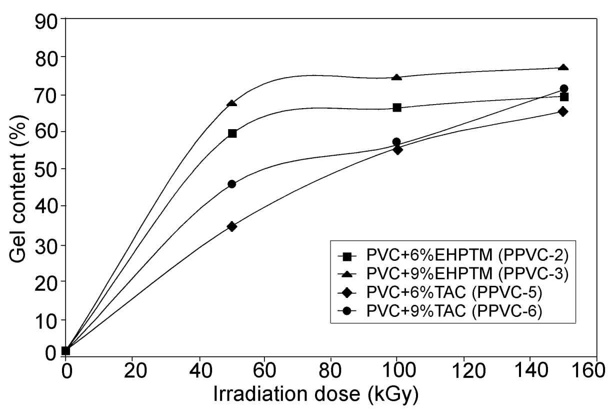


**Fig. 1.** Variation of gel content as a function of radiation dose for samples: PPVC-2, PPVC-3, PPVC-5 and PPVC-6.

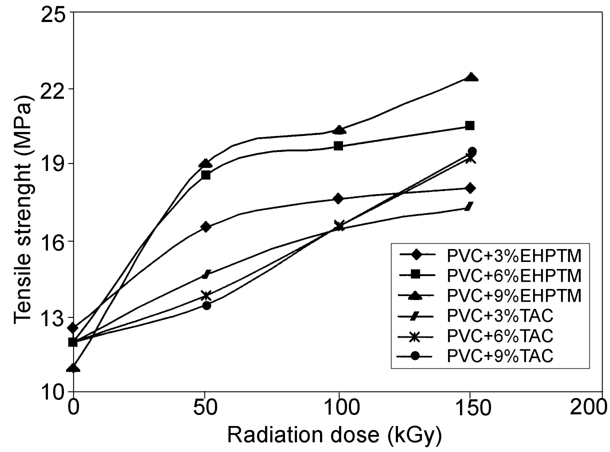


**Fig. 2.** Variation of TS as a function of radiation dose measured for different samples.

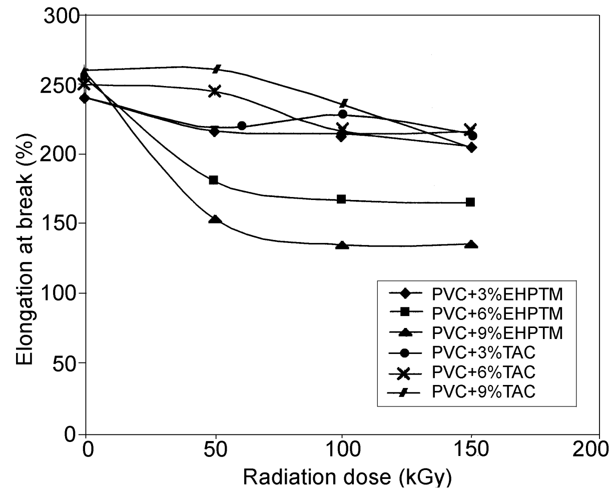


**Fig. 3.** Variation of EB as a function of radiation dose measured for different samples.

enhanced properties due to irradiation. The active sites are formed on PVC backbones and monomers produce high yields of radicals, giving good contact with PVC chains and create three dimensional networks [9]. Hence, the addition of radiation sensitizer leads to efficient cross-linking reaction. Figure 2 represents the variation of tensile strength as a function of radiation dose for different samples. Figures 3 and 4 show the variation of elongation at break and modulus as a function of radiation dose for irradiated samples.

For all loaded samples, tensile strength and modulus increase with radiation dose (Figs. 2 and 4). However, modulus and tensile strength values for EHPTM loaded samples were higher than that of TAC loaded samples at all radiation doses. At constant radiation dose, tensile strength and modulus increase with increasing EHPTM loading. Modulus and tensile strength are directly proportional to cross-linking densities. When cross-linked density continues to increase, chain mobility is reduced, resulting in an increase in tensile strength and a decrease in elongation at break. The augmentation of tensile strength and modulus follows the same trend as the gel content. With increasing of radiation dose linking of the PVC molecules to the network continues and homogeneous network through PVC mass is formed

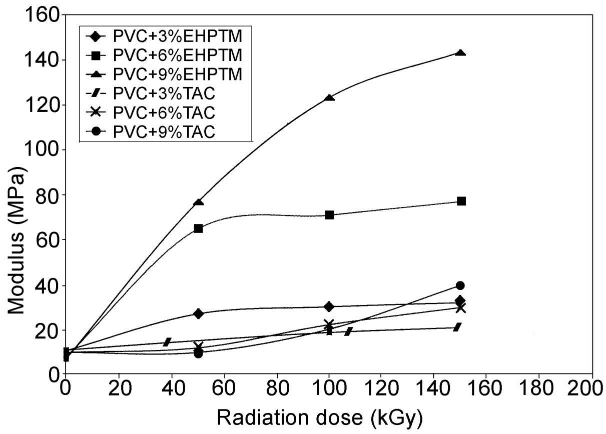


**Fig. 4.** Variations of modulus at 100% elongation as a function of radiation dose for different samples.

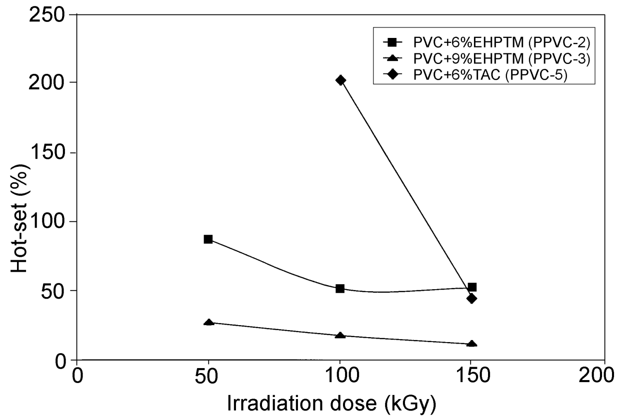


**Fig. 5.** Hot-set measurements as a function of radiation dose for three types of samples PPVC-2, PPVC-3 and PPVC-5.

and cross-linking density increases. This is made possible by some optimal concentration of a monomer. Our experimental data show that 9% concentration of EHPTM in PPVC compound is a suitable level for efficient cross-linking. Also, elongation at break (Fig. 3) decreases in EHPTM (6 and 9%) loaded samples as radiation dose increases due to cross-linking, but for TAC (6 and 9%) loaded samples the trend of decreasing is slow.

## Thermal properties

Thermal expansion of samples was studied in a hot-set apparatus. It was observed that the elongation of samples under fixed specific load changed as a function of amount and type of monomer. Before irradiation, the samples containing monomers (and also control samples) had very large elongation in the hot-set apparatus. In other words, they failed under elevated temperature and a given load. However, the irradiated samples containing monomers did not fail. The thermal expansion of samples continuously decreased with increasing radiation dose. This means that the increase in radiation dose causes a higher degree of cross-linking. The elongation of samples in the hot-set apparatus is a good indicator for mechanical performance and the dimensional stability of cross-linked PPVC products. At a given load, lower the elongation means the broader applicability at high temperatures. Figure 5 shows the thermal expansion at 150°C under 20 $N/cm^2$ as a function of radiation dose for three different samples PPVC-2, PPVC-3, and PPVC-5. The curve for sample PPVC-5 (6% TAC) shows clearly that for radiation doses up to 100 kGy all the samples fail or break in less than 15 min. This is due to lesser formation of cross-linking within the samples. Also, $\pi$ system of TAC triazine rings might play a role of protective agent due to efficient dissipation of adsorbed radiation energy into heat. Such a process increases radiation resistance and simultaneously decreases yield of radicals and consequently cross-linking. Therefore, in the presence of TAC efficiency of cross-linking, especially for low doses, is restricted. This is also confirmed from the gel content measurements (Fig. 1). With increasing radiation dose towards 150 kGy, the thermal expansion decreases sharply. The curve for sample PPVC-2 (6% EHPTM) shows that the samples fail for radiation doses up to 50 kGy (Fig. 5) and above 50 kGy, thermal expansion decreases. This trend of reduction is slowed down towards 150 kGy. Some measured data for higher doses are presented in Table 2. The curve for sample PPVC-3 (9% EHPTM) is the lowest curve and thermal expansion of this sample is smaller for all doses compared with PPVC-5 and PPVC-2 samples. From these experimental data, it is concluded that the sample PPVC-3 is more heat resistant than other examined samples.

## Volume resistivity

Volume resistivity of the polymeric insulation depends largely on the presence of low molecular additives. During irradiation, interaction of charged particles with the insulation material occurs and various species like excited ions and molecules and free radicals are formed. It is reported [5] that reduction of electrical conductivity may happen due to attachment of ions to the polymeric system which limits their mobility. This reduction of the electrical conductivity or increase in volume resistivity depends on the concentration of ions. Besides, due to cross-linking, the volume resistivity increases as a result of structural changes. From Table 3 it can be seen that the volume resistivity of PPVC-2 and PPVC-3 samples increase with increasing doses up to 100 kGy. This may be due to the increase in cross-linking densities which reduce the mobility of chains due to the formation of network structure, by increased radiation dose [15]. Decrease in the volume resistivity in some samples at high radiation dose (e.g. 150 kGy) is observed which may be due to degradation resulted from dehydrochlorination. Therefore, there is no special trend in observed changes. Dielectric strength of the samples increases slightly with raising radiation dose (Table 2) which can be due to the augmentation in cross-linking densities in agreement with the results of volume resistivity measurements.

## LOI measurements

Flammability of the polymeric compound can be characterized by LOI. The minimum oxygen concentration

**Table 3.** Volume resistivity, dielectric strength and limiting oxygen index (LOI) of irradiated PPVC samples

| Formulation code | Dose (kGy) | Volume resistivity (Ω-cm) at room temperature | Dielectric strength (KV/mm) | LOI (%) |
|---|---|---|---|---|
| PPVC-1 | 0 | $7.41 \times 0^{13}$ | 20.1 | 19.0 |
| | 50 | $1.08 \times 10^{13}$ | 20.2 | 22.0 |
| | 100 | $2.65 \times 10^{13}$ | 21.2 | 22.3 |
| | 150 | $2.62 \times 10^{13}$ | 21.7 | 22.5 |
| PPVC-2 | 0 | $7.41 \times 0^{13}$ | 20.1 | 18.4 |
| | 50 | $1.31 \times 10^{14}$ | 21.1 | 21.0 |
| | 100 | $1.59 \times 10^{14}$ | 21.3 | 21.0 |
| | 150 | $3.59 \times 10^{13}$ | 21.3 | 22.5 |
| PPVC-3 | 0 | $7.41 \times 0^{13}$ | 19.7 | 18.4 |
| | 50 | $2.61 \times 10^{14}$ | 20.9 | 21.6 |
| | 100 | $1.33 \times 10^{14}$ | 21.4 | 21.4 |
| | 150 | $8.02 \times 10^{13}$ | 21.4 | 22.0 |
| PPVC-4 | 0 | $7.41 \times 0^{13}$ | 19.1 | 18.5 |
| | 50 | $1.05 \times 10^{14}$ | 19.8 | 21.4 |
| | 100 | $7.88 \times 10^{13}$ | 20.8 | 22.5 |
| | 150 | $2.64 \times 10^{13}$ | 21.0 | 23.0 |
| PPVC-5 | 0 | $7.41 \times 0^{13}$ | 18.8 | 18.5 |
| | 50 | $3.47 \times 10^{13}$ | 20.4 | 21.4 |
| | 100 | $1.33 \times 10^{14}$ | 20.7 | 22.0 |
| | 150 | $7.88 \times 10^{13}$ | 21.4 | 22.5 |
| PPVC-6 | 0 | $7.41 \times 0^{13}$ | 20.8 | 18.6 |
| | 50 | $2.75 \times 10^{13}$ | 20.2 | 21.2 |
| | 100 | $8.12 \times 10^{13}$ | 20.5 | 22.0 |
| | 150 | $1.08 \times 10^{14}$ | 21.8 | 21.3 |

required to sustain burning was measured. As shown in Table 2, LOI measurements of the irradiated samples in all cases increase slightly with increasing radiation dose in the range of 50–150 kGy. The reason for the rise of LOI may be due to the increase of thermal stability of PPVC resulting from the cross-linking.

## Conclusion

From the analysis of our experimental results, it can be concluded that:

1. PPVC loaded with EHPTM and TAC were cross-linked by high energy electron beam irradiation and cross-linking increased with increasing radiation dose. The influence of radiation dose on the cross-linking of PPVC samples loaded with EHPTM was more than the TAC loaded ones.
2. Hot-set test experiments agreed with the results of gel content measurements. The thermal expansion of samples decreased with the increase in radiation dose due to cross-linking effects. The irradiated samples containing EHPTM had more thermal stability compared to TAC loaded samples. LOI value was raised with increasing radiation dose that may be due to increasing thermal stability.
3. Tensile strength and modulus of loaded PPVC samples increased with raising the radiation dose up to 150 kGy. The tensile strength increase for EHPTM loaded samples was higher than the corresponding values for TAC loaded samples. Also, elongation at break for loaded samples decreased with increasing radiation dose. The decrease in EB was significant for EHPTM loaded samples compared to the values of TAC loaded samples. Thus, the results indicated that the enhancement in mechanical properties of the EHPTM loaded samples was better than the TAC loaded ones at 150 kGy doses.
4. The electrical properties of irradiated samples did not change significantly.

Therefore, in general, the EHPTM (9%) loaded PPVC irradiated samples show better mechanical, thermal and electrical properties compared with the other samples.

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