

ORIGINAL ARTICLE

The use of polyfunctional monomers in the radical cure of chlorinated polyethylene

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An investigation has been undertaken to find out the effect of different polyfunctional monomers (PFMs) on the physical properties of chlorinated polyethylene (CPE) crosslinked by electron beam (EB). The following PFMs were used: triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), trimethylolpropane trimethacrylate (TMPT) and ethylene glycol dimethacrylate (EDMA). The physical properties of EB-irradiated CPE sheets were evaluated by measuring the tensile strength, elongation at break, hardness, elasticity and tear strength. The efficiency of the PFMs studied in enhancing crosslinking has been followed up by measurement of physical and mechanical properties of the vulcanized CPE. Physico-mechanical properties of EB-irradiated samples were compared with the dibenzoyl peroxide-cured samples. Dependence of properties on irradiation dose was determined from a dose range of 0–20 Mrad. The results showed an increase in physico-mechanical properties as a result of introducing PFMs; the most efficient being TAC and TAIC. Moreover, on the basis of the comparison between EB and dibenzoyl peroxide vulcanization efficiency, the results show that EB irradiation offers the best results.

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INTRODUCTION

Chlorinated polyethylene (CPE) is a synthetic elastomer produced by the means of controlled chlorination of polyethylene and has been commercially produced since the late 1960s.¹ The properties of the CPE product are influenced by a number of factors, which include the molecular weight and molecular weight distribution of initial polyethylene, chlorine content and chlorine distribution. Typical commercial grades of CPE contain 25–42 wt% chlorine. The saturated backbone of CPE imparts outstanding ozone, oxidative and heat resistance to a compound's performance.² The addition of chlorine to the backbone creates polarity in the polymer structure that imparts oil and chemical resistance to the polymer, and subsequently to the compounded material. In addition, the chlorine on the backbone can help provide inherent flame retardance by providing a halogen source in a fire situation.³

The molecular saturation of CPE elastomers results in excellent property retention but requires the use of vulcanization systems other than conventional sulfur systems. Cure agents for CPE compounds are typically based on (1) peroxide cure systems with coagents; (2) thiadiazole-based chemistries; or (3) irradiation crosslinking techniques.⁴ The choice of cure system depends upon a number of factors such as compound cost, processing equipment and curing equipment.

Peroxide cures are preferred when extra scorch safety, shelf life, bin stability, low permanent set and high-temperature performance

are desired. Thiadiazole cure provides the ability to cure over a wider range of temperature and pressure conditions while generating fewer volatile by-products than do peroxide cures. Irradiation-curable compounds are usually formulated in a manner similar to the peroxide-curable compounds, except that no peroxide is necessary.⁵

Chemical additives known as coagents are used in conjunction with radical cure systems such as organic peroxides and electron beam (EB) irradiation. They are used in the cure of elastomers to promote crosslinking reactions and improve physical properties. Coagents are typically polyfunctional monomers (PFMs) and can participate in a number of radical reaction mechanisms, the most beneficial being grafting and radical addition. By increasing the crosslink density of the compound, network performance can be improved. Coagents can be grouped according to their influence on cure kinetics and ultimate physical properties. Type I coagents are highly reactive and increase both the rate and state of cure. Typically monomeric, such coagents contain acrylate, methacrylate or maleimide functionality. They are very polar structures with limited solubility in most elastomer grades. Type II coagents are based on allyl reactive sites and increase the state of cure only. Monomeric forms include allyl-containing cyanurates, isocyanurates and phthalates. Polymeric forms of Type II coagents include poly(butadienes) with pendant vinyl unsaturation.^{6,7}

Radiation curing has historically been used as an alternative to peroxides in applications in which the curatives themselves or side

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products of vulcanization are viewed as impurities in the final product. Peroxide cure progresses through a series of radical intermediates, each of which can undergo side reactions, which may not necessarily contribute to crosslink density. Radiation cure, on one hand, is known to be a cleaner and more homogeneous cure process.⁶

Improvements in physical properties take place in EB curing when crosslinking is achieved in the presence of PFMs. To improve the heat stability of poly (l-lactic acid), for example, it has been demonstrated that EB irradiation at 100 kGy in the presence of 3% triallyl isocyanurate (TAIC) formed quantitative gel fraction and improved heat stability of poly (l-lactic acid).⁸

In this study, the influence of EB radiation dosage and types of PFMs on characteristics of CPE was investigated. The data was compared with a sample standard crosslinking with peroxide-cured system also containing the same PFMs. The results of this study will help us improve the curing of CPE blends (lower irradiation dose, usage of the most efficient PFM, producing better products and so on).

EXPERIMENTAL PROCEDURE

Materials

Materials used in the study:

- Chlorinated polyethylene CPE TX10 (35% chloride content, 2% percentage of ash, density 1.16 g/cm⁻³).
- Polyfunctional monomers: triallyl cyanurate (TAC) Luvomaxx TAC DL 70 (26% percentage of ash, density 1.34 g/cm⁻³, 30% active synthetic silica),

Table 1 Chemical structure of PFMs used

Polyfunctional monomer	Type	Functionality
Trimethylolpropane trimethacrylate (TMPT)	I	3
Ethylene glycol dimethacrylate (EDMA)	I	2
Triallylcyanurate (TAC)	II	3
Triallylisocyanurate (TAIC)	II	3

TAIC Luvomaxx TAIC DL 70C (pH 2.6, density 1.34 g cm⁻³), trimethylolpropane-trimethacrylate (TMPT) Luvomaxx TMPT DL 75 (22% percentage of ash, pH 9.2, density 1.36 g cm⁻³, 75 ± 3% active ingredient), ethylene glycol dimethacrylate (EDMA) Luvomaxx EDMA DL 75 (23% percentage of ash, 75 ± 3% active ingredient, density 1.25 g cm⁻³). Table 1 presents the chemical structure of PFMs.

- Dibenzoyl peroxide Perkadox 14-40B (density 1.60 g cm⁻³, 3.8% active oxygen content, 40% peroxide content) as a vulcanizing agent for vulcanization of control samples.

Specimen preparation

Blends have been prepared by means of blending technique, on a laboratory roll with electric heating at 120 ± 5 °C, total blend time of 5' and friction of 1:1.1. The blend constituents were added in the following sequence and amounts: 100 phr CPE and 3 phr PFMs (TAC, TAIC, TMPT and EDMA, respectively).

Plates required for physico-mechanical tests have been prepared by compression molding, using an electrically heated hydraulic press, at a temperature of 160 °C, pressure of 150 MPa and time of 3 min to obtain sheets of 11.5 × 11.5 × 0.2 cm³.

Control samples were prepared similarly with the following specifications: 8 phr of dibenzoyl peroxide as vulcanizing agent was added and the blend vulcanization was achieved in a hydraulic press at 160 °C; the vulcanization time was measured by means of Monsanto Rheometer (Table 2).

Experimental installations and sample irradiation

The resulting plates were subjected to EB vulcanization with ILU-6M accelerator of 1.8 MeV and 10.8 kW output power. The ILU-6M is a resonator-type

Table 2 Rheometric and physico-mechanical characteristics of samples crosslinking with peroxide

Characteristics/PFMs	Control	TMPT	EDMA	TAC	TAIC
<i>Rheometric characteristics</i>					
The minimum torque ML, (dNm)	12.7	12.1	13	7	8.5
The maximum torque MH, (dNm)	23.5	30	31.5	28	30.8
M90, (dNm)	22.42	28.2	29.7	25.9	28.6
ΔM , (dNm)	10.8	17.9	18.5	21	22.3
Curing time, t_{90} , min	13'30"	9'15"	9'	9'25"	9'
Shorter time t_{min} , min	1'15"	1'15"	45"	1'15"	1'15"
Scorch time, t_{s2} , min	3'15"	3'	1'55"	2'7"	2'20"
Cure rate index, (CRI), min^{-1}	9.75	16	14.1	14	15
<i>Physical-mechanical characteristics</i>					
Hardness, °ShA,	61	64	64	66	64
Elasticity, %,	24	20	22	18	20
100% Module, N mm^{-2}	1.6	1.6	1.3	1.8	1.7
Tensile strength, N mm^{-2}	5.6	10.4	5.9	5.3	4.5
Elongation at break, %	367	447	400	200	253
Elongation set, %	43	52	47	12	21
Tear strength, N mm^{-1}	25	32.5	27.5	30	27

Abbreviations: EDMA, ethylene glycol dimethacrylate; PFM, polyfunctional monomer; TAC, triallylcyanurate; TAIC, triallylisocyanurate; TMPT, trimethylolpropane trimethacrylate.

accelerator, operating at 115 ± 5 MHz. This accelerator generates EB pulses of 0.375 ms duration, up to 0.32 A current peak intensity and up to 6 mA mean current intensity. The cross-sectional size of the scanned EB at the ILU-6M vacuum window exit is 1100 mm \times 65 mm. The EB effects are related to the absorbed dose (D), expressed in Gray or J kg^{-1} . The single-pass dose with conveyor under the ILU-6M scanner is adjustable from 12.5 to 50 kGy. For EB treatment, the rubber sheets were cut in a rectangular shape of $0.15 \times 0.15 \text{ m}^2$. The layers of three sandwiched sheets were irradiated by repeatedly passing on a conveyor under the ILU-6M scanner in atmospheric conditions and at a room temperature of 25 °C. Distance between ILU-6M vacuum window exit and conveyor surface was $33 \times 10^{-2} \text{ m}$. The conveyor speed was $2.36 \times 10^{-2} \text{ m s}^{-1}$. Single-pass dose measured with ceric-cerous sulfate dosimetry system was 25 kGy. For the samples passing several times under the scan, the accumulated dose was from 50 to 200 kGy.

According to the Technical Report Series No. 277,⁹ the absorbed dose is the major parameter in the accelerated electron radiation. The vulcanizing and grafting process performances are provided by the strict control of this parameter.

The relation defining the absorbed dose is as follows:

$$D = d\varepsilon/dm$$

where $d\varepsilon$ is the mean energy given up by the ionizing radiation to the mass amounts dm of the substance interacting with this ionizing radiation.

dm is emphasized to be very low, but not so low that the mean energy $d\varepsilon$ given up by the radiation would undergo a significant fluctuation.

Absorbed dose is measured in J kg^{-1} . The SI unit measure for the absorbed dose is the gray (Gy):

$$1 \text{ Gy} = 1 \text{ J kg}^{-1}$$

The rad unit is also used, with the following relation between the Gy and rad:

$$1 \text{ Gy} = 100 \text{ rad}$$

A relevant example: a material irradiated by 2 Mrad (20 kGy) indicates that accelerated EB has deposited 2.10^8 ergs or $\sim 10^{19}$ eV per gram substance.

Laboratory tests

Tensile strength and tearing strength tests were carried out with a Schoppler strength tester with a testing speed of 460 mm min^{-1} , using dumb-bell-shaped specimens according to ISO 37/2005, respectively, angular test pieces (type II) according to SR EN 12771/2003. Hardness was measured by using a hardener tester according to the ISO 7619-1/2004, using 6-mm-thick samples. Elasticity

was evaluated with a Schob type rubber elasticity tester using 6-mm thick samples, according to the ISO 4662/1986. All measurements were recorded several times and the resulting values were averaged on 5 to 8 measurements. Curing characteristics were determined by an oscillating disk rheometer (Monsanto Company, Hertfordshire, UK), at 160 °C for 30 min, according to the SR ISO 3417/1997.

RESULTS AND DISCUSSION

Characteristics of samples crosslinking with peroxide

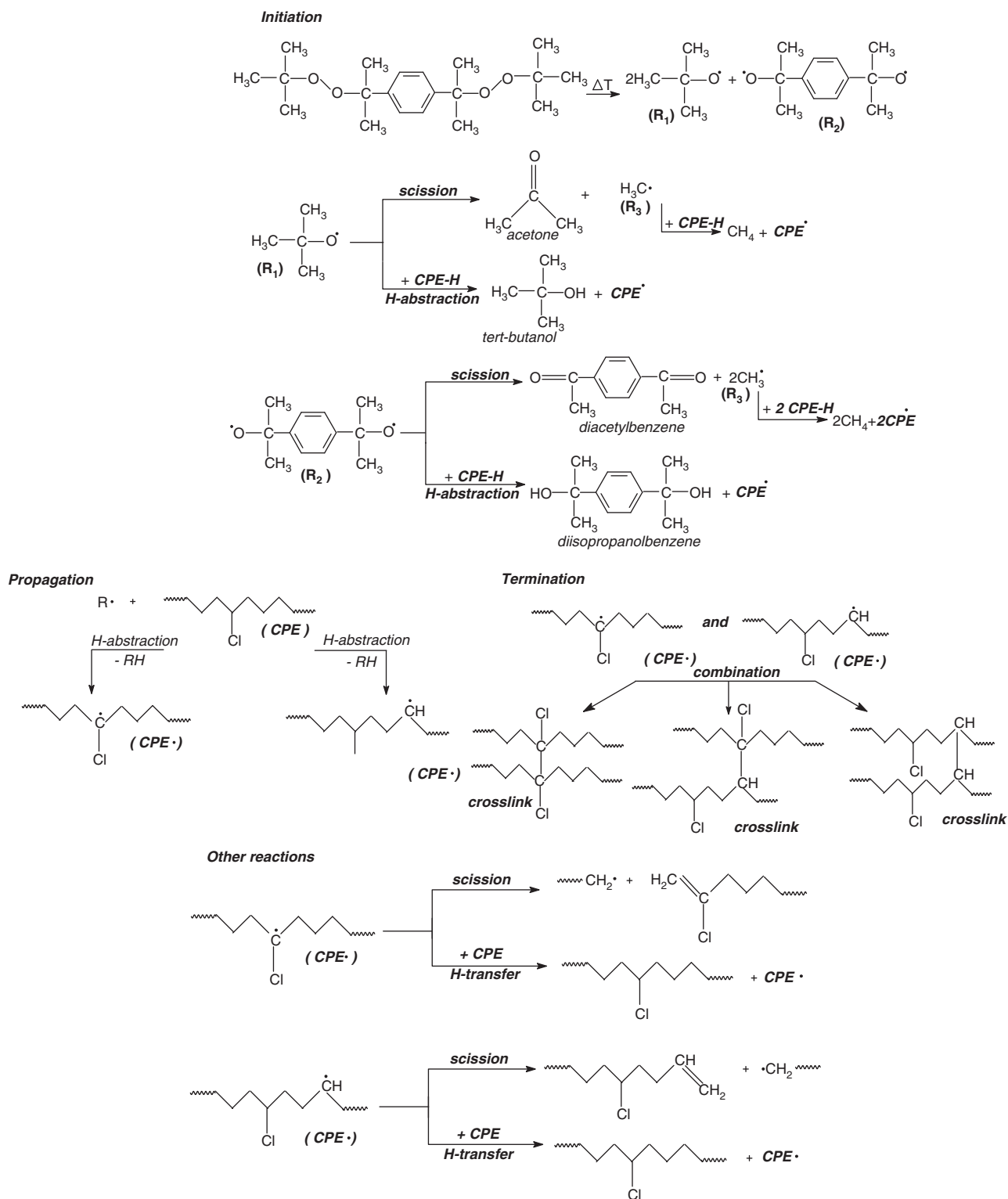
Figure 1 suggests a mechanism of the crosslinking reaction of CPE with Perkadox 14-40B. Vulcanization with peroxides is done by radicalic mechanism when bonds form between C-C macromolecules. The basic stages in the generally accepted mechanism of peroxide cure are initiation, propagation and termination. Initiation is induced by homolytic decomposition of the peroxide into radicals (R_1 and R_2) at 160 °C. The initiation step follows first-order reaction kinetics;^{10,11} therefore, the cleavage of the peroxide molecule is only proportional to the concentration of peroxide at any time. The R_1 and R_2 (primary radicals) formed by scission-stable species (acetone and diacetylbenzene) and the second radical (R_3), and continue the propagation in the presence of CPE rubber. The formed primary radicals react with CPE rubber (CPE-H) under H-abstraction, accompanied by formation of CPE rubber radicals (CPE^\bullet) and stable species (tert-butanol and diisopropanolbenzene). The recombination of CPE rubber radicals (CPE^\bullet) results in a crosslinking reaction (CPE-CPE). The reaction of CPE rubber radicals (CPE^\bullet) with peroxide radicals (R^\bullet — R_1 , R_2 or R_3) results in a crosslinking-inactive reaction (CPE-R).^{11–14} Final crosslinking density of CPE vulcanized with peroxide is the sum of crosslinking densities that form by combining two macroradicals. Theoretically, crosslinking density is proportional to the peroxide quantity, but in practice it is lower because of secondary reactions leading to the formation of inert compounds.¹⁵ Simultaneously, secondary reactions take place, such as hydrogen transfer reactions or splitting reactions of the macromolecular chain.¹⁶

Rheometric characteristics of samples crosslinking with peroxide. The cure characteristics of the CPE samples with different types of PFMs are presented in Table 2. Scorch times (t_{s2}) provide a measurement of process safety, indicating the latent period at a given temperature before appreciable vulcanization occurs. It can be seen that scorch time decreases depending on the type of PFM introduced, a fact also reported by other researchers.⁶ Therefore, a shorter time was required for the beginning of the vulcanization process for the CPE compounds. A decreasing trend of the optimum cure time t_{90} from 13'30" to 9'–9'25" was also observed.

At the same time, the variation of maximum torque and minimum torque value in different types of PFMs are also given in Table 2. A minimum torque, ML, is a measure of stiffness of the unvulcanized test specimen taken at the lowest point of the cure curve. A maximum torque, MH, is a measure of stiffness or shear modulus of the fully vulcanized test specimen at vulcanization temperature. In other words,^{17,18} it is also a measure of crosslink density. Both the maximum torque and the difference of delta torque between the maximum and minimum torque increased with the formation of crosslinks between the macromolecular chains; the other reasons, as aforementioned, such as the addition of PFM increased the crosslink density. Crosslink density increased with PFM addition. The highest increase in crosslink density was found for TAC, TAIC—Type II coagents.

The cure rate index (CRI) of the recipe at different PFMs was calculated according to the following formula:

$$\text{CRI} = 100 / (t_{90} - t_{s2})$$



The cure rate index is a measure of the rate of vulcanization based on the difference between optimum vulcanization time, t_{90} , and incipient scorch time, t_{s2} . As shown in Table 2, cure rate index increases by 43.6–64.1% in PFM blends, indicating that using PFMs, the crosslinking rate increases, because of the change in the crosslinking

reaction mechanism. Most Type I coagents can homopolymerize and graft to form viable crosslinks through radical addition reactions. Certain Type II coagents, containing extractable allylic hydrogen, have been shown to participate in intramolecular cyclization reactions as well as in intermolecular propagation reactions.^{19,20} Trifunctional

allylic coagents (TAC and TAIC) may form crosslinks through the cyclopolymerization products as well as grafting through pendant allyl groups. The polymeric coagents simply increase the concentration of reactive pendant unsaturation, further promoting crosslinking reactions.

Physico-mechanical characteristics of samples crosslinking with peroxide. Physico-mechanical characteristics of samples crosslinking with peroxide (Table 2) indicate the following:

Hardness increased by 3 °ShA and 5 °ShA, respectively, compared with that of the blend without PFM, indicating an increase of blend reinforcement by increasing crosslinking density due to PFM introduction; the blend containing TAC had a hardness of 66 °ShA and those with TAIC, TMPT and EDMA had a hardness of 64 °ShA.

Elasticity decreased as a result of reinforcing blends using PFMs, the lowest value was obtained for the blend with TAC.

100% modulus increases when introducing type II PFMs TAC and TAIC in the blend. Modulus values typically follow delta torque, as both can be directly correlated to crosslink density.

Tensile strength presents different values depending on the type of PFM used.

Tear strength significantly increased (by maximum 37.25%), obtaining the best results for blends with TMPT and TAC. All blends have a higher tear strength compared with the value of the control sample.

Elongation at break and residual elongation have dropped by introducing PFMs in blends, obtaining the lowest values for blends with Type II coagents: TAC and TAIC (a significant decrease of 31–45.5% for the elongation at break and of 51–72% for the elongation set), because the involved coagents have been shown to participate in intramolecular cyclization reactions, as well as in intermolecular propagation reactions, leading to a higher crosslinking density and a decrease in the degree of crystallization.^{19,20}

The obtained results prove the fact that PFMs have led to the increase of crosslinking density and the decrease of the degree of crystallization of CPE blends, which determined, particularly for blends containing type II crosslinking coagents (TAC, TAIC), an increase in hardness, 100% modulus and tear strength, as well as a decrease in elongation at break and residual elongation.

Physico-mechanical characteristics of blends irradiated with accelerated electrons

Vulcanization by EB irradiation involves the interaction of high-energy electrons and an elastomer. Ionizing radiation produces an excitation of polymer molecules in the vicinity of the impinging radiation. The energies associated with the excitation are dependent on the irradiation dosage and voltage (velocity) of electrons.^{21,22} The interaction results in formation of free radicals formed by dissociation of molecules in the excited state or by interaction of molecular ions. The free radicals or molecular ions can react by connecting the polymer chains directly or by initiating grafting reactions.²³ The mechanism of EB cure of CPE is suggested in Figure 2. The chemistry of the process is based on macroradical formation from elastomer chains, which recombine causing structuring.^{24,25} High-energy ionizing radiation produces excited polymer molecules and abundant secondary electrons that are capable of interacting with other molecules including PFMs. Depending on the energies involved and the sample size, these excited molecules can further react to form radicals or can absorb the energy and slow down (thermalize) without producing further reactions. Optimization of an elastomeric network using PFMs in EB irradiation is dependent on forming crosslinks

through radical addition reactions. An increased concentration of molecules in the excited state leads to a higher percentage of crosslinking reactions, thus improving the physical properties. The enhancement in physical properties is related to the intensity of the EB.⁶

From the analysis of characteristics of samples crosslinked with accelerated electrons, the following features are noticed:

Hardness (Figure 3) decreases through irradiation for the sample without PFMs by maximum 6 °ShA, reaching, for an irradiation dose of 15–20 Mrad, a hardness of 61 °ShA corresponding to the control sample crosslinked with peroxide. This decrease of hardness may be due to the change in the morphology of the sample by irradiation, namely C–C link formation affecting the degree of crystallization of the sample. Instead, for samples containing PFM, hardness variations of maximum 3 °ShA are noticed (for the blend containing TAIC it has not changed)—a slight decrease by irradiation with 5 Mrad and then an increase as a result of crosslink density increase by augmenting the irradiation dose. Moreover, for the conventional curing method, the samples were cured at high pressure and temperature influencing the sample morphology.

Elasticity (Figure 4) had an opposite behavior compared with that noticed in hardness variation, namely an increase by augmenting the irradiation dose from 18% to maximum 28% and a slight decrease by using PFM, because of morphology change and reinforcement of blend by crosslinking as a result of irradiation. For the sample without PFM, higher elasticity values than those of the control sample crosslinked with peroxide have been obtained.

The 100% modulus (Figure 5) depends directly on the crosslink density. Thus, the increase in crosslink density is reflected by the enhancement in the 100% modulus with irradiation dose. The higher modulus achieved with the addition of PFMs further supports the fact that the increase in modulus with irradiation dose is associated with irradiation-induced crosslinking of the rubber phase. In some cases, it has a maximum and then decreases (the blend without PFMs at 10 Mrad, with TAC at 15 Mrad); for blends containing PFMs, higher values than that for the control sample crosslinked with peroxide have been obtained for irradiation doses of 15 and 20 Mrad. The best values of 100% modulus have been obtained using TAIC and TAC.

Tensile strength (Figure 6) and tear strength (Figure 7) for blends without PFM decrease with the increase in irradiation dose as a result of reducing the crystallization degree, and at a dose of 15 Mrad it has similar values for the control sample vulcanized with peroxide. Instead, for blends containing PFM, these characteristics increase when augmenting the irradiation dose, a maximum is obtained (for TAC and EDMA at 5 Mrad, for TMPT at 10 Mrad), and then a slight decrease is noticed. This was because of the occurrence of excessive crosslink in CPE chain, which in turn produced a brittle material and thus reduced the tensile strength. The reduction of tensile strength at doses higher than that at the maximum tensile strength could not be assigned to scission reactions that generally occur in competition with crosslinking reactions during irradiation process. This is supported by the fact that the modulus of the rubber remains essentially unchanged at higher doses.²⁶

Elongation at break (Figure 8) and residual elongation (Figure 9) decrease significantly when augmenting the irradiation dose. Such decline is expected as the rubber becomes increasingly rigid as a consequence of the increase in crosslink density with irradiation. An increased crosslinking degree and intramolecular cyclization reactions that take place especially in blends containing TAC or TAIC, result in an important decrease in the degree of crystallization, altering the sample morphology as a result of the decrease in crystalline domains

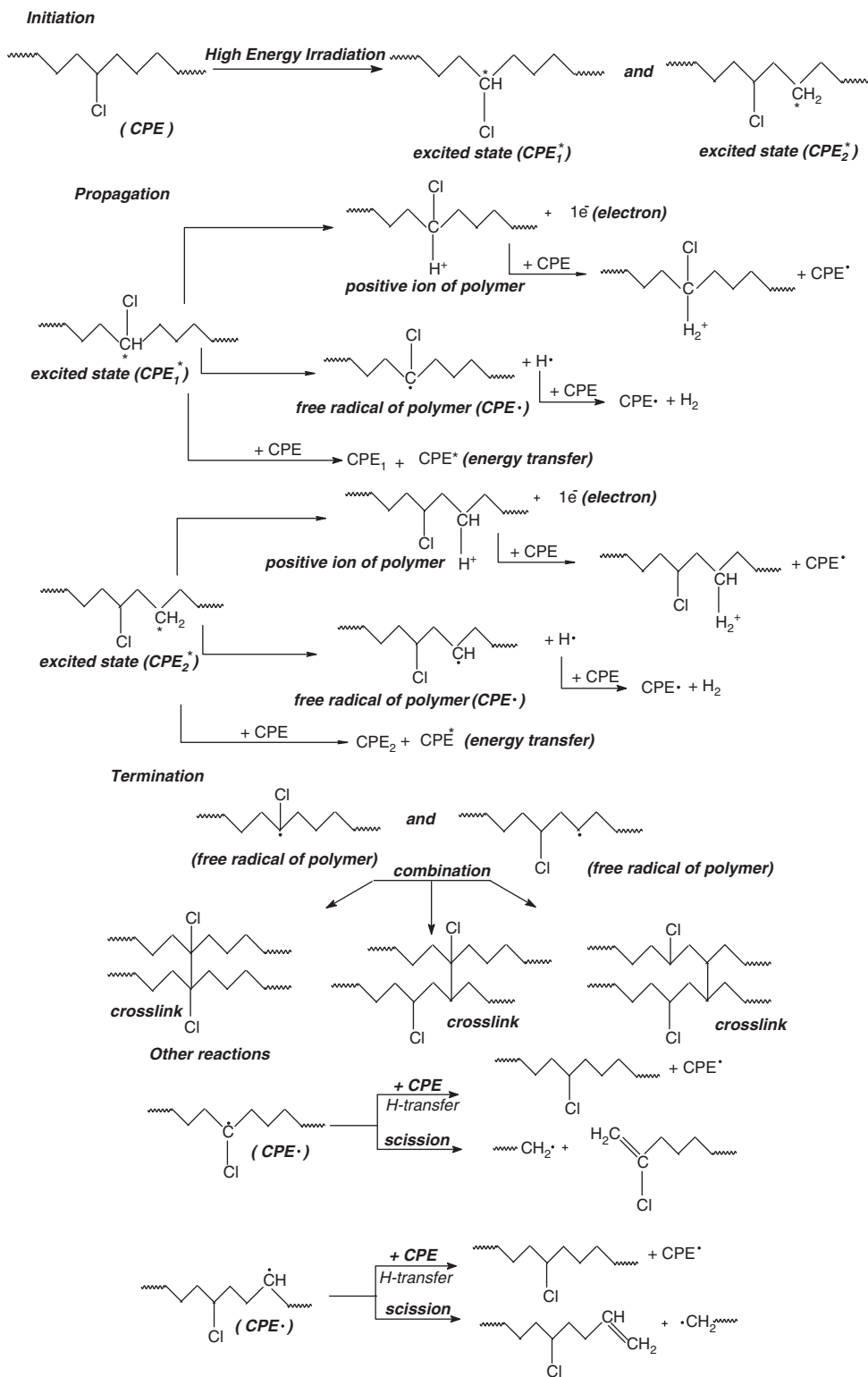


Figure 2 Mechanism of the crosslinking reaction of chlorinated polyethylene (CPE) with electron beam (EB).

specific to plastic materials in favor of the amorphous one specific to elastomers that leads to lower values of the residual elongation (therefore, a better return to the initial shape after applying a force) and a decrease in the elongation at break (there is no thermoplastic-specific necking).^{19,20,27} The values of these characteristics for the

sample without PFMs at the dose of 15 Mrad have similar values for the control sample crosslinked with peroxide. The high values of elongation at break of the non-irradiated sample indicate a slip of macromolecules against each other; by increasing the irradiation dose, C–C links form between them limiting this shift. The non-irradiated

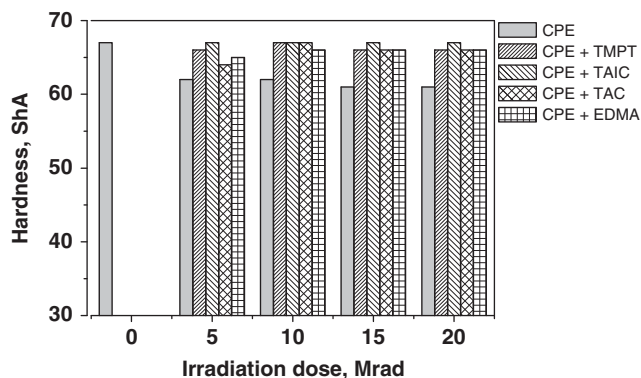


Figure 3 Hardness versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

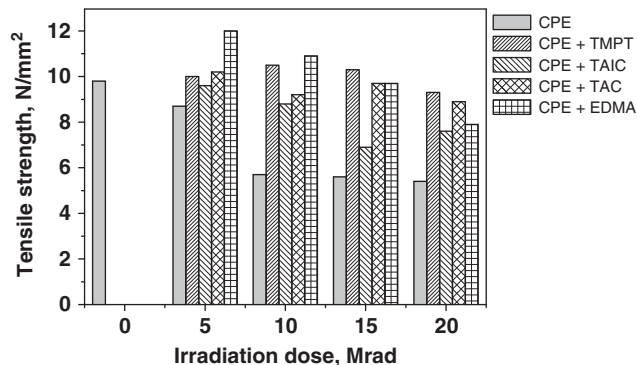


Figure 6 Tensile strength versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

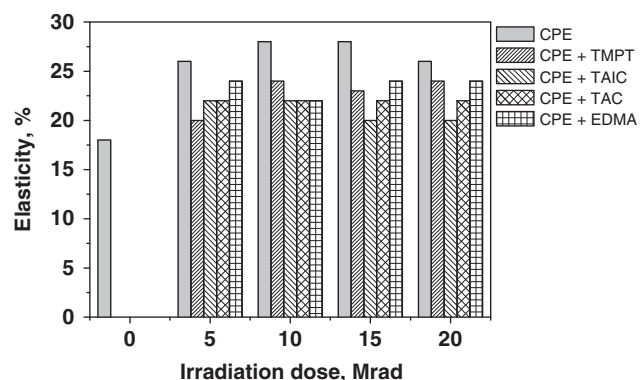


Figure 4 Elasticity versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

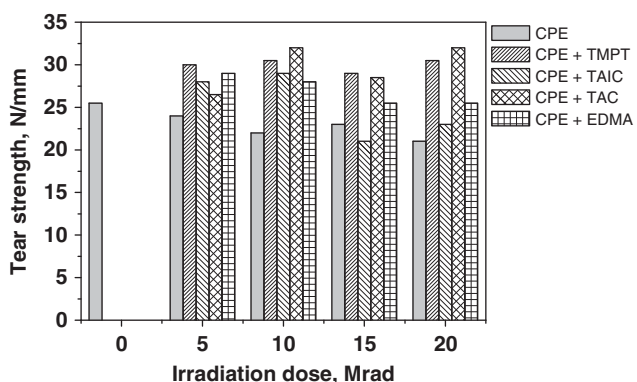


Figure 7 Tearing strength versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

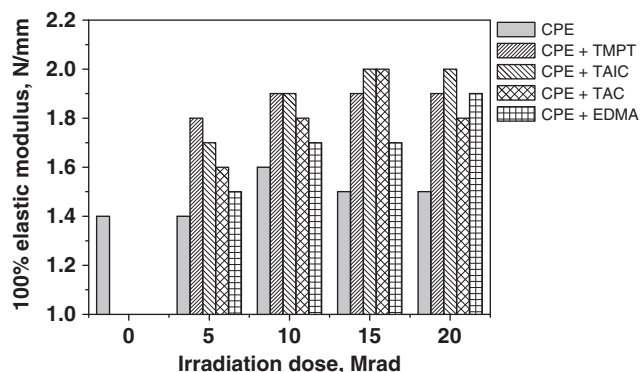


Figure 5 100% elastic modulus versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

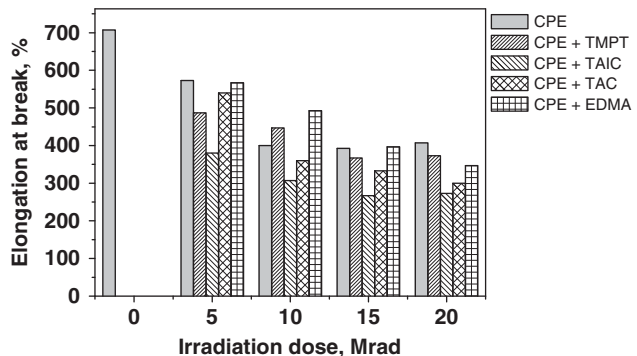


Figure 8 Elongation at break versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

sample has a high residual elongation value specific to plastics, and by augmenting the irradiation dose, a very good recovery of samples is noticed after application of a force as a result of blend crosslinking. Although the elongation reduces in proportion with the tightness of the rubber networks, the elongation values remain high enough to be useful for most applications.

Comparing peroxide and EB curing

Radiation curing has historically been used instead of peroxide curing in which the curatives themselves or side products of vulcanization are

seen as undesirable. Peroxide cure progresses through a series of intermediates, each of which can undergo side reactions that may not necessarily contribute to crosslinking. Radiation curing, on the other hand, has been promoted as a cleaner and a more homogenous process. Although both peroxide and EB cure involve radical-based intermediates, differences between the mechanisms do exist. Although peroxide cure is a thermally initiated event with cure temperatures routinely in the 160–180 °C range, EB cure is performed at room temperature. Peroxide cure is initiated by oxygen-centred radicals that can be differentiated from the carbon-centred radicals produced by

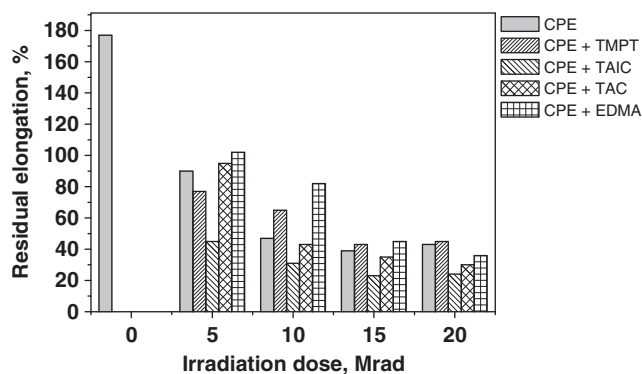


Figure 9 Residual elongation versus electron beam (EB) irradiation dose and polyfunctional monomer (PFM) type.

polymer excitation in radiation cure. The length of cure time in each system is also very different. In peroxide cure, cure time is governed by the half-life of the peroxide at a given temperature, and can be longer than 30 min to reach >99% decomposition. In contrast, EB cure is practically instantaneous. The cure temperature and cure time differences can result in significantly less energy applied to the EB cure process, a fact that may contribute to variations in PFM performance between the disparate systems.^{6,19–23}

Crosslinking and grafting CPE blends by accelerated electron radiation was proved by comparing physico-mechanical characteristics of the irradiated blends with those of the control blends with the same composition but crosslinked using the classical method with peroxides.

The resulting physical mechanical characteristics have revealed the following features:

- Hardness and elasticity of samples crosslinked with peroxide and PFMs compared with similar ones crosslinked by irradiation have lower values; the highest differences are of 3 °ShA (the ones with TMPT) for hardness, and a decrease of 22%, respectively, (samples with TAC).
- 100% modulus of samples crosslinked with peroxide is slightly low or corresponding to an irradiation dose of 5 Mrad (for the sample with TAIC) and 10 Mrad, respectively, (for the sample without PFMs); similar effects have been also noticed for tensile strength, elongation at break and residual elongation.
- Tear strength of samples crosslinked with peroxide has values similar to those of samples crosslinked with EB with doses of 5–10 Mrad.

The use of PFMs provides benefits in both peroxide and radiation cure mechanisms. However, there are clear differences in the efficiency with which certain PFM structures contribute to crosslink density, based on cure chemistry and process. To realize the greatest improvements in a given application or cure type, it is crucial to understand the structure–property relationships directing the performance of PFM.

CONCLUSION

PFMs can be used to increase the crosslink density of peroxide- or EB-cured systems by increasing the efficiency of productive radical reactions. These have led to the improvement of physico-mechanical properties of CPE; the most efficient PFM for CPE have been TAC and

TAIC, respectively. Moreover, based on the comparison between EB and benzoyl peroxide vulcanization efficiency, the results show that EB irradiation yielded the best results. Comparing mechanical parameters of the samples obtained by EB vulcanization with those vulcanized with dibenzoyl peroxide, it is easy to observe that the first one showed greater efficiency. For blends containing TAIC and TAC, respectively, an irradiation dose of 5 Mrad is enough to obtain superior/similar properties to those of blends crosslinked with benzoyl peroxide. In addition, crosslinking by EB also shows a series of advantages such as reduced crosslinking time and power expenditure, no polymer degradation due to high temperature as EB crosslinking occurs at room temperature, the process is very fast and can be controlled precisely; the EB can be steered very easily to meet the requirements of various geometrical shapes of the products to be cured, very high productivity, perfect for thin products, lack of wastes and the resulting products are sterile.²⁸

End-use elastomeric applications for CPE are wide in range; for example, wire and cable, automotive, industrial and general rubber markets.²⁹

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