

Crosslinking and grafting ethylene vinyl acetate copolymer with accelerated electrons in the presence of polyfunctional monomers

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Abstract In this study, we have studied the effects of polyfunctional monomers (PFMs) on physical properties of ethylene vinyl acetate (EVA) copolymer crosslinked with electron beam (EB) or peroxides. The PFMs used were triallylcyanurate, triallylisocyanurate, trimethylolpropane trimethacrylate, zinc diacrylate, and ethylene glycol dimethacrylate. Using PFMs has led to (1) optimum cure time t_{90} decrease from 19'25'' to 17'30''–18'45'', (2) scorch time increase from 2' to maximum 3'45'', (3) increasing the crosslink density of peroxide or EB-cured systems by increasing the efficiency of productive radical reactions. The most efficient PFM for EVA copolymer blends has been triallylisocyanurate. Tensile strength and tear strength of samples crosslinked with EB for all irradiation doses are significantly better than those obtained for samples crosslinked with peroxides (differences up to 190%). The results show that EB irradiation gave the best results

Keywords Vulcanization · Ethylene vinyl acetate · Polyfunctional monomer · Electron beam

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Introduction

Ethylene vinyl acetate (EVA) copolymers are randomly structured polymers which offer excellent ozone resistance, weather resistance, and excellent mechanical properties. EVA is one of the widely used polymers for cable insulants. But new applications have now been developed and EVA has been recognized as an oil-resistant material, which can be used for automotive applications, such as gaskets, seals, and hoses [1]. It is also frequently used as a long-lasting plasticizer to improve the mechanical and processing properties of polyvinyl chloride (PVC). EVA is available as a plastic, thermoplastic elastomer, and rubber type depending on the vinyl acetate (VA) content in the copolymer. EVA containing 28% VA is a thermoplastic elastomer, and 50% VA is a rubber type [2].

In this study, we have studied the effects of polyfunctional monomers (PFMs) on physical properties of electron beam (EB) or peroxides crosslinked EVA. This is very important from the viewpoint of finding out optimum types of PFM required to obtain desired properties. The following work will evaluate Type I (trimethylolpropane trimethacrylate, zinc diacrylate, ethylene glycol dimethacrylate) and Type II (triallylcyanurate, triallylisocyanurate) PFMs. This will facilitate the use of the most efficient type of PFM in order to obtain EVA products with characteristics fit for the field of use. Establishing the optimum dose required for achieving the desired crosslinking will further help avoiding the exposure of the EVA to doses higher than what is necessary.

Issues regarding EVA crosslinking

An important stage in the EVA processing technology is crosslinking. It consists in introducing crosslinking bridges between macromolecules, thus leading to a significant improvement of thermal and dimensional stability of products. Since it has a fully saturated backbone, EVA does not crosslink by means of sulfur. They have to be cured radically by means of peroxides or high-energy radiation.

Polyfunctional monomers

The mechanism of the crosslinking reaction is first an abstraction of a hydrogen atom from the polymer chain, leading to the formation of a reactive radical site. Then, two polymer radicals can combine, which results in a polymer network. The network formed by those reactions is very irregular [1]. In order to improve the network, the addition of compounds with PFMs is necessary. The effect is described as an addition to the radical site at the polymer chain and transfer of the radical to the PFM. The network is formed by reaction of the transferred radical with another chain. The performance and efficiency of all PFMs are not alike. Researchers have classified PFMs as either Type I or Type II depending on their effect on the curing characteristics of the rubber.

Type I: addition and hydrogen abstraction reactions

These PFMs consist of rather polar molecules with a low molecular weight and activated double bonds. Their main characteristic is that they are highly reactive toward radicals, so scorch takes place very fast, which sometimes can be a disadvantage [3]. By using this kind of PFMs not only the rate of cure, but also the crosslink density are increased. A disadvantage that may be present when using this type of PFMs is that, due to polarity, the compatibility of these PFMs with the polymer matrix is limited [4]. Some examples of Type I PFMs are acrylates, methacrylates, bismaleimides, and zinc salts.

Type II: addition reactions

These PFMs are, in general, less polar molecules, which form more stable free radicals, so scorch does not take place as fast as with the previous type of PFMs. The use of these PFMs leads to an increase in crosslink density of the vulcanizate but, unlike Type I, they are not capable of increasing the cure rate. Owing to their low polarity, these PFMs have a good compatibility with many elastomers. Some examples are high vinyl 1,2-polybutadiene, divinylbenzene, allyl esters of cyanurates, isocyanurates, and sulfur.

Despite the fact that the mechanism of PFM reaction during vulcanization is still being investigated, it has been proven that PFMs get incorporated into the polymer network [5–7], as they create bridges between polymer chains, thus contributing to an increase in crosslinking efficiency by generating extra crosslinks. Further, since they have a major affinity for radicals, they help to minimize chain scission and disproportioning reactions. From a morphological point of view, there can be two ways for PFM incorporation into the polymer network: either by polymerization—forming an interpenetrating network by homopolymerization of PFM molecules, or by being grafted onto the polymer backbone [3, 8–10]. Figure 1 shows these two options.

Probably, what takes place in real practice is a combination of the two mechanisms. PFMs are in general rather polar materials, especially Type I PFMs. This means that they are not very miscible with the non-polar rubber and will tend to phase separate and homopolymerize [4, 11, 12]. These phase-separated domains

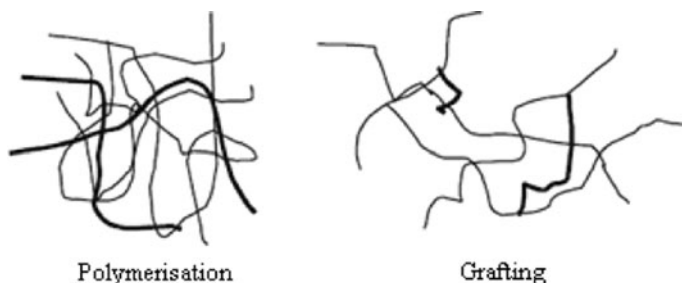


Fig. 1 Incorporation of PFMs into the rubber network [3]

will also be covalently attached to the rubber network [12, 13]. Ultimately, the extent of homopolymerization compared with grafting will depend on several factors, such as the readiness of the PFM to homopolymerize, the PFM concentration, the difference in polarity between the PFM and the rubber matrix, namely solubility, and the adequacy of mixing [9, 14].

Ethylene vinyl acetate peroxide crosslinking

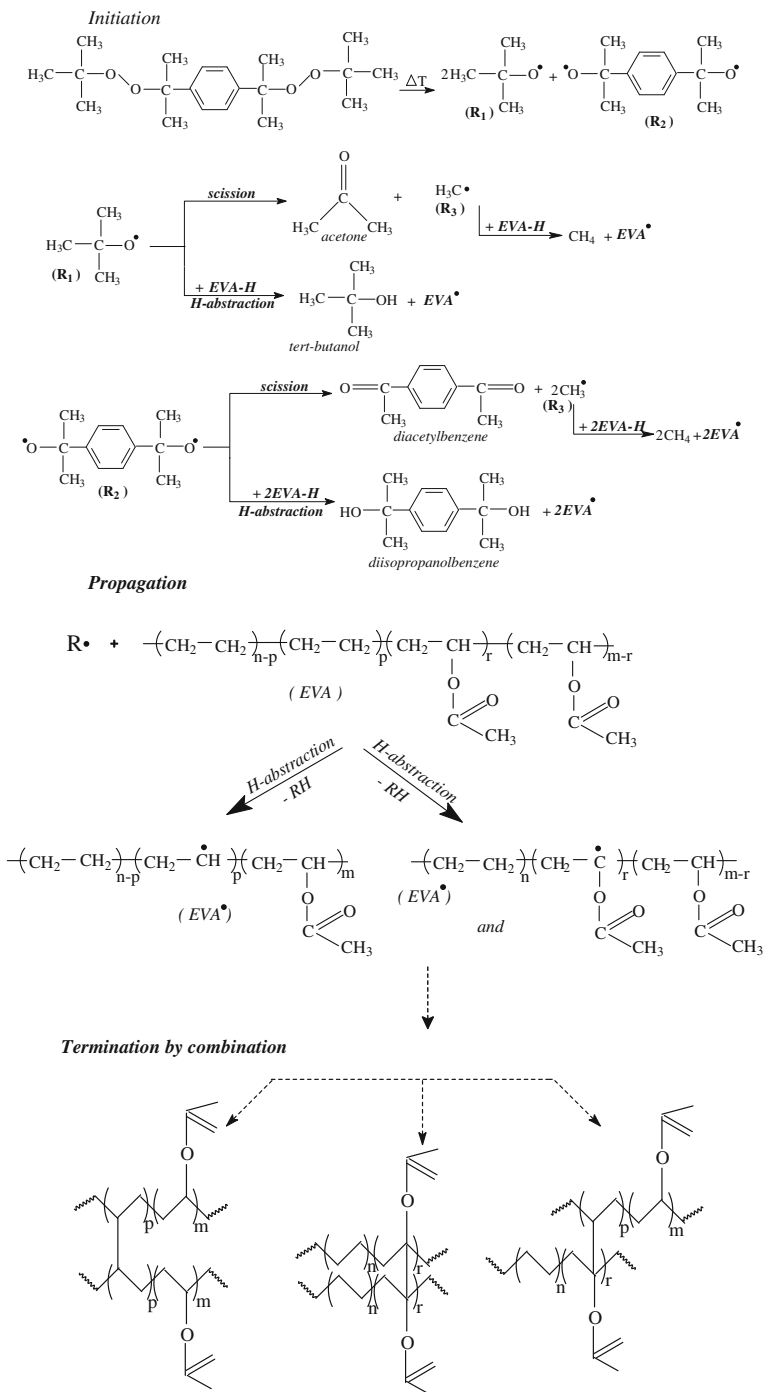
Crosslinking of the copolymer EVA is commonly performed through a thermochemical process using peroxides [15–22]. This process follows a well-known free radical mechanism where thermally decomposed peroxide radicals abstract mainly the hydrogen bonded to the tertiary carbon of the acetate group of VAc comonomers, followed by crosslinking through mutual termination of EVA macroradicals. It leads to a network structure with covalent C–C crosslinks, which generally provides excellent heat aging and high temperature properties. Scheme 1 suggests a mechanism of EVA crosslinking reaction with peroxides. It is noticed that in the first stage, the “initiation,” the initiator decomposition takes place—benzoyl peroxide which leads to free radical formation. This operation is carried out at high temperatures. Free radicals formed are very reactive chemical species which initiate “propagation” reactions. Only the formation of two types of macroradicals is presented. The formed macroradicals can recombine—see “termination” reactions—thus leading to crosslinked structures [3, 9, 15]. Other secondary reactions that can occur in EVA crosslinking with peroxide are those with H transfer or scission/degradation reactions with formation of aldehydes, carboxylic acids, ketones, vinyl groups, etc. (Aldehydes, vinylidene, carboxylic acid formation) (Scheme 2) [3, 16].

Several commercially available PFMs were tested in the peroxide cure of EVA in order to evaluate their influence on the vulcanization reaction, as well as on the final properties of the material. Since different PFMs not only differ in molecular weight but they also have other amounts of reactive functionalities in their molecular structures, comparisons were done in terms of equivalents of unsaturation. In this way a fair comparison, independent of molecular weight and number of functionalities, can be carried out amongst the different PFMs.

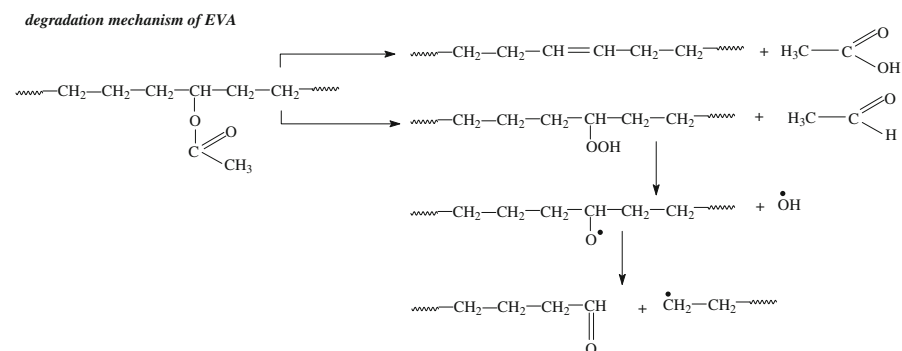
Schemes 3 and 4 suggest two reaction mechanisms for EVA crosslinking and grafting in the presence of PFMs with 2 and 3 functionality, respectively. It is noticed that PFMs are actually incorporated into the EVA elastic network [3, 6, 11], unlike peroxides, which only initiate the crosslinking reactions. After reaction initiation, these PFMs are quickly crosslinked by free radical addition reactions and cyclopolymerization, forming small vitrified thermoreactive particles [11, 14]. These particles act as multi-nodal crosslinking centres, binding a large number of EVA chains.

Ethylene vinyl acetate EB crosslinking

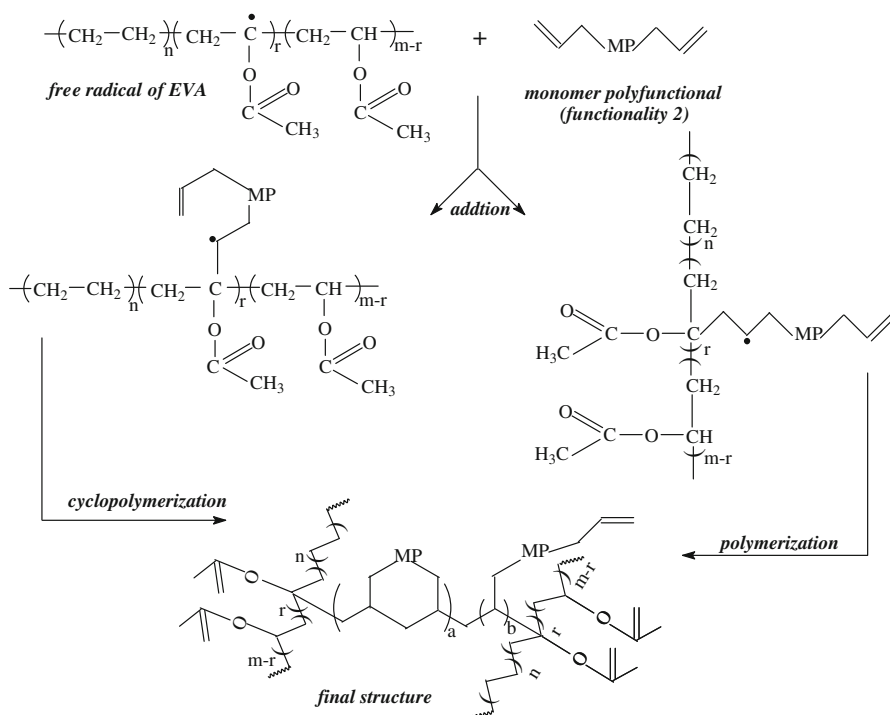
Radiation curing has historically been used as an alternative to peroxides in applications where the curatives themselves or side products of vulcanization are



Scheme 1 Scheme crosslinking mechanism of EVA chains by peroxide



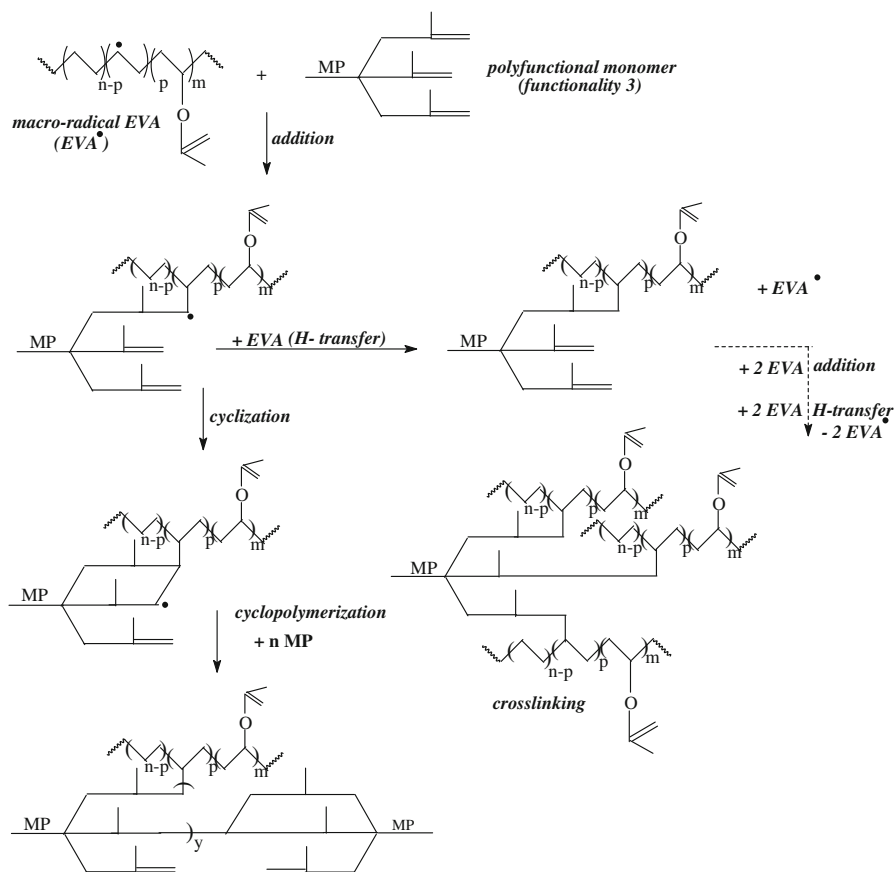
Scheme 2 Degradation mechanism of EVA



Scheme 3 Chemical reactions which can occur by using a monomer with 2 functionality

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 [21]. Radiation cure, on the one the hand, is known to be a cleaner and more homogeneous cure process.

The effects of ionizing radiation on polymers have been investigated by many researchers [23, 24] over the past few decades. Among the effects is that high-energy irradiation causes crosslinking and degradation in polymers. These reactions

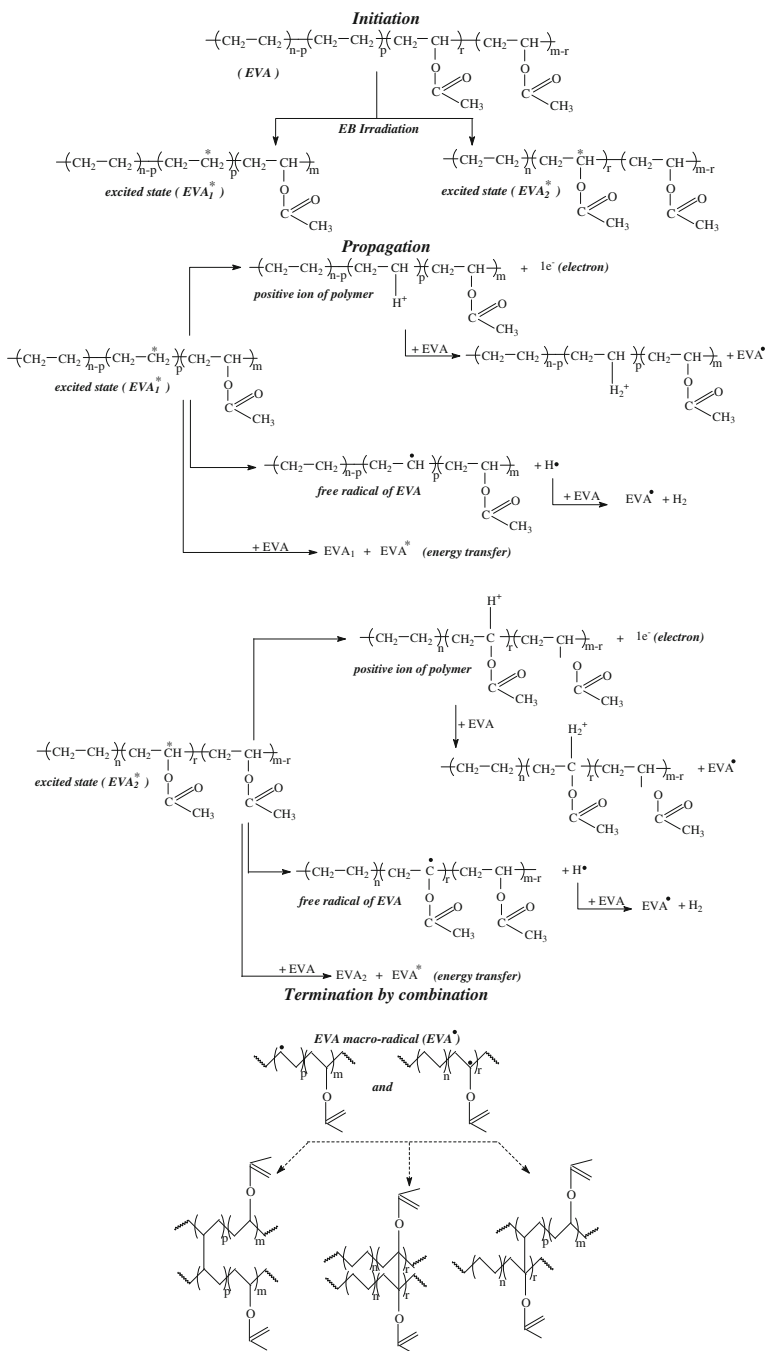


Scheme 4 Chemical reactions which can occur by using a monomer with 3 functionality

are reported to follow the free radical mechanism. As a result of crosslinking, the tensile strength, elasticity, and modulus increase while the elongation at break decreases. Degradation, on the other hand, leads to a decrease in tensile strength, elasticity, and modulus [24].

Crosslinking most likely occurs due to combinations of the macromolecular EVA radicals created during irradiation [25]. One of the proposed mechanisms for the radiation crosslinking of EVA is presented in Scheme 5. 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. 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 initiating grafting reactions [22].

High-energy ionizing radiation produces excited polymer molecules, as well as abundant secondary electrons which are capable of interacting with other molecules



Scheme 5 Radiation crosslinking mechanism of EVA chains

including PFMs. Depending on the energies involved and sample size, these excited molecules can further react to form radicals or can absorb the energy and slow down (thermalize) without producing further reactions.

Appropriate PFMs in polymer matrix can be used to obtain the desired crosslinking density at lower irradiation doses [26, 27].

Experimental

Materials

Materials used in the study: (1) EVA copolymer Elvax 260 (27.8% wt% VA content, flow index (MFI) 5.5 g/10 min at 190 °C and 2.16 kg load), (2) antioxidant Irganox 1010, (3) dibenzoyl peroxide Perkadox 14-40B (1.60 g/cm³ density, 3.8% active oxygen content, 40% peroxide content, pH 7.) as vulcanizing agent for vulcanization of control samples and (4) PFMs such as triallylcyanurate Luvomaxx TAC DL 70, triallylisocyanurate Luvomaxx TAIC DL 70C, trimethylolpropane-trimethacrylate Luvomaxx TMPT DL 75, ethylene glycol dimethacrylate Luvomaxx EDMA DL 75, and zinc-diacrylate ZDA GR 75. Table 1 presents the chemical structure, type, functionality, and characteristics of PFMs used.

Sample preparation

Blends were prepared by means of blending technique, on a laboratory electrically heated roller mill. The blend constituents were added in the following sequence and amounts: 100 phr EVA, three parts to a 100 parts of rubber (phr) PFMs (TAC, TAIC, TMPT, EDMA, and ZDA, respectively), and 1 phr Irganox 1010. Process variables: temperature 70 ± 5 °C, friction 1:1.1, and total blending time 6 min.

Plates required for physico-mechanical tests have been made by compression molded, using a electrically heated hydraulic press, at a temperature of 120 °C, pressure of 150 MPa, and time of 5 min to obtain sheets of dimension $11.5 \times 11.5 \times 0.2$ cm³.

Dibenzoyl peroxide vulcanized samples were prepared similarly with the experimental ones 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 and pressure of 150 MPa. All cure times were adjusted to bring the respective cures to T90 for each PFM—the vulcanization time was measured by means of Monsanto Rheometer (see Table 4).

Electron beam irradiation

The samples were packed in a polyethylene film and were irradiated at doses ranging from 5 to 20 Mrad irradiation in the *ILU-6M cavity* electron accelerator in atmospheric conditions and at room temperature. The accelerator consists mainly of two systems: the electron acceleration system (including resonator, RF generator, vacuum pumps for the accelerating structure, etc.) or accelerated electron generator,

Table 1 Comparison of chemical structure of PFMs used

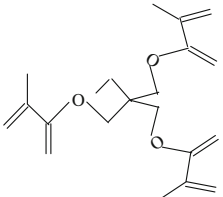
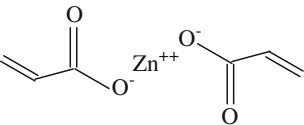
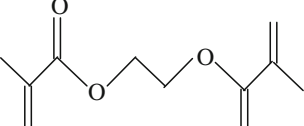
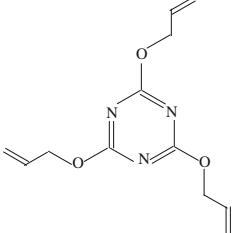
PFM	Type	Functionality	Characteristics	Chemical structure
Trimethylolpropane-trimethacrylate Luvomaxx TMPT DL 75 (TMPT)	I	3	Melting point: −25 °C; Boiling point: >200 °C; 22% percentage of ash; pH 9.2; Density: 1.36 g/cm ³ ; 75 ± 3% active ingredient.	
Zinc-diacrylate ZDA GR 75 (ZDA)	I	2	Melting point: 240–244 °C; Boiling point: 141 °C; Density: 1.23 g/cm ³ ; 75 ± 3% active ingredient.	
Ethylene glycol dimethacrylate Luvomaxx EDMA DL 75 (EDMA)	I	2	Melting point: −40 °C; Boiling point: 85 °C; 23% percentage of ash; Density: 1.25 g/cm ³ ; 75 ± 3% active ingredient	
Triallylcyranurate Luvomaxx TAC DL 70 (TAC)	II	3	Melting point: 26–28 °C; Boiling point: 119–120 °C; 26% percentage of ash, Density: 1.34 g/cm ³ ; 30% active synthetic silica.	

Table 1 continued

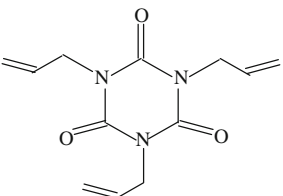
PFM	Type	Functionality	Characteristics	Chemical structure
Triallylisocyanurate Luvomaxx TAIC DL 70C (TAIC)	II	3	Melting point: 26–28 °C; Boiling point: 149–152 °C; pH 2.6; Density: 1.34 g/cm ³ ; 30% active synthetic silica.	

Table 2 The main characteristics of cavity electron accelerator ILU-6M

Characteristic	Value
EA energy	1.8 MeV
EA power in impulse	0–1 A
EA impulse duration	$\tau_B = 500 \mu s$
EA impulse repeat frequency	2, 3, 5 10, 15, 25, 50 Hz
Mean power	0–6 mA
Maximum mean power	10.8 kW
Electron scattering method	Electromagnetic scanning device
Useful section of EA field at scanning device output	100 cm × 6.5 cm
Conveyor belt for samples to be irradiated with the following characteristics	
Moving speed	$V_{belt} = 1.56\text{--}12.8 \text{ cm/s}$
Dimensions	Length: 125 mm; width: 290 mm; thickness: 160 mm
Distance between terminals	1282 mm
Distance from the scanning device output window	$H = 100\text{--}500 \text{ mm}$
Dimensions of sample holder	500 mm × 300 mm (with possibility of extension up to 1500 mm × 600 mm)

and accelerated electron scanning system. The main characteristics of the ILU-6M electron accelerator are presented in Table 2.

According to the Technical Report Series No. 277 [28], the absorbed dose is the major parameter in the accelerated electron radiation. The vulcanizing and grafting process performances are provided by the severe control of this parameter.

The relation defining the absorbed dose is

$$D = d\varepsilon/dm$$

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. The SI unit measure for the absorbed dose is the gray (Gy):

$$1 \text{ Gy} = 1 \text{ Joule/kg.}$$

To control the radiation dose EA, the methodology used was that of measurements of absorbed dose in accelerated electron beams with the chemical system “ceric sulfate–cerous sulfate” according to ISO/DIS 15555/1997 and Manual on Radiation Dosimetry by Holm and Berry [29].

Laboratory tests

Mechanical properties of the vulcanizates were measured on a Schoppler tensile tester with a nominal rate of the traverse of the moving grip of 460 mm/min. Modulus at 100% strain, tensile strength, and elongation at break tests were carried out according to the conditions described in ISO 37/2005, on dumb-bell shaped specimens of Type 2. Residual elongation is the elongation of a specimen measured 1 min after rupture in a tensile test. It was calculated using the formula:

$$\text{Residual elongation (\%)} = [(L - L_0) / L_0] \times 100$$

where L_0 is the initial length between two marks and L is the length between the marks 1 min after the sample broke in a tensile test.

Tearing strength tests were carried out using angular test pieces (type II) according to SR EN 12771/2003. Hardness of the vulcanized materials was measured using the Shore A scale with vulcanized samples of 6-mm thickness, by using a hardener tester according to ISO 7619-1/2004. Elasticity was evaluated with a Schoob test machine using 6-mm thick samples, according to ISO 46662/1986. All measurements were taken several times and the result values were averaged on three to five measurements.

The cure characteristics of the compounds were determined by an oscillating disk rheometer (Monsanto), at 160 °C and 30 min, according to the SR ISO 3417/1997. Delta torque or extent of crosslinking is the maximum torque (MH) minus the minimum torque (ML). Scorch time (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum. The cure rate index (CRI) of the recipe 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} .

Toluene resistance of irradiated samples was tested according to ISO 1817/2005. Specimens in the form of rectangular having dimensions of $20 \times 20 \times 2 \text{ mm}^3$ were immersed in the toluene at room temperature for 22 h. The test specimens were then removed from the toluene, wiped with tissue paper to remove excess toluene from the surface, and weighed. The percentage mass swell was calculated as follows:

$$\text{Change in mass (\%)} = [(W_2 - W_1)/W_1] \times 100$$

where W_1 is initial mass of specimen (g), W_2 is mass of specimen after immersion (g). Volume variation was calculated similarly.

Results and discussions

Characteristics of sample crosslinking with peroxide

Peroxide cure of EVA in the absence of PFMs

In order to understand the effect of PFMs in peroxide cure, it is necessary to previously perform the cure in the absence of PFMs, in order to have a later reference for the extent of the PFMs effect. Therefore, tests were carried out with only master batch and peroxide in the formulation.

Control blends crosslinked with peroxide have been crosslinked at 160 °C and vulcanization time was chosen depending on curves obtained on the Monsanto rheometer (rheologic characteristics) of blends in order to obtain the following blend samples: subvulcanized (T_{50}), vulcanized (T_{90}), and supravulcanized (T_{140}). Thus, the time needed to obtain T_{50} and T_{90} blends was determined from rheograms and corresponds to T_{50} (8' is the time to reach 50% of the delta torque above minimum and was determined according to the rheogram) and T_{90} (19'25'', see Table 4) and the time needed to obtain T_{140} supravulcanized blends was 30'.

Comparing physical–mechanical properties (Table 3) of non-vulcanized, sub-vulcanized (T_{50}), vulcanized (T_{90}), and supravulcanized (T_{140}) samples of EVA blend, it is noticed that, as the vulcanization time increases, (a) hardness, elasticity, and 100% module increase, (b) elongation at break and residual elongation decrease; (c) tensile strength and tear strength have a maximum and then a slight decrease. These effects occur as a result of EVA macromolecular chain crosslinking; it is noticed that, as the crosslinking time increases at high temperature, the crosslinking density increases (the number of free radicals increases).

Table 3 Physical–mechanical characteristics of control EVA blends crosslinked by means of peroxides

Characteristics	Non-vulcanized EVA	Vulcanized EVA		
		T_{50}	T_{90}	T_{140}
Hardness (°ShA)	81	83	83	84
Elasticity (%)	40	43	44	46
100% module (N/mm ²)	2.8	3.6	3.7	3.8
Breaking strength (N/mm ²)	4.7	10.9	8.5	8.2
Elongation at break (%)	527	420	327	300
Elongation set (%)	226	180	126	105
Tear strength (N/mm)	46	48	42	39

Table 4 Rheometric characteristics of samples crosslinking with peroxide and PFMs

Rheometric characteristics/Tip de PFMs	Control	TMPT	ZDA	EDMA	TAC	TAIC
The minimum torque ML (dNm)	0.7	2.0	2.0	3.0	0.7	3.0
The maximum torque MH (dNm)	38.0	39.5	38.0	37.0	44.7	44.7
M90 (dNm)	34.27	35.75	34.40	33.60	40.30	40.53
ΔM (dNm)	37.3	37.5	36.0	34.0	44.0	41.7
Curing time, t_{90} (min)	19'25"	17'45"	20'15"	18'45"	17'30"	18'00"
Shorter time t_{\min} (min)	1'0"	1'0"	1'0"	1'0"	1'15"	1'0"
Scorch time, t_{s2} (min)	2'0"	2'7"	2'0"	3'45"	2'30"	2'15"
Cure Rate Index, CRI (min^{-1})	5.71	6.40	5.48	6.67	6.67	6.56

Characteristics of samples crosslinking with peroxide and PFMs

Rheometric characteristics of samples crosslinking with peroxide and PFMs Rheometry for each compound is shown in Table 4.

Scorch time (t_{s2}) is a measure of time when the premature vulcanization of the material occurs. Therefore, a shorter time was required for the beginning of the vulcanization process for the EVA compounds. A decreasing trend of the optimum cure time t_{90} from 19'25" to 17'30"–18'45" as a result of using PFMs was also observed.

Scorch time increases from 2' to maximum 3'45" as a result of introducing PFMs, therefore, improves (blends will not have the risk of premature vulcanization during processing).

At the same time, the variation of maximum torque and minimum torque value in different types of PFMs are also given in Table 4. 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, 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, the addition of PFMs increased the crosslink density. The highest increase in crosslink density was found for TAC, TAIC–Type II PFMs. The cure rate index is a measure of the rate of vulcanization. As shown in Table 4, cure rate index increases by 12–16.8% in PFM blends.

The exception to these trends was the blend containing ZDA. This is probably due to the formation of an ionic type of crosslink rather than carbon–carbon bond crosslinks which results in a slight increase of the optimal curing time and a decrease of CRI and ΔM compared with the control blend, as ionic bonds are thermostable and determinations are carried out at 160 °C.

Physical–mechanical characteristics of samples crosslinking with peroxide and PFMs Physical–mechanical characteristics of samples crosslinking with peroxide and PFMs are presented in Table 5. The data demonstrates that all PFMs exhibited

Table 5 Physical-mechanical characteristics of blends based on EVA and PFMs, crosslinked with peroxides

Characteristics/PFMs	Control	TMPT	ZDA	EDMA	TAC	TAIC
Hardness (°ShA)	83	84	81	84	81	82
Elasticity (%)	44	42	42	42	40	40
100% module (N/mm ²)	3.7	3.7	3.6	3.8	3.8	3.6
Breaking strength (N/mm ²)	8.5	8	8.4	6.8	6.4	6.4
Elongation at break (%)	327	328	307	273	200	227
Elongation set (%)	126	124	117	97	53	75
Tear strength (N/mm)	42	48.5	47	39	49	30.5

decreased tensile strength, elongation at break, and residual elongation, which demonstrates increased crosslink density. The lowest values have been obtained for blends containing TAC and TAIC. Elongation at break of the samples depends upon the nature of the polymer and PFM, as well as on the degree of crosslink, which restricts the movement of the polymer chain against the applied force.

In addition, results agree to the studies conducted by Dikland et al. [11], it was reported that the PFMs of Type II form PFM domains during vulcanization, which co-vulcanize with the polymer matrix. These domains are therefore covalently bound to the rubber matrix and behave as filler particles, such effect on mechanical properties of these PFM domains depends on the rigidity of the PFM molecules.

Physical–mechanical characteristics of blends irradiated with accelerated electrons

Physical–mechanical characteristics of samples irradiated with accelerated electrons indicate the following:

Hardness (Fig. 2) increases by irradiation as a result of increasing crosslink density, so that at a dose of 5 Mrad higher values than peroxide-crosslinked plates are obtained; by further increasing the irradiation dose, small and irregular variations are noticed (max 2°ShA). The hardness of peroxide-cured control/PFMs sample was 83 °ShA/81–84 °ShA corresponding to the hardness of the irradiated sample at the lowest level of 5 Mrad dose.

Elasticity (Fig. 3) increases (by max 14.3%) with irradiation dose increase and has a maximum around the dose of 15 Mrad; except for the EDMA blend, where elasticity has an irregular variation by increasing the irradiation dose. The obtained values are higher than those obtained by peroxide crosslinking.

Modulus at 100% strain (Fig. 4) shows that increases (by max. 64%) in the irradiation dose increase the crosslink in the EVA and thus enhance the stiffness; the most prominent increase is in the 0–5 Mrad range (by max 43%). The modulus depends directly on the number of closed loops in the network, or in other words, a perfect network (network with no chain end). Variations are not uniform.

The tensile strength (Fig. 5) was increased as the irradiation dose was increased up to 5 Mrad. The tensile strength shows an optimum dose where tensile strength

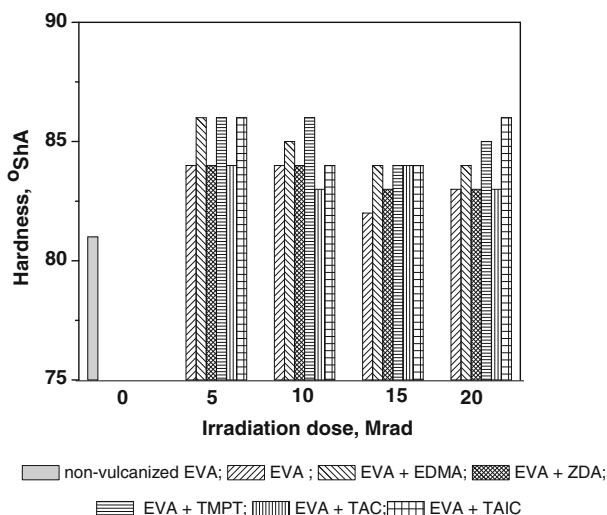


Fig. 2 Hardness versus EB irradiation dose and PFMs type

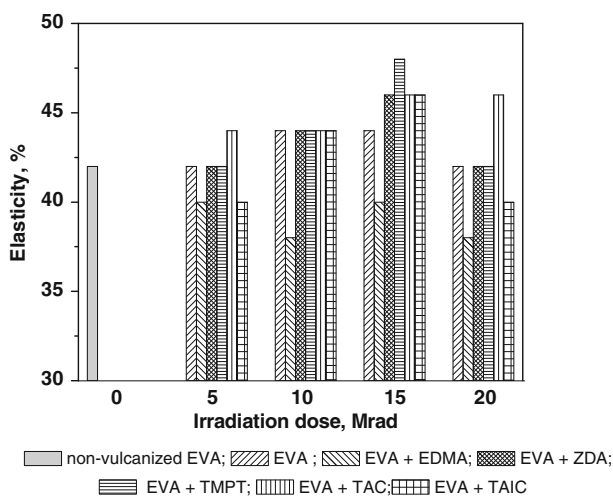


Fig. 3 Elasticity versus EB irradiation dose and PFMs type

passes through a maximum. For instance (1) for the TAIC blend at a dose of 5 Mrad where a four times increase of tensile strength was obtained (18.6 N/mm^2); (2) for the EDMA blend at a dose of 10 Mrad where a 4.25 times increase of tensile strength was obtained (20 N/mm^2), (3) given the variation of tensile strengths of samples, it could be assumed that the maxima of the other samples could be between 5 and 10 Mrad. In general, the reactivity of PFMs depends on a combination of factors including their ability to dissolve and diffuse into the polymer matrix, the reactivity of unsaturated bond, and the influence by the aromatic ring [30]. The different behavior of TAIC may be explained on the basis of the reactivity of its

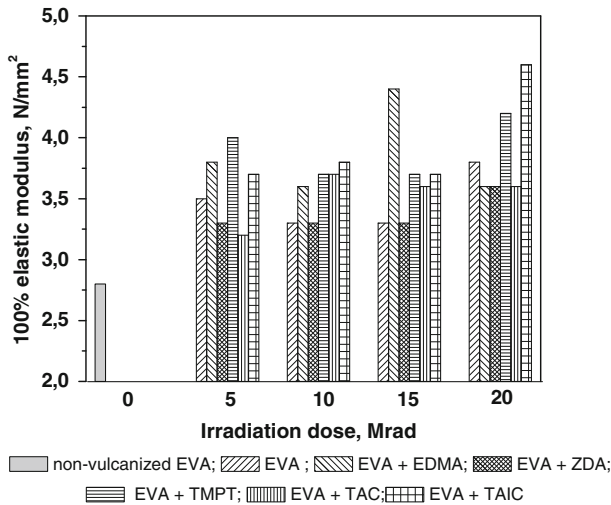


Fig. 4 100% elastic modulus versus EB irradiation dose and PFMs type

unsaturated bonds and its ability to dissolve and diffuse into the polymer matrix of the EVA compared with that of the TMPT. This behavior is obviously due to the difference in polarity of the two PFMs.

This is because at higher doses than 15 Mrad, the crosslinked network of the rubber becomes excessively tighter and flexibility of the rubber is diminished, leading to less ductile behavior and thus lower tensile strength. The reduction of tensile strength at doses higher than the dose 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

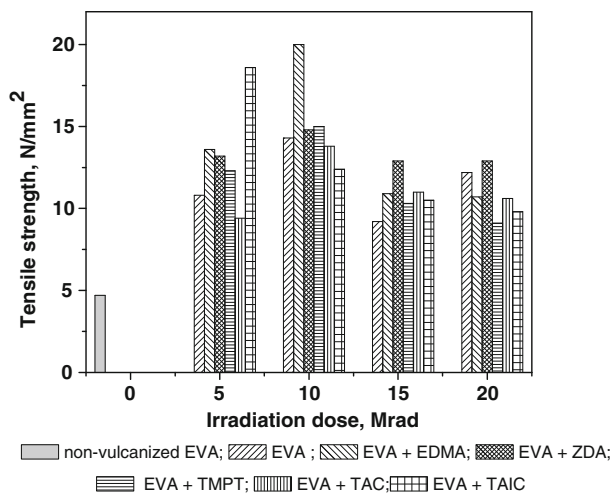


Fig. 5 Tensile strength versus EB irradiation dose and PFMs type

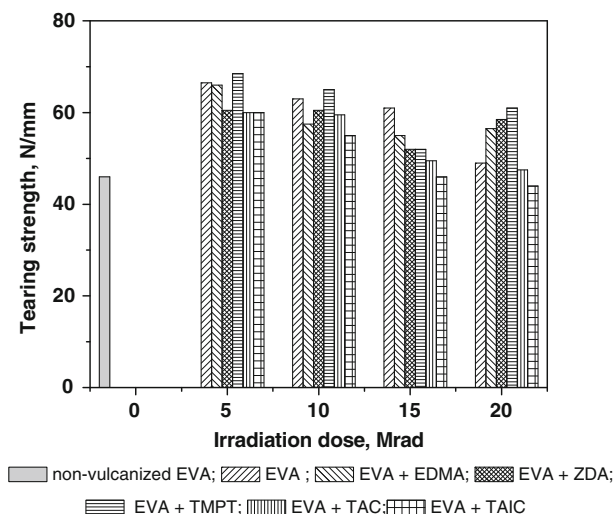


Fig. 6 Tearing strength versus EB irradiation dose and PFMs type

the modulus of the EVA remains essentially unchanged at higher doses as shown in Fig. 4. Tensile strength of irradiated doses of 15–20 Mrad EVA samples remains higher than the peroxide-cured sample.

Tear strength (Fig. 6) in increasing the irradiation dose has a maximum situated in the 0–10 Mrad region, and then exhibits a slight decrease, similar to the effect noticed in tensile strength. The highest values were obtained at a dose of 5 Mrad for TMPT blends (68.5 N/mm, increase by 48.1%) and EDMA blends (66 N/mm, increase by 43.5%).

The steadily decrease in elongation at break (Fig. 7) with increase at radiation dose level indicates that the network structure of the crosslinked rubbers becomes tighter and less flexible so that molecular movements are restricted. As mentioned earlier, increases in irradiation dose will enhance the brittleness of the EVA thus reduce its elongation at break. Crosslink in EVA will impart the stiffness behavior, which reduce the elongation at break of the materials. The elongation at break of samples are affected by PFMs functionality as it can be observed by comparing the results of TAC and TAIC with ZDA and EDMA. The elongation at break of blends with trifunctional monomer was lower than that of those with the bifunctional monomer. Although the elongation reduces in proportion with the tightness of the rubber networks as depicted in Fig. 5, however, the elongation values remain high enough to be useful for most applications.

Increases in irradiation dose will decrease the residual elongation (Fig. 8) of EVA. Thus, by increasing the irradiation dose, as a result of crosslink density increase, a very good recovery of samples is noticed after force application.

Mass (Fig. 9) and volume variation (Fig. 10) of samples after 22 h immersion in toluene provides clear signs on crosslink density. They indicate the fraction of shorter, uncrosslinked chains, which will remain in toluene. Upon increasing the irradiation dose, as a result of sample crosslinking, a decrease of mass and volume

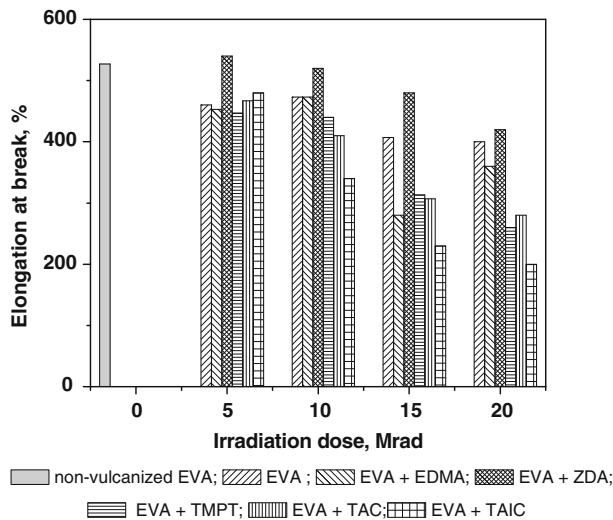


Fig. 7 Elongation at break versus EB irradiation dose and PFMs type

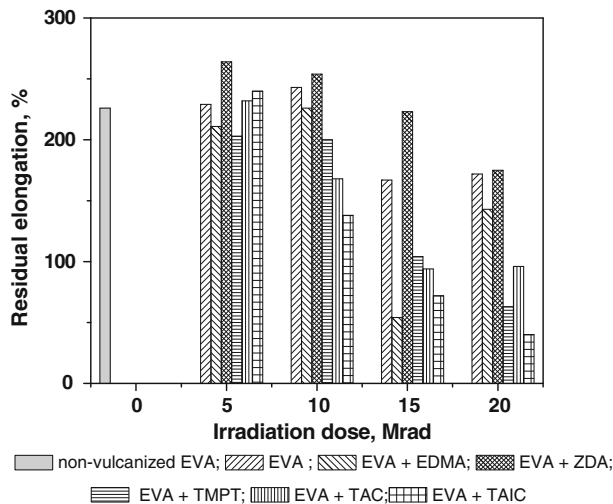


Fig. 8 Residual elongation versus EB irradiation dose and PFMs type

variation occurs after immersion in toluene. It is noticed that these characteristics decrease significantly by irradiating samples with 5 Mrad, then, upon increasing the irradiation dose, a slight decrease of these characteristics occurs as a result of further increase of the crosslinking degree. At doses of 20 Mrad, in some samples a slight increase of these characteristics is noticed indicating the share of copolymer degradation reactions. It is known that by sample irradiation, polymerization, grafting, crosslinking or degradation reactions can take place simultaneously. Depending on the irradiation dose, working conditions, blend composition, etc., a certain reaction prevails.

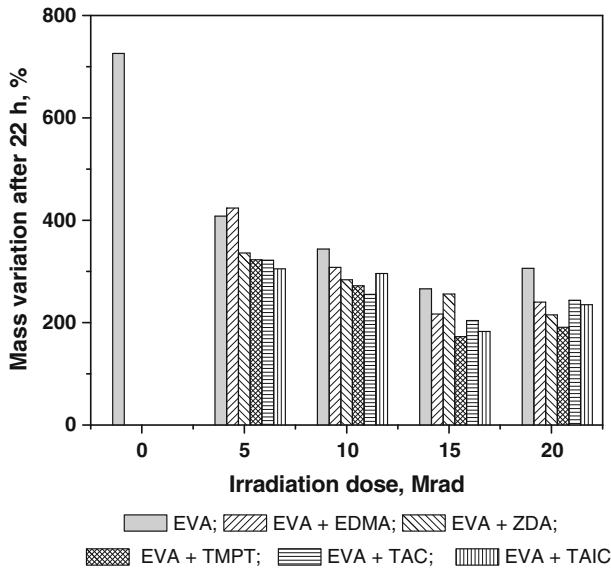


Fig. 9 Mass variation after 22 h immersion in toluene

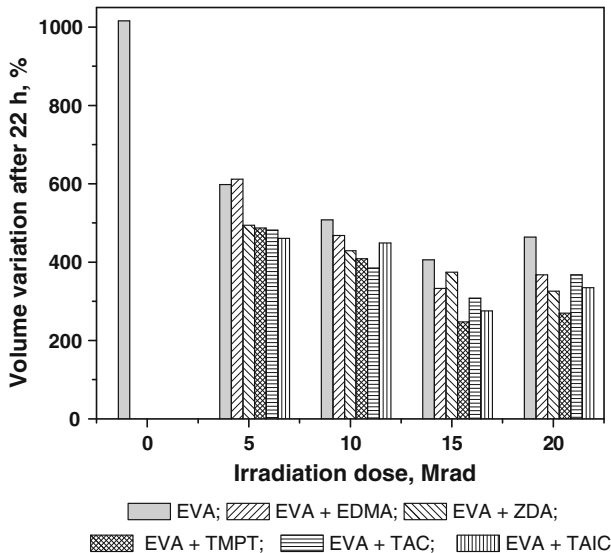


Fig. 10 Volume variation after 22 h immersion in toluene

Conclusion

Crosslinking of elastomers with the help of ionizing radiations is done without heating and in the absence of vulcanization agents. The chemistry of the process is based on microradical formation from elastomer chains which recombine, causing

structuring. The reaction mechanism is similar to that of the peroxide method, but in this case, the initiation of the reaction is due to the action of accelerated electrons [31]. Vulcanization processes by means of accelerated electrons are “clean and efficient” as compared with the classical processes (by heating resulting from black oil or gas combustion) and show some major advantages [32], such as (1) the resulted products are pure as no peroxide is added, (2) lack of wastes, (3) reduced crosslinking time and power expenditure, (4) the resulted products are sterile, and (5) improved characteristics of crosslinked products [32–34].

The crosslinking and grafting of EVA blends by accelerated electron radiation was proved by comparing physical–mechanical characteristics of the irradiated blends with those of the control blends with the same composition but crosslinked by 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 4 °ShA (the ones with TAIC) for hardness, and of 15%, respectively (samples with TAC) for elasticity.
- 100% modulus of samples crosslinked with peroxide is corresponding to an irradiation dose of 5–10 Mrad.
- elongation at low doses was higher than that of chemically cured samples and only at doses above 15 Mrad it followed a descending trend.
- tensile and tear strength of samples crosslinked with EB for all irradiation doses are significantly better than those obtained for samples crosslinked with peroxides (differences of up to 190%).
- the results show that EB irradiation gave the best results.

Using PFMs in EVA blends has led to (1) decreasing of the optimum cure time t_{90} from 19'25" to 17'30"–18'45", (2) scorch time increase from 2' to maximum 3'45", (3) increasing the crosslink density of peroxide or EB-cured systems by increasing the efficiency of productive radical reactions. The most efficient PFM for EVA copolymer blends has been triallylisocyanurate.

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