Vulcanization of Ethylene-Propylene–Terpolymer-Based Rubber Mixtures by Radiation Processing

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ABSTRACT: Elastomers are materials used in a large range of industrial and household applications. A common physical-chemical treatment is curing (crosslinking), imparting the rubber mechanical and thermal stability. Elastomers show low thermal conductivity values, and therefore, require complex and high-cost heating methods; thus, the ionizing (accelerated electrons) method shows high interest for the grafting and crosslinking processes. In addition to the lack of environmental impact, reliability, flexibility, and low costs render the radiation technologies especially attractive. The article presents the results concerning trimethylolpropane-trimethacrylate coagent concentration effect, on the mechanical properties of the ethylene-propylene–terpolymer (EPDM) rubber vulcanized by electron beam (EB). Mechanical properties of EB irradiated samples were compared with the dibenzoyl peroxide cured samples. Dependence of mechanical properties on irradiation dose was determined from a dose range of 0 kGy to 200 kGy. Dibenzoyl peroxide vulcanization at 160°C was carried out on the EPDM samples as well. Two types of blends have been analyzed: fillers and nonfillers. The results showed an increase in mechanical properties as a function of increasing polyfunctional monomer level. Also, based on the comparison between EB and dibenzoyl peroxide vulcanization efficiency, the results show that EB irradiation gave the best results. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Ethylene-propylene copolymers and ethylene-propylene-diene terpolymers (EPDM) are among the most versatile synthetic rubbers. In EPDM the ethylene and propylene comonomers form a saturated polymer backbone with randomly distributed, nonconjugated diene monomers, which provide unsaturations attached to the main chain. The physical, thermal, and chemical properties of EPDM can be tuned by adjusting the copolymer structure, the diene type and content and the molecular weight distribution. In the main chain, the distribution of ethylene and propylene is irregular, this makes EPDM elastic. As there is no polar group or big lateral groups to obstruct molecular motion, the cohesive force of EPDM is low and the molecular chain can keep its flexibility and elasticity over a wide temperature range. This special structure gives it excellent heat aging (or aging) property and outstanding ozone and weather resistance. As nonpolar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalis, phosphate esters, and many ketones and alcohols. EPDM is widely used to make automotive rubber parts, rubber sheet, and as insulation material for wire and cable.[1,2]

The most important stage in the EPDM rubber processing technology is vulcanization/crosslinking. During vulcanization/crosslinking, rubber molecules with chain configuration are linked by chemical bridges/bonds, and the rubber mass turns from its plastic mass into an elastic one.[3] This is normally done by sulfur and accelerator for general purpose rubbers. Although the fatigue resistance is very good with this type of network, aging and set suffer. An alternative curing system has been developed using peroxide. All the above curing systems involve chemicals by which the purity of the processed products is not maintained. Even dispersion of these vulcanizing agents is vital for a viable product. Excessive milling or mixing will cause scorch (premature cure), and render the product unstable. In the Green drive, i.e., to make the world pollution-free, the electron beam (EB) radiation technology takes an important position.

The process is very clean, requires less energy, permits greater processing speed and operates at ambient temperature. Physical and chemical changes in some polymers and mechanisms of crosslinking and chain scission under exposure to radiation energies have been investigated first in the 1950s. Ionizing radiation can induce chemical reactions at any temperature in the solid, liquid, and gas phase without using catalyst. This feature brings unique advantages of radiation processing for industries, such as energy saving, and capabilities inducing reaction at room temperature and in solid state. EB vulcanization has demonstrated extremely positive results compared with the conventional curing system such as: no polymer degradation due to high temperature as EB crosslinking occurs at room temperature, no oxidative degeneration in polymers as observed in classical crosslinking, direct crosslinking by C—C linkage by EB, extremely strong bonds, high degree of crosslinking, extremely short curing cycles, very high productivity, perfect for thin products, lower material waste.[4–6] Radiation vulcanization is applicable, but the dose required for EPDM vulcanization is very high.[7–9] To reduce the dose for vulcanization of EPDM, some researches have worked on the introduction of coagents/polyfunctional monomers such as ethylene glycol dimethacrylate, triallyl cyanurate, triallyl isocyanurate, trimethylolpropane-trimethacrylate etc.[10,11]

Many investigations have been undertaken to find out the effect of different polyfunctional monomers on the physical properties of the different rubber types vulcanized by EBs.[4,12–15] Poyfunctional monomers are effective on modification of material by crosslinking. It is suggested that the reaction be depicted as a two-step process: (1) rapid initial polymerization of the polyfunctional monomer and (2) reaction of the polymerized polyfunctional monomer with EPDM chains which "ties" the latter with the former to form a crosslinked EPDM-polyfunctional monomer network.[7] Appropriate polyfunctional monomers in polymer matrix can be used to obtain desired crosslinking density at lower irradiation doses.[16,17]

It is known that one of EB elastomer crosslinking is that increasing the radiation dose leads to an increase of degradation reactions versus crosslinking reactions. That's why it would be ideal to reduce the radiation dose necessary for crosslinking to improve the product quality. As shown above an efficient method to reach this objective would be to use polyfunctional monomers. One of the most efficient polyfunctional monomers for EPDM crosslinking is trimethylolpropane-trimethacrylate (TMTP).[18,19] The article presents the results concerning TMPT concentration effect, as polyfunctional monomer, on the mechanical properties of the ethylene-propylene–terpolymer (EPDM) rubber vulcanized by EB. Mechanical properties of EB irradiated samples were compared with the dibenzoyl peroxide cured samples. Dependence of mechanical properties on irradiation dose was determined from a dose range of 0 kGy to 200 kGy. Two types of blends have been analyzed: fillers and nonfillers. One of the major drawbacks in the use of TMPT, from an industrial point of view, is its high-cost; thus, it appears to be a very important goal to verify which is its minimum amount necessary to optimize the EB vulcanization process of blends based on EPDM and to guarantee the best performances of the

final compounds. Some studies[20,21] have reported that EB initiated vulcanization and grafting of trimethylol propane triacrylate (TMPT) onto ethylene-propylene diene monomer (EPDM) has been carried out over a wide range of irradiation doses (0–200 kGy) using a fixed concentration (10%) of TMPT. The values of tensile strength of the surface modified samples have not changed very significantly, while the modulus and elongation at break values have increased.

The results obtained in this study can contribute to the set-up of a database to optimize the EB vulcanization process of blends based on EPDM. This will facilitate the use of the most efficient TMPT concentration in order to obtain EPDM 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 EPDM to doses higher than what is necessary. The results of this study will help us to improve the curing of EPDM blends (lower irradiation dose, usage of the optim concentration of TMPT, and producing better products etc).

EXPERIMENTAL

Materials

The following raw materials were used: EPDM rubber (Nordel 4760) (Mooney viscosity is 70 ML_{1+4} at 120°C, 70% ethylene content, 5-ethylidenenorbornene (ENB) 4.9 wt %, density 0,88 g/cm^3, 10% crystalline degree), polyfunctional monomer TMPT Luvomaxx TMPT DL 75 (22% percentage of ash, pH 9.2, density 1.36 g/cm^3, 75 ± 3 % active ingredient), precipitated silica Ultrasil VN$_3$ (volatile materials at 105°C, max. 4.9 %), zinc oxide first quality (min 99% purity, max. 0.2% humidity), stearic acid, polyethylene glycol, antioxidant Irganox 1010, and dibenzoyl peroxide Perkadox 14-40B (1.60 g/cm^3 density, 3.8% active oxygen content, 40% peroxide content, pH 7) as vulcanizing agent.

Sample Preparation

Blends were prepared on a laboratory electrically heated roller mill.

For EPDM+TMPT preparation, the blend constituents were added in the following sequence and amounts: EPDM (100 p), 1 phr Irganox 1010 and 3 phr TMPT (KT$_3$), 6 phr TMPT (KT$_6$), 9 phr TMPT (KT$_9$), and 12 phr TMPT (KT$_{12}$).

For EPDM+TMPT+ingredients preparation, the blend constituents were added in the following sequence and amounts: EPDM (100 p), 3 phr TMPT (EIT$_3$), 6 phr TMPT (EIT$_6$), 9 phr TMPT (EIT$_9$), and 12 phr TMPT (EIT$_{12}$) and 50 phr Ultrasil VN3, 5 phr zinc oxide, 0.5 phr stearic acid, 3 phr polyetylen glycol, 1 phr antioxidant (Irganox 1010), called forward ingredients (ING).

Process variables: temperature 60–80°C, friction 1 : 1.1, and total blending time 7 min. for EPDM+TMPT blends and 11–15 min for EPDM+TMPT+ingredients blends. Plates required for physicomechanical tests were obtained by pressing in a hydraulic press at 120 ± 5°C and 150 MPa. 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; the best vulcanization time was measured by means of Monsanto Rheometer.

Experimental Installations and Sample Irradiation

The resulted plates were subjected to the following vulcanization methods:

- Conventional vulcanization with dibenzoyl peroxide (DP-V) at 160°C and 150 MPa by using an electrical hydraulic presser and the best curing time was established by means of the Monsanto rheometer;
- EB vulcanization (EB-V) with ILU-6M accelerator of 1.8 MeV and 10.8 kW output power.

The ILU-6M accelerator was built in Russia, Institute of Nuclear Physics-Novosibirsk. It is placed at Electrical Project and Research Institute from Bucharest, Romania. The ILU-6M is a resonator-type accelerator, operating at 115±5 MHz. This accelerator generates EB pulses of 0.375 ms duration, upto 0.32 A current peak intensity and upto 6 mA mean current intensity. The cross-sectional size of the scanned EB at the ILU-6M vacuum window exit is 1100 mm × 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 kGy to 50 kGy. For EB treatment, the rubber sheets were cut in rectangular shape of 0.15 × 0.15 m^2. The layers of three sandwiched sheets (covered in polyethylene foils) were irradiated by repeatedly passing on a conveyor under the ILU-6M scanner in atmospheric conditions and at room temperature of 25°C.

Distance between ILU-6M vacuum window exit and conveyor surface was 33 × 10^{-2} m. The conveyor speed was 2.36 × 10^{-2} 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 kGy to 200 kGy.

Laboratory Tests

Tensile strength and tearing strength tests were carried out with a Schoppler strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/1997, respectively angular test pieces (Type II) in according to ISO 34-1/2000. Hardness was measured by using a hardener tester according to ISO 7619/2001. Elasticity was evaluated with a test machine of type Schob. The cure characteristics of the compounds were measured at 160°C using an oscillating disk rheometer (Monsanto), 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) is a measure of the rate of vulcanization based on the difference between optimum vulcanization time (t_{90}) and incipient scorch time (t_{s2}). It was calculated according to the following formula (1):

$$CRI = \frac{100}{t_{90} - t_{s2}} \quad (1)$$

The sol-gel analysis was performed on crosslinked EPDM rubber to determine the mass fraction of insoluble EPDM (the network material resulting from network-forming crosslinking process) samples (gel fraction). The samples were swollen in toluene and extracted after 72 h in order to remove any scissioned fragments and unreacted materials. The networks were then dried in air for 6 days, and reweighed. The gel fraction was calculated as:

$$\text{Gel fraction} = \frac{m_s}{m_i} \times 100 \quad (2)$$

where m_s and m_i are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively.[3]

The crosslink density of the samples was determined on the basis of equilibrium solvent-swelling measurements (in toluene at 23–25°C) by application of the well-known modified Flory-Rehner equation for tetra functional networks. The samples (2 mm thick) were initially weighed (m_i) and immersed in toluene for 72 h. The swollen samples were removed and cautiously dried to remove excess solvent before being weighed (m_g) and, during this operation, the samples being covered to avoid toluene evaporation during weighing. Traces of solvent and other small molecules were then eliminated by drying in air for 6 days. Finally, the samples were weighed for the last time (m_s), and volume fractions of polymer in the samples at equilibrium swelling v_{2m} were determined from swelling ratio G, and calculated as follows:

$$v_{2m} = \frac{1}{1 + G} \quad (3)$$

where

$$G = \frac{m_g - m_s}{m_s} \times \frac{\rho_e}{\rho_s}; \quad (4)$$

ρ_e and ρ_s are the densities of elastomer samples and solvent, respectively.

The samples crosslink densities, v, were determined from measurements in a solvent, using the Flory–Rehner relationship, given by:

$$v = -\frac{Ln(1 - v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2}{V_1 \left(v_{2m}^{1/3} - \frac{2}{\Phi} v_{2m} \right)} \quad (5)$$

where $V_1 = 106.5$ cm^3/mol is the molar volume of solvent (toluene), v_{2m} is the volume fraction of polymer in the sample at equilibrium swelling, $\Phi = 4$ is the crosslink functionality and $\chi_{12} = 0.49$ is the EPDM-toluene interaction parameter[12,22,23]

RESULTS AND DISCUSSION

Characteristics of the Blends Vulcanized by Dibenzoyl Peroxide

Mechanism of Crosslinking EPDM Rubber with Peroxide. Peroxide crosslinking of EPDM covers about 15% of the commercial applications because of the enhanced performance in high temperatures. Based on results obtained and existing literature studies,[24–26] reaction mechanisms are suggested for crosslinking EPDM rubber using the crosslinking systems
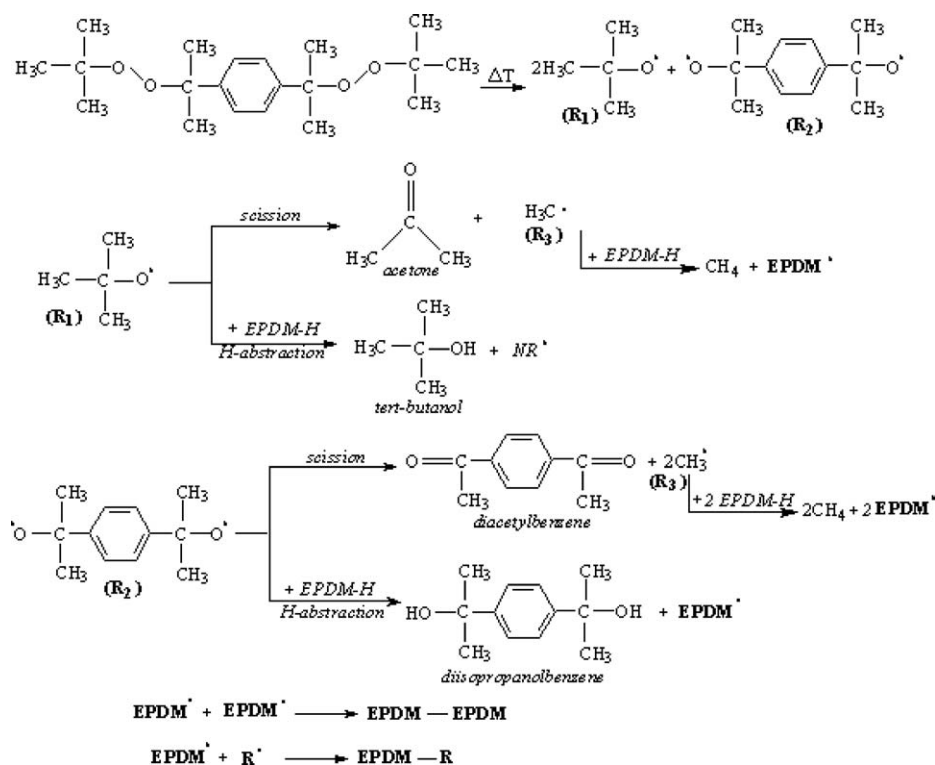
Figure 1. Mechanism of peroxide cure of EPDM.

presented above. 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 of EPDM are presented in Figure 1. It is initiated by the thermal decomposition of the peroxide, which results in the formation of two radicals (R_1 and R_2), which subsequently abstract H atoms from the EPDM polymer, yielding macroradicals EPDM and stable species (tert-butanol and diisopropanolbenzene). 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 EPDM rubber. All these radicals abstract H-atoms from the EPDM polymer, both at the CH_2 and CH units in the EPDM main chain and at the allylic positions of the diene unit, yielding EPDM alkyl and allyl macroradicals.

The termination by recombination (alkyl-alkyl, allyl-allyl, alkyl-allyl) of two EPDM macroradicals (EPDM˙) results in a crosslinking reaction (EPDM-EPDM) (Figure 2). The reaction of EPDM macroradicals (EPDM˙) with peroxide radicals (R˙ – R_1, R_2 or R_3) results in a crosslinking-inactive reaction (EPDM-R).[27,28]

Cure Characteristics of the Blends Vulcanized by Dibenzoyl Peroxide. In Tables I and II are presented the results of rheological measurements made on EPDM + TMPT (PKT$_0$, PKT$_3$, PKT$_6$, PKT$_9$, PKT$_{12}$ series) and EPDM + TMPT + ingredients (PEIT$_0$, PEIT$_3$, PEIT$_6$, PEIT$_9$, PEIT$_{12}$ series) samples, vulcanized by dibenzoyl peroxide. For every measured sample, the ML, the MH, optimum curing time (T_{90}), shorter time (t_{min}), scorch time (t_{s2}), CRI, and the difference of delta torque between the maximum and minimum torque (ΔM) were determined by

reading the variables on the curing curves obtained with the Monsanto rheometer.

For EPDM+TMPT samples (Table I), scorch time and curing time decrease with TMPT concentration increasing. TMPT is indeed improving the crosslinking efficiency of peroxide in the present system. The delta torque increases with increasing TMPT concentration. The delta torque values are a measure of the dynamic shear modulus and related to the crosslink density of the blends. As the value increases, the crosslink densities are expected to increase, reflecting the increase in stiffness.[29] Also the cure rate index is higher at blends with the TMPT amount introduced. This increase in cure rate may be due to the fact that an increasing concentration of TMPT caused the vulcanization reaction to increase and create more active crosslink sites in the rubber compound.

For EPDM+TMPT+ingredients samples (Table II), the increase of CRI is noticed and optimum curring time decreases with TMPT concentration increasing, similar effect to that noticed in nonfillers.

Tables I and II shows the torque values of fillers are higher than those of nonfillers. The increment of torque values is caused by the increase in stiffness of the composite due to the restriction of the mobility of the rubber chains as fillers are incorporated.[30]

The results obtained are in accordance with those obtained by other researchers, who reported that Type I cure coagents (such as TMPT) are highly reactive toward radicals, so scorch takes place very fast, which sometimes can be a disadvantage. Moreover, not only the rate of cure (CRI) is increased, but also the crosslink density or state of cure.[31,32]
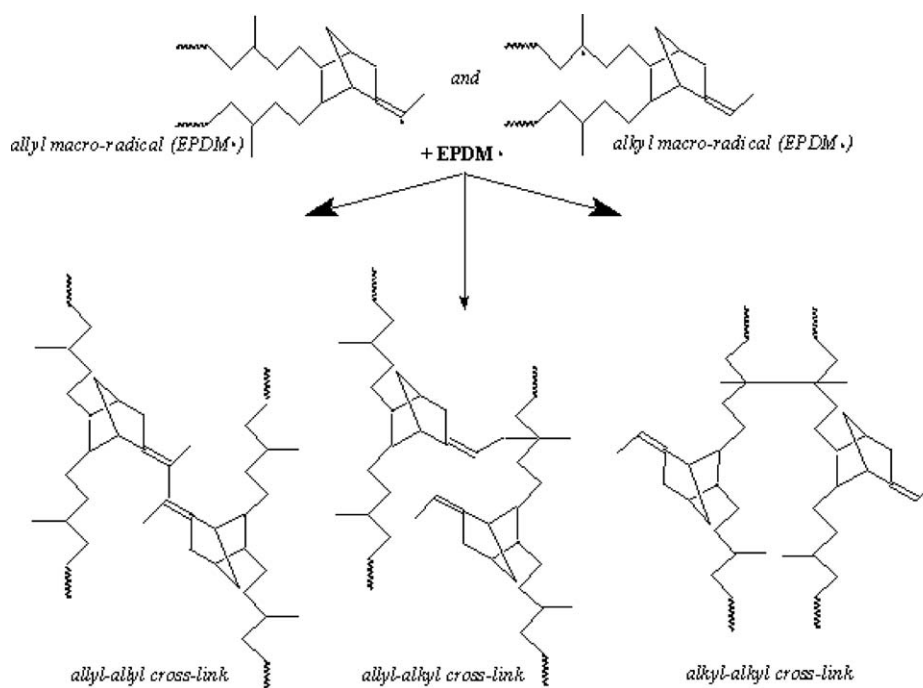
Figure 2. Scheme crosslinking mechanism of EPDM chains by peroxide.

Physicomechanical Characteristics of the Blends Vulcanized by Dibenzoyl Peroxide. Analyzing the physical-mechanical characteristics (Tables I and II) of nonfillers (PKT$_0$, PKT$_3$, PKT$_6$, PKT$_9$, PKT$_{12}$ series), and fillers, respectively (PEIT$_0$, PEIT$_3$, PEIT$_6$, PEIT$_9$, PEIT$_{12}$ series), it is noticed that, as TMPT amount increases in the blends, an increase of hardness occurs

(by max. 9°ShA and 6° ShA, respectively), modulus at 100% strain (by 60% and 42%, respectively) and an increase of tear strength (by 54% and 10.23%, respectively), elongation at break decreases (by 16.7% and 26.7%, respectively) as a result of crosslinking density increase. Tensile strength increases for non-fillers (by 53%) and has high values and an irregular variation

Table I. Cure and Physicomechanical Characteristics of the EPDM+TMPT Mixtures Vulcanized by Dibenzoyl Peroxide

Characteristics	Mixture symbol				
	PKT$_0$	PKT$_3$	PKT$_6$	PKT$_9$	PKT$_{12}$
Cure characteristics					
The minimum torque ML, (dNm)	7.5	1	1	1	2.5
The maximum torque MH, (dNm)	43	46.8	49.5	55.5	56.8
M90, (dNm)	39.5	42.2	44.7	50	51.4
ΔM, (dNm)	35.5	45.8	48.5	54.5	54.3
Curing time, t_{90}, min	23'45"	23'30"	19'30"	16'45"	16'15"
Shorter time t_{min}, min	1'15"	55"	45"	35"	30"
Scorch time, t_{s2}, min	2'30"	2'15"	1'30"	1'	1'
CRI, min^{-1}	4.71	4.71	5.56	6.35	6.56
Physical-mechanical characteristics					
Hardness, °ShA,	61	64	67	69	70
Elasticity, %,	52	60	58	52	52
Modulus at 100% strain	1.5	1.7	1.9	2.4	–
Tensile strength, N/mm^2	1.7	2.1	2.2	2.5	2.6
Elongation at break, %	120	120	113	113	100
Elongation set, %	5	5	4	5	5
Tear strength, N/mm	11	13.5	13.5	14	17

Table II. Cure and Physicomechanical Characteristics of the EPDM+TMPT + Ingredients Mixtures Vulcanized by Dibenzoyl Peroxide

Characteristics	Mixture symbol				
	$PEIT_0$	$PEIT_3$	$PEIT_6$	$PEIT_9$	$PEIT_{12}$
Cure characteristics					
The minimum torque ML, (dNm)	47	44	45.5	56.2	58
The maximum torque MH, (dNm)	78	71.8	70	81.5	81.5
M90, (dNm)	74.9	69.03	67.55	78.9	79.15
ΔM, (dNm)	31	27.8	24.5	25.3	23.5
Curing time, t_{90}, min	21′15″	21′	20′	18′45″	17′
Shorter time t_{min}, min	45″	45″	45″	45″	30″
Scorch time, t_{s2}, min	2′	2′	2′	1′30″	1′30″
CRI, min^{-1}	5.19	5.26	5.55	5.80	6.45
Physical-mechanical characteristics					
Hardness, °ShA,	83	84	86	88	89
Elasticity, %,	34	36	34	34	36
Modulus at 100% strain	4	4	4.8	5.6	5.7
Tensile strength, N/mm^2	18.3	16.1	16.3	17.3	17.3
Elongation at break, %	560	553	460	447	410
Elongation set, %	99	93	67	70	62
Tear strength, N/mm	88	88	91	95	97

for fillers. Residual elongation has very low values and an irregular variation for nonfillers and has high values and decreases with the increase TMPT amount in the blends for fillers.

Comparing the two series of blends, it is noticed that in fillers, due to strong interactions between rubber and filler, elasticity is reduced and restricts the movements of the rubber chain, resulting in more rigid and tough blends. As a result, introducing the filler in the blends led to a significant increase of hardness, tensile strength, elongation at break, residual elongation and tear strength, and a decrease of elasticity, also reported by other researchers.[33,34]

Gel Fraction and Crosslink Density of the Blends Vulcanized by Dibenzoyl Peroxide. Table III shows the gel fraction (mass fraction of the network material resulting from a network-forming polymerization or crosslinking process; the gel fraction comprises a single molecule spanning the entire volume of the material sample) and crosslink density (number of crosslinks per unit volume in a polymer network) of the samples vulcanized by dibenzoyl peroxide and TMPT as a function of the TMPT content. The determination is based on the absorption of a proper solvent and subsequent swelling of the rubber.[35] It is noticed that, as the TMPT quantity increases, there is a decrease of swelling ratio G (toluene soluble polymer quantity) and a

slight increase of gel fraction, volume fractions of polymer in the samples at equilibrium swelling (v_{2m}) and of crosslink density (v). Crosslink density has effect on physical and chemical properties of vulcanized rubber. The experimental results showed that with the increase in crosslink density, modulus at 100% strain, hardness, tensile strength, and tear strength increased, whereas the elongation at break decreased, confirmed by other works.[36]

Characteristics of Blends Vulcanized by EB
Mechanism of Crosslinking EPDM Rubber with EB. Elastomer crosslinking by means of EB is done without heating and in the absence of vulcanization agents. Increased utilization of electron-beams, for modification and enhancement of polymer properties, has been well documented over the past 40 years. EB processing of crosslinkable plastics has yielded materials with improved dimensional stability, reduced stress cracking, improved heat resistance, reduced solvent and water permeability, and significant improvements in other thermomechanical properties.[37]

The reaction mechanism is similar to that presented in crosslinking with peroxides, but in this case, reaction initiation is due to the action of EB and in the presence of the polyfunctional monomers. Ionizing radiation produces an excitation of

Table III. Gel Fraction and Crosslink Density of Samples Vulcanized by Dibenzoyl Peroxide and TMPT

Sample	m_i(g)	m_g (g)	m_s(g)	φ_e(g/cm^3)	Gel fraction (%)	G	v_{2m}	v (10^{-4} mol/cm^3)
PKT0	1.2955	3.0018	1.2644	0.8225	97.5994	1.3051	0.4338	7.4421
PKT3	1.1078	2.4331	1.0886	0.8173	98.2668	1.1656	0.4617	9.2178
PKT9	1.2266	2.7231	1.2191	0.8025	99.3885	1.1432	0.46666	9.5567

Figure 3. Mechanism for EB curing.

Figure 5. Hardness versus EB irradiation dose and TMPT concentration.
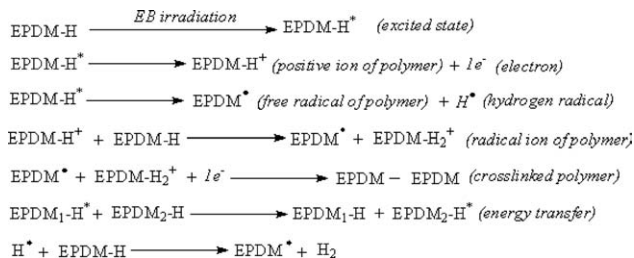
polymer molecules. The energies associated with the excitation are dependent on the irradiation dosage of electrons. The interaction results in formation of free radicals formed by dissociation of molecules in the excited state or by interaction of molecular ions. The free radicals or molecular ions can react by connecting the polymer chains directly or initiating grafting reactions. The mechanism of EB cure of EPDM is summarized in Figure 3. The chemistry of the process is based on macroradical formation from elastomer chains (Figure 4), which recombine, causing structuring.[38–42]

Physicomechanical Characteristics of the Blends Vulcanized by Eb. Several representative results are further presented. They show the relation between several rubber physical and mechanical properties, TMPT concentration and EB absorbed dose. In the Figures 1–6 EPDM control samples with ingredients but without TMPT and EPDM control samples without ingredients and TMPT are presented, as reference values. It has been represented by comparing, variation of physical and mechanical properties of EPDM + TMPT blends with and without ingre-
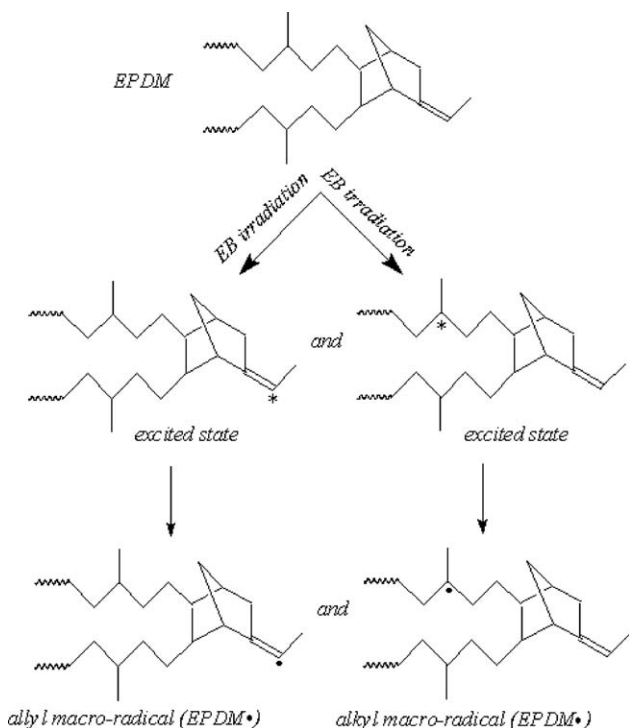
dients, unvulcanized (0 point on the graphics) and EB of 50, 100, 150, and 200 kGy.

As it is shown in Figure 5, hardness increases as the TMPT amount increases in the blends, similar to the effect noticed in blends crosslinked with peroxide. At the same time, an increase of hardness is noticed by irradiation of samples with 50 kGy as a result of samples reinforced by crosslinking, then, upon further increase of the irradiation dose, this characteristic changes insignificantly.

Elasticity (Figure 6) presents a significant variation by irradiation of samples with 50 kGy as a result of the elastomer going from plastic to elastic state by crosslinking. Upon the further increase of the irradiation dose, small variations of this characteristic occur.
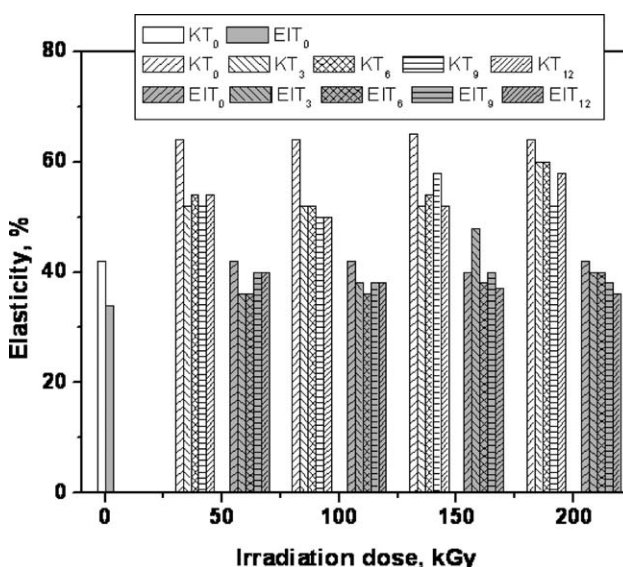

Figure 4. Scheme to obtain allyl and alkyl macro-radicals of EPDM by EB.

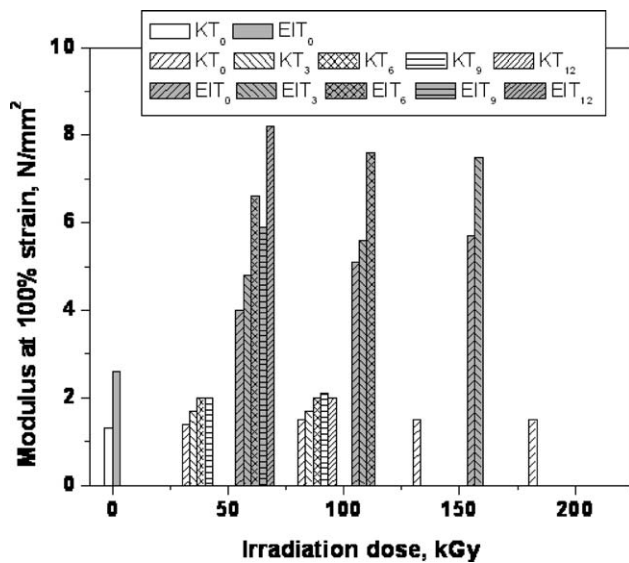**Figure 6.** Elasticity versus EB irradiation dose and TMPT concentration.

Figure 7. Modulus at 100% strain versus EB irradiation dose and TMPT concentration.

Modulus at 100% strain (Figure 7) shows that increases in the irradiation dose will increase the crosslink density in the EPDM+TMPT and EPDM+TMPT + ingredients. Significant increases can be noticed in fillers, which might indicate that EB leads to an improvement of filler-elastomer interactions.[43,44]

Upon increasing the TMPT amount in the blends, the increase of modulus at 100% strain is noticed as a result of the increase of rubber crosslinking degree.[45]

Tensile strength (Figure 8) and tear strength (Figure 9) for fillers vulcanized by EB irradiation present maximum values for irradiation dose of 50 kGy, indicating elastomer crosslinking. For irradiation dose of 100, 150, and 200 kGy, the tensile strength and tear strength decrease with the EB irradiation dose increas-
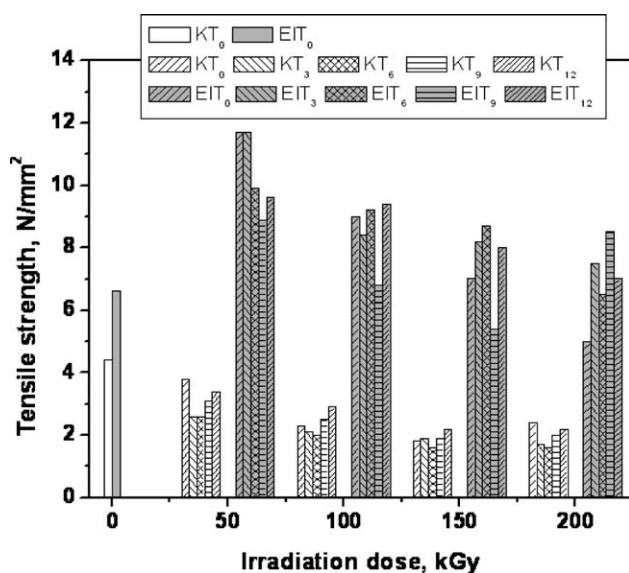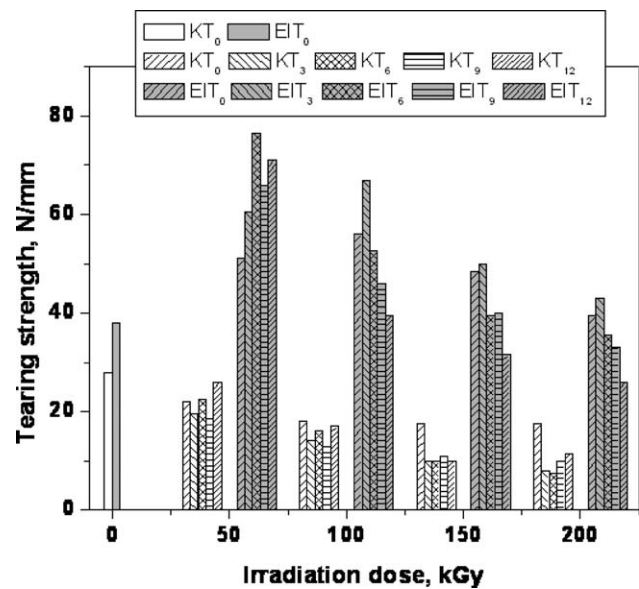

Figure 9. Tearing strength versus EB irradiation dose and TMPT concentration.

ing. This might be due to degradation taking place at the same time with vulcanization: polyethylene crosslinks under irradiation in air and polypropylene, generally, degrades under irradiation in air. However, given the data obtained for modulus at 100% strain, we can deduce that this does not necessarily indicate degradation of the elastomer at doses higher than 50 kGy, but it can be due to the occurrence of excessive crosslink in EPDM chain, which in turn produced a brittle material. Similarly, in nonfillers, a decrease of these characteristics occurs upon the increase of EB dose. However, in this case, by irradiation with 50 kGy a decrease of tensile strength and tear strength occurs as a result of reducing the crystallization degree by EPDM crosslinking.[15,16]
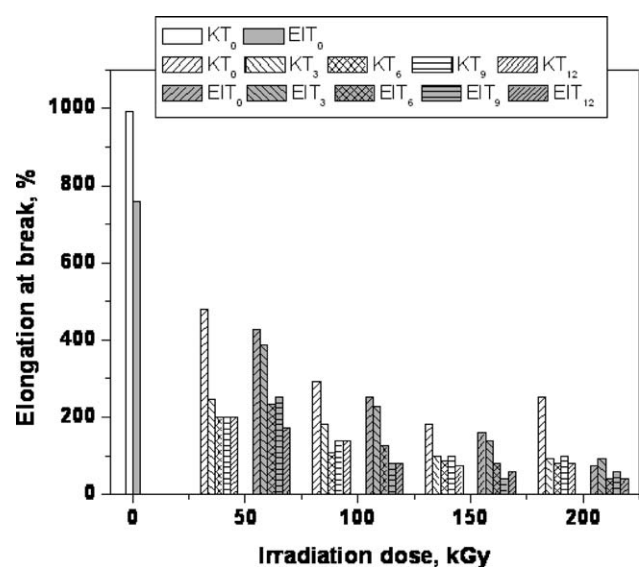

Figure 8. Tensile strength versus EB irradiation dose and TMPT concentration.

Figure 10. Elongation at break versus EB irradiation dose and TMPT concentration.
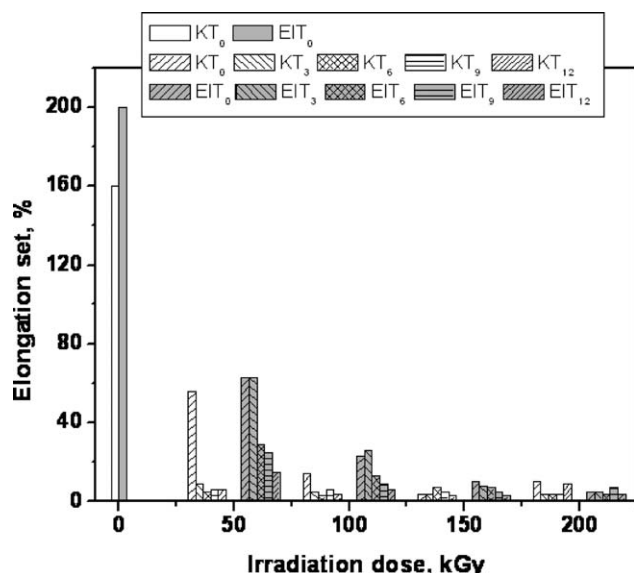
Figure 11. Residual elongation versus EB irradiation dose and TMPT concentration.

Elongation at break (Figure 10) and residual elongation (Figure 11) present a significant decrease with irradiation dose increasing from 0 to 100 kGy and then a slow decrease; TMPT concentration increase is followed by an elongation at break and residual elongation decrease. These effects indicate the increase of intermacromolecular links (crosslink density increase respectively) by increasing the irradiation dose which restricts the shift of macromolecules among themselves and moreover, a very good recovery of samples is noticed after force application.

Gel Fraction and Crosslink Density of the Blends Vulcanized by Eb. The induced crosslinking was evaluated with gel fraction (crosslinked polymer content) and crosslink density (number of crosslinks per unit volume in a polymer network) determination.

Note: The samples were not subjected to crosslinking treatment (with benzoyl peroxide or by irradiation treatment) were completely dissolved in toluene – in the same conditions.

The results presented in Table IV show that as the TMPT quantity and EB dose increases, there is a decrease of swelling ratio G (toluene soluble polymer quantity) and a slight increase of gel fraction, volume fractions of polymer in the samples at equilibrium swelling (v_{2m}) and of crosslink density (v), the highest values were obtained for blend with 9 phr TMTP radiated with 200 kGy. Thus, in an irradiation cured system, the gel content and crosslink density of samples increases with increase in irradiation dose and the TMPT quantity. This is due to the formation of a three-dimensional network structure.[46]

Comparison Between Crosslinking with Peroxide and with EB
While both peroxide and EB cure involve radical-based intermediates, differences between the mechanisms do exist. While peroxide cure is a thermally initiated event with cure temperatures routinely in the 160°C to 180°C range, EB cure is performed at room temperature. Peroxide cure is initiated by oxygen-centered radicals that can be differentiated from the carbon-centered radicals produced by 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 which may contribute to variations in coagent performance between the disparate systems.

That was necessary for pointing out how the studied physical and mechanical properties are influenced by dibenzoyl peroxide and EB vulcanization, respectively.

Table IV. Gel Fraction and Crosslink Density of Samples Vulcanized by EB

Sample	Dose (kGy)	m_i (g)	m_g (g)	m_s (g)	φ_e (g/cm^3)	Gel fraction	G	v_{2m}	v (10^{-4} mol/cm^3)
KT0	50	1.0485	5.4700	1.0204	0.8275	97.3200	4.1668	0.1935	0.6252
	100	1.1145	4.0691	1.0970	0.8275	98.4298	2.5888	0.2786	1.8152
	150	1.0893	3.7835	1.0742	0.8275	98.6138	2.4100	0.2933	2.1202
	200	1.0713	3.4673	1.0573	0.8275	98.6932	2.1780	0.3146	2.6336
KT3	50	1.1198	4.4660	1.0946	0.8133	97.7496	2.8926	0.2569	1.4227
	100	1.0796	3.5156	1.0658	0.8133	98.7217	2.1587	0.3166	2.6841
	150	1.0244	2.9239	1.0139	0.8133	98.9750	1.7692	0.3612	4.0661
	200	1.0996	2.9699	1.0916	0.8133	99.2725	1.6160	0.3823	4.8877
KT9	50	1.1061	3.5036	1.0858	0.8025	98.1647	2.1126	0.3213	2.8097
	100	1.1219	2.9236	1.1110	0.8025	99.0284	1.5478	0.3925	5.3284
	150	1.1906	3.0279	1.1834	0.8025	99.3953	1.4787	0.4034	5.8344
	200	1.2052	2.9884	1.1992	0.8025	99.5022	1.4155	0.4140	6.3579

Note: The samples were not subjected to crosslinking treatment (with benzoyl peroxide or by irradiation treatment) were completely dissolved in toluene – in the same conditions.
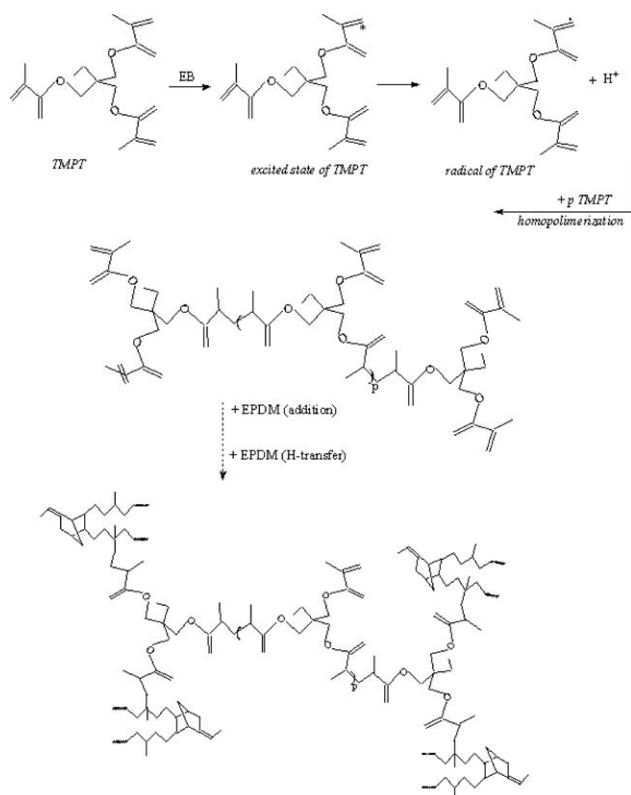
Figure 12. Scheme to obtain EPDM – TMPT crosslinking by EB.

Comparing experimental data obtained by crosslinking with peroxide (Tables I and II) to those obtained by irradiation with EB, the following remarks can be made:

1. The hardness and elasticity values obtained for unfiller samples vulcanized by irradiation are similar with those obtained for vulcanized by dibenzoyl peroxide samples. For filler samplers, it is noticed that hardness of blends irradiated with 50 kGy is 3–4°Sh A higher than that of corresponding blends vulcanizated with peroxide. Hardness increases by max 3°ShA as the irradiation dose increases from 50 to 200 kGy. Similarly, elasticity is higher in irradiated fillers compared to those crosslinked with peroxide. This can be determined by the fact that: (1) irradiation leads to the improvement of the interaction between filler and elastomer, which implicitly leads to obtaining better properties, and (2) as a result of the high radiation penetration ability, an efficient and uniform vulcanization occurs in the whole mass of rubber articles, thus obtaining homogenous samples.

2. In nonfillers, it was noticed that a dose of 50 kGy leads to obtaining very low values of residual elongation, similar to those obtained by vulcanization with peroxide. These values indicate an efficient vulcanization and a very good recovery after applying a force. Corresponding to this dose of EB, it is noticed that irradiated blends have higher values of tensile strength, tear strength, and elongation at break than those of blends crosslinked with peroxide.

3. Similarly, in fillers it was noticed that a dose of 50 kGy dose to obtaining very low values of residual elongation,

similar to those obtained by vulcanization with peroxide. Corresponding to this dose of EB, it is noticed that irradiated blends have lower values of tensile strength, tear strength, and elongation at break than those of blends crosslinked with peroxide. This effect, correlated to the values of modulus at 100% strain may indicate that 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, elongation at break and tear strength.

4. Crosslink density values for the mixtures crosslinked with peroxide are higher than those obtained from mixtures crosslinked with EB, but gel fraction shows similar values for both types of samples. In both cases the crosslink density and gel fraction increases with increasing concentration of TMPT in mixtures.

In conclusion, crosslinking with EB is much more efficient that one with peroxide because it leads to an efficient crosslinking in the whole mass of the elastomer and to obtaining better physical-mechanical characteristics. The optimal irradiation dose is of max 50 kGy, it is lower in filler blends in comparison with the nonfiller blends. The optimal vulcanization time is reduced by minimum 10 times.

Influence of TMPT on Characteristics of Blends

Polyfunctional monomers are effective on modification of polymer material by crosslinking. Generally speaking, there are two factors which affect the functionality of polyfunctional monomers in the polymer: one is the unsaturation of polyfunctional monomers and the other is the solubility of polyfunctional monomers in the polymer.[42] The polyfunctional monomers are coagents and can participate in a number of radical reaction mechanisms, including grafting and radical addition. These polyfunctional monomers can be grouped according to their influence on cure kinetics and ultimate physical – mechanical properties. Type I polyfunctional monomers are highly reactive and increase both the rate and state of cure (acrylate, methacrylate, or maleimide functionality). Type II polyfunctional monomers are based on allyl reactive sites and increase the state of cure only. Monomeric forms include allyl – containing cyanurates, isocyanurates, and phthalates. In our study, we used as a polyfunctional monomer: TMPT (trimethylopropane trimethacrylate), of Type II.

Polyfunctional monomers are effective on modification of material by crosslinking. It is suggested that the reaction be depicted as a two-step process: (1) rapid initial polymerization of the polyfunctional monomer and (2) reaction of the polymerized polyfunctional monomer with EPDM chains which "ties" the latter with the former to form a crosslinked EPDM-polyfunctional monomer network.[7] Appropriate polyfunctional monomers in polymer matrix can be used to obtain desired crosslinking density at lower irradiation doses.[17,18]

TMPT coagent is actually built into elastic EPDM network in contrast to the peroxide, wich only initiates the crosslinking reaction.[47] After peroxide decomposition, these coagents are quickly crosslinked by addition reactions of free radicals and homopolymerization, forming small vitrified thermoreactive

particles.[48] These particles act as multinodal crosslinking centers, binding a large number of EPDM chains. Figures 12 present the mechanism of EPDM crosslinking by EB in the presence of TMPT coagent, achieved based on existing literature data.[48]

Analyzing the obtained results, it is noticed that the introduction of TMPT in blends leads to an improvement of cure and physicomechanical characteristics of the blends vulcanized by dibenzoyl peroxide or EB.

With the increase of TMPT amount in blends crosslinked with peroxide, a significant decrease of vulcanization time and an increase of MH, ML, delta M, CRI, gel fraction, and crosslink density occur. This may be due to the fact that an increasing concentration of TMPT caused the vulcanization reaction to increase and create more active crosslink sites in the rubber compound. As a result, crosslink density of the blend increases, thus leading to an increase in reinforcement.

In blends vulcanized by irradiation with EB, upon the increase of TMPT amount in the blends, an increase of hardness, modulus at 100% strain, gel fraction and crosslink density, and a decresce of elongation at break and residual elongation occur.

These effects indicate the increase of intermacromolecular links, crosslink density increase respectively, which leads to a reinforcement of the samples, restriction of macromolecule shifting and moreover, a very good recovery of samples is noticed after force application.

CONCLUSIONS

Comparing physicomechanical parameters of the composites obtained by EB vulcanization with those vulcanized with dibenzoyl peroxide, it is easy to observe higher efficiency first of all, as it leads to a more efficient crosslinking in the whole mass of the elastomer and to obtaining better physical-mechanical characteristics. The optimum values of physicomechanical rubber parameters present a strong dependence on TMPT concentration and irradiation dose. So, there are optimum irradiation doses (50 kGy) which confer maximum values to the analyzed samples. The results obtained in this study can contribute to an optimization of the vulcanization process by EB of blends based on EPDM.

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