

EFFECT OF IRRADIATION DOSE ON CROSS-LINK DENSITY OF EPDM RUBBER

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Abstract

This paper presents the effect of irradiation dose on the gel fraction and crosslink density of the ethylene-propylene-terpolymer (EPDM) rubber blended with polyfunctional monomer trimethylolpropane-trimethacrylate (TMPT) and cross-linked by electron beam (EB). Dependence of gel fraction and crosslink density on irradiation dose was determined from a dose range of 0 kGy to 50kGy. The results indicate that the application of new technologies will lead to a significant improvement in physical properties of finished products and to optimize the curing stage, the most important operation of the technological process for obtaining elastomeric materials.

Key words: ethylene-propylene-terpolymer rubber, cross-linking, electron beam, cross-link density.

1. INTRODUCTION

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.

Ethylene-propylene elastomers are one of the most versatile, fastest growing and interesting synthetic rubber polymers. Excellent resistance to heat, oxidation, ozone and weather aging are expected to provide continued value in demanding automotive, construction, and mechanical goods applications. Current and emerging advanced polymerization and catalyst technologies also provide the ability to design polymers to meet application and processing needs that are important to meeting the ever-increasing demands for product quality, uniformity and performance [1].

Ethylene-propylene rubbers use the same chemical building blocks or monomers as polyethylene (PE) and polypropylene (PP) thermoplastic polymers. These ethylene (C2) and propylene (C3) monomers are combined in a random manner to produce rubbery and stable polymers. A wide family of ethylene-propylene elastomers can be produced ranging from amorphous, non-crystalline to semi-crystalline structures depending on polymer composition and how the monomers are combined [1-3]. These polymers are also produced in an exceptionally wide range of Mooney viscosities (or molecular weights). The ethylene and propylene monomers combine to form a chemically saturated, stable polymer backbone providing excellent heat, oxidation, ozone and weather aging. A third, non-conjugated diene monomer can be terpolymerized in a controlled manner to maintain a saturated

backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification chemistry. The terpolymers are referred to as EPDM (or ethylene-propylene-diene with “M” referring to the saturated backbone structure). An EPDM polymer structure is illustrated in Figure 1. The ethylene-propylene copolymers are called EPM.

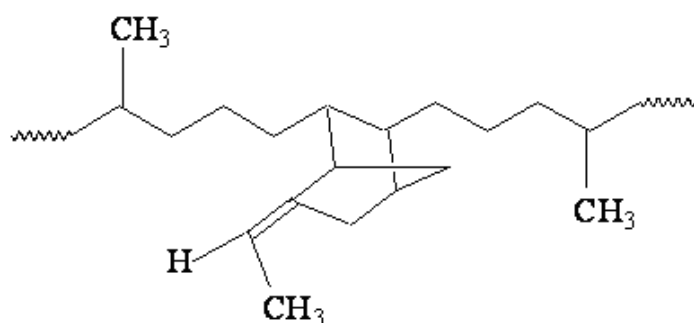


Figure 1. Structure of EPDM (*ethylene-propylene-terpolymer rubber*)

Vulcanisation is the process by which rubber is changed from essentially a plastic material to either an elastic or a hard material.[4-6] In this process, an elastomer is transformed from a ‘plastic’, ‘formable’ material into an ‘elastic’ material by the formation of a three-dimensional network with different types of junctions. The word vulcanisation derives from *Vulcan*, the Roman God of fire. Not accidentally, it also means volcano, a hot place where quite some sulphur species can be found. The term vulcanisation was therefore originally exclusively applied to the crosslinking reaction achieved by sulphur at high temperatures. Nowadays this term is also applied to refer to other crosslinking processes, such as peroxide cure. There are several possibilities for the crosslinking of rubber. The already mentioned sulphur vulcanisation was the first to be discovered and still is today’s most common cure system. The sulphur vulcanisation process requires the presence of carbon-carbon unsaturation in the polymer and it leads to a three-dimensional rubber network in which the polymer chains are linked to each other by sulphur bridges. As a result, sulphur cured articles have good tensile and tear strength, good dynamic properties, but poor high temperature properties like ageing, for instance.[5, 6] Other vulcanisation systems, i.e. peroxides, ultraviolet light, electron beam, microwave, resins, etc. were later discovered and gained more importance with the progressive development of synthetic rubbers.

Vulcanization with peroxides is done by radicalic mechanism when bonds form between C-C macromolecules. The chain of free radical reactions is initiated by thermal decomposition of the peroxide into primary radicals formed by scission stable species (acetone and diacetylbenzene) and the second radical that continue the propagation in the presence of rubber.

Radiation curing has historically been used as an alternative to peroxides in applications where the curatives themselves or sideproducts 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 the other hand, has been promoted as a cleaner and more homogeneous cure process. Electron beam irradiation has been used in the wire and cable industry for longer than 30 years and applied to a wide range of commodity and specialty elastomers. A survey of the types of elastomers susceptible to radiation curing is available, as are review articles describing the electron-beam curing of commercially significant grades [7, 8]. Variables such as radiation dosage and the effect of polymer microstructure

and chemical additives on the efficiency of electron beam cure have been studied. Some researchers [9-11] studied radiation-induced crosslinking in thermoplastic elastomers based on ethylene-propylene rubber (EPDM) and polyethylene (PE) or polypropylene (PP) plastics.

Elastomer crosslinking by means of electron beam is done without heating and in the absence of vulcanization agents. The reaction mechanism is similar to crosslinking with peroxides, but in this case, reaction initiation is due to the action of EA and in the presence of the polyfunctional monomers. Ionizing radiation produces an excitation of 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.

Electron beam (EB) vulcanization has demonstrated extremely positive results compared to the conventional curing system such as: no polymer degradation due to high temperature as EB cross-linking occurs at room temperature, no oxidative degeneration in polymers as observed in classical cross-linking, direct cross-linking by C-C linkage by EB, extremely strong bonds, high degree of cross-linking, extremely short curing cycles, zero blooming effects; extremely high tensile strength; extremely high resistance to compression set; extremely high resistance to oils, grease, lubricants; highly improved accelerated ageing properties, very high productivity, perfect for thin products, lower material waste [12, 13]. However, the radiation cross-linking of rubbers was not used in larger technical applications because of the high cost of irradiation to bring about vulcanization, but could become an industrial process when the radiation dose decreased with the use of some sensitizers.

Reported papers suggest that appropriate polyfunctional monomers (co-agents) in polymer matrix [14-16] could be used to obtain desired rubber physical properties at lower irradiation doses [17-20]. Co-agents are multi-functional organic molecules which are highly reactive towards free radicals.[5] They are used as reactive additives to boost the vulcanization efficiency.[21, 22]. The most used coagents are molecules with maleimide groups, (meth)acrylate groups, or allylic groups, [23-25] but polymeric materials with a high vinyl content, i.e. 1,2-polybutadiene, can also act as co-agents. Some authors have even studied the action of sulphur, or sulphur donors as co-agents.[26-32, 6]. The co-agents can be divided into two groups: Type I and Type II co-agents. Type I: Addition and hydrogen abstraction reactions: these co-agents consist of rather polar molecules with a low molecular weight and activated double bonds. Their main characteristic is that they are highly reactive towards radicals, so scorch takes place very fast, which sometimes can be a disadvantage. By using this kind of coagents not only the rate of cure is increased but also the crosslink density or state of cure. A disadvantage that may be present when using this type of co-agents is that, due to polarity, the compatibility of these co-agents with the polymer matrix is limited. Some examples of Type I co-agents are: acrylates, methacrylates, bismaleimides and zinc salts. Type II: Addition reactions: these co-agents 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 co-agents. The use of these co-agents leads to an increase in crosslink density of the vulcanisate but, unlike Type I, they are not capable of increasing the cure rate. Due to their low polarity, these co-agents have a good compatibility with many elastomers. Some examples are: high-vinyl 1,2-polybutadiene, divinylbenzene, allyl esters of cyanurates, isocyanurates and sulphur.

This paper presents the effect of irradiation dose on the gel fraction and crosslink density of the ethylene-propylene-terpolymer (EPDM) rubber blended with polyfunctional monomer trimethylolpropane-trimethacrylate (TMPT) and cross-linked by electron beam (EB). Dependence of gel fraction and crosslink density on irradiation dose was determined from a dose range of 0 kGy to 50kGy.

2. MATERIALS AND METHODS

2.1. Materials

The following materials were used in the study: *ethylene-propylene-terpolymer rubber*, EPDM (Nordel 4760) (Mooney viscosity is 70 ML₁₊₄ at 120°C, 70% ethylene content, ENB 4.9 W_t %, density 0,88 g/cm³, 10% crystalline degree), antioxidant Irganox 1010 and polyfunctional monomer *trimethylolpropane-trimethacrylate*, TMPT, Luvomaxx TMPT DL 75 (22% percentage of ash, pH 9.2, density 1.36 g/cm³, 75 ± 3 % active ingredient).

2.2. Preparation of samples and irradiation

Blends have been made by means of blending technique, on a laboratory roll, total blend time of 7', friction of 1:1.1. The blend constituents were added in the following sequence and amounts: 100 phr EPDM rubber, 1 phr Irganox 1010, and 3 phr TMPT (for EPDM/TMPT -3 samples), 9 phr TMPT (for EPDM/TMPT -9 samples). Plates required for physical tests have been made by compression molded, using an electrically heated hydraulic press, pressure of 150 MPa and time of 3 min. to obtain sheets of 11.5 x 11.5 x 0.2 cm³.

The resulted plates were subjected to the EB vulcanization 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 electron beam 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 x 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 x 0.15 m². 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.

2.3. Laboratory tests

The *sol-gel analysis* was performed on cross-linked EPDM rubber to determine the mass fraction of insoluble EPDM (the network material resulting from network-forming crosslinking process) samples (*gel fraction*). The samples (1.0x1.0 cm) 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:

$$Gel\,fraction = \frac{m_s}{m_i} \times 100 \quad (1)$$

Where m_s and m_i are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively [33].

The *cross-linking 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:

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

where:

$$G = \frac{m_g - m_s}{m_s} \times \frac{\rho_e}{\rho_s} \quad (3)$$

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

The samples cross-link densities, ν , were determined from measurements in a solvent, using the Flory–Rehner relationship, given by

$$\nu = - \frac{Ln(1 - v_{2m}) + v_{2m} + \chi_{12}v_{2m}^2}{V_1 \left(v_{2m}^{1/3} - \frac{2}{\Phi} v_{2m} \right)} \quad (4)$$

where $V_1 = 106.5 \text{ cm}^3/\text{mol}$ 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 cross-link functionality and $\chi_{12} = 0.49$ is the EPDM-toluene interaction parameter [34, 35].

3. RESULTS AND DISCUSSION

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 polymer: one is the unsaturation of polyfunctional monomers and the other is the solubility of polyfunctional monomers in polymer [21]. The polyfunctional monomers 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), and type II polyfunctional monomers are based on allyl reactive sites and increase the state of cure only. In our study we used TMPT – trimethylolpropane-trimethacrylate (figure 2) as polyfunctional monomer (type I and functionality 3).

The EB irradiation method, applied to the above mentioned rubber type, is based on our research reported [36-40] that demonstrate the efficiency of EB curing process.

Vulcanization by EB irradiation involves the interaction of 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 [18]. 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 [17]. The chemistry of the process is based on macroradical formation from elastomer chains, which recombine causing structuring [19, 20].

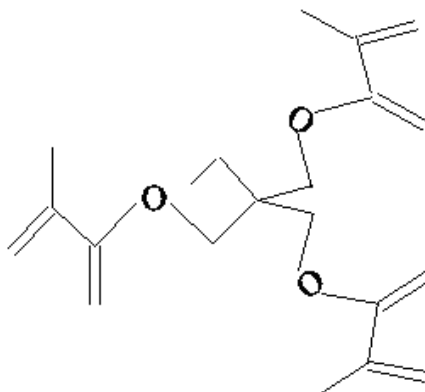


Figure 2. Chemical structure of trimethylolpropane-trimethacrylate

In this paper the induced crosslinking was evaluated with *gel fraction* (crosslinked polymer content), and *cross-link density* (number of crosslinks per unit volume in a [polymer network](#)) determination and the results were represented in figure 3 and figure 4, respectively. The samples were not subjected to crosslinking treatment (by irradiation with electron beam) were completely dissolved in toluene – in the same conditions. Sol-gel studies revealed higher sensitivity of EPDM and EPDM/TMPT to irradiation. Even at a low dose (12.5 kGy) gel fractions were found 52.30%, 76.15% and 85.76% for pure EPDM, EPDM/3 phr TMPT and EPDM/9 phr TMPT respectively. Slowly increase is observed for all samples when irradiation dose increasing from 12.5 to 50 kGy. It was noted that for all irradiated samples the sol-gel fraction slightly increase with dose increasing, the best results being obtained for the series EPDM / 9 phr TMPT: 93.07%, 94.26% and 96.23% for 2.50 kGy, 3.75 kGy and 5.00 kGy respectively. Also, on the base of the obtained results, it was observed small differences between the results obtained for EPDM / 3 phr TMPT series and EPDM / 9 phr TMPT series.

Similar results are obtained for crosslinking degree, too. Fig. 4 shows that, for every series (EPDM, EPDM/3 phr TMPT and EPDM/9 phr TMPT), the crosslinking degree increase with irradiation dose increasing. The weaker variation is for EPDM series for which the degree of crosslinking increases slowly: from 1.05×10^{-4} mol/cm³ at dose of 12.5 kGy to only 2.44×10^{-4} mol/cm³ at 5.00 kGy. For EPDM/ 3 phr TMPT series it was observed a slightly higher variation of crosslinking degree: from 1.28×10^{-4} mol/cm³ at dose of 12.5 kGy to 6.82×10^{-4} mol/cm³ for de 5.00 kGy. As expected (as with sol-gel parameter) the spectacular increase in the degree of crosslinking was obtained for EPDM/ 9 phr TMPT series. Thus, were obtained values of 1.34×10^{-4} mol/cm³ for the smallest dose (12.5 kGy) and 12.39×10^{-4} mol/cm³ for the the biggest tested dose (5.00 kGy).

4. CONCLUSION

The variation in gel content and of the crosslinking density, when different concentration of TMPT (polyfunctional monomer) were added to the blend and irradiated at various doses, has shown, as it was expected, an increase for both parameters because the TMPT employed in this study are well known reactive additives that form bridges by radiation-induced free radical mechanism and produce a network structure even at lower doses. The highest values were obtained for mixtures that contain 9 phr TMPT irradiated at 50 kGy. So, in radiation treatment system, the gel content and the crosslinking density of samples increase with irradiation dose and the TMPT quantity increasing. This is due to the formation of a three-dimensional network structure. [40].

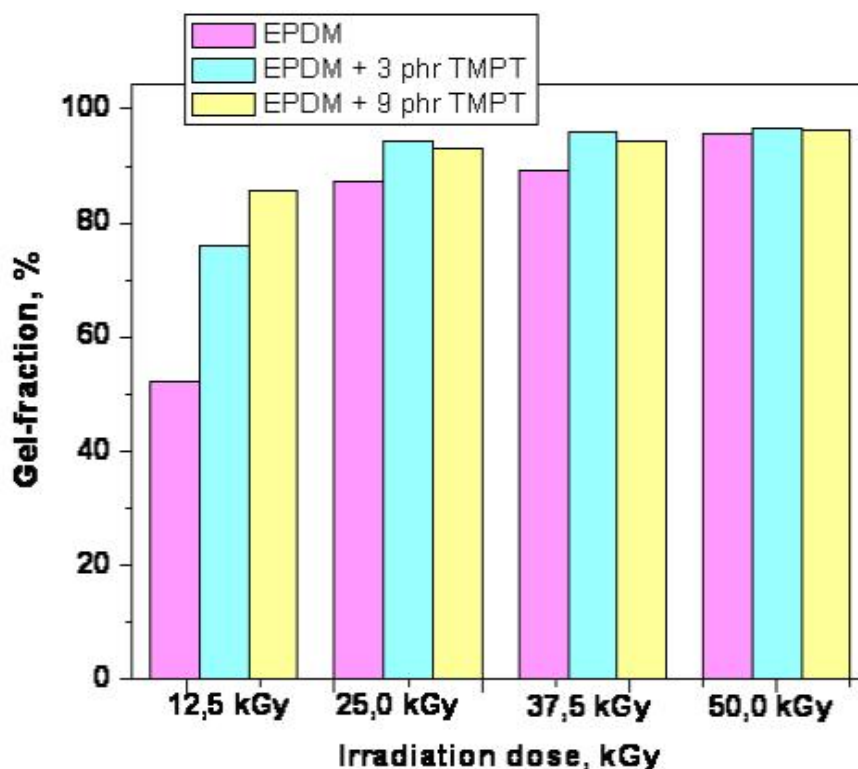


Figure 3. Change of *gel fraction* with irradiation dose for different compositions of EPDM with TMPT (EPDM, EPDM + 3 phr TMPT and EPDM + 9 phr TMPT)

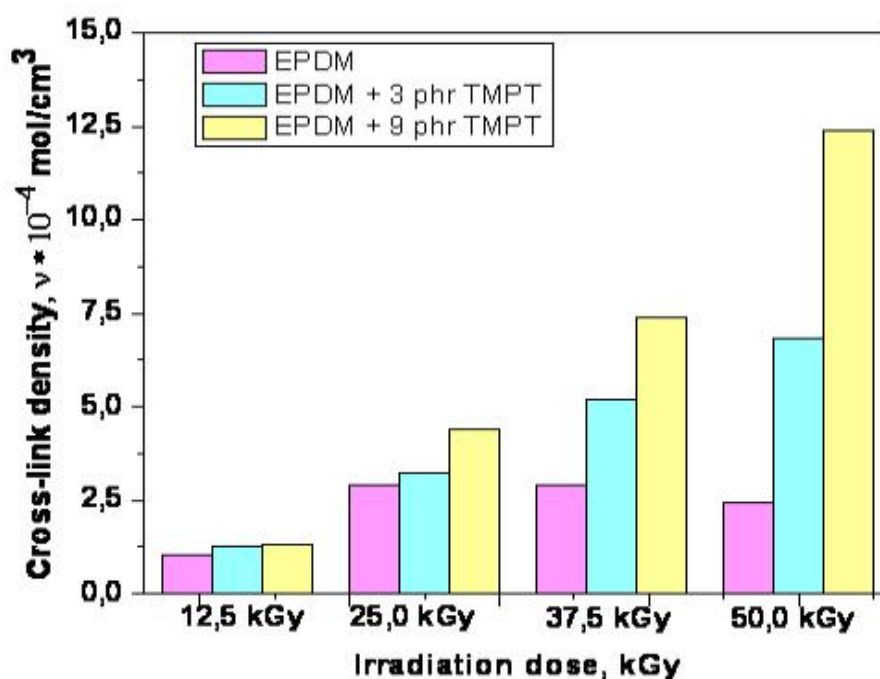


Figure 4. Change of *cross-link density* with irradiation dose for different compositions of EPDM with TMPT (EPDM, EPDM + 3 phr TMPT and EPDM + 9 phr TMPT)

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