

Electron Beam Processing of Ethylene-Propylene-Terpolymer-Based Rubber Mixtures

M. D. Stelescu, E. Manaila, G. Craciun, D. Ighigeanu

Abstract—The goal of the paper is to present the results regarding the influence of the irradiation dose and amount of multifunctional monomer trimethylol-propane trimethacrylate (TMPT) on ethylene-propylene-diene terpolymer rubber (EPDM) mixtures irradiated in electron beam. Blends, molded on an electrically heated laboratory roller mill and compressed in an electrically heated hydraulic press, were irradiated using the ALID 7 of 5.5 MeV linear accelerator in the dose range of 22.6 kGy to 56.5 kGy in atmospheric conditions and at room temperature of 25 °C. The share of cross-linking and degradation reactions was evaluated by means of sol-gel analysis, cross-linking density measurements, FTIR studies and Charlesby-Pinner parameter (p_0/q_0) calculations. The blends containing different concentrations of TMPT (3 phr and 9 phr) and irradiated with doses in the mentioned range have present the increasing of gel content and cross-linking density. Modified and new bands in FTIR spectra have appeared, because of both cross-linking and chain scission reactions.

Keywords—Electron beam irradiation, EPDM rubber, crosslinking density, gel fraction.

I. INTRODUCTION

ELECTRON beam applications are based on different physical action principles: generation of strong local heating (electron beam treatment), Coulomb interaction with electrons in organic and organic materials generating molecular excitation and ionization (chemical processing) or defects (semiconductor treatment) and bremsstrahlung generation (materials inspection) [1]-[3]. When electrons are absorbed in matter, secondary electrons are produced as a result of the energy degradation process. By Coulomb interaction of these electrons with the atoms or molecules of the absorber, finally ions, thermalized electrons, excited states and radicals are formed. Radiation chemical processing as polymerization, crosslinking, grafting and degradation of polymers is based on the generation of chemical reactive species [3].

The way in which polymers behave to radiation depends on several external and internal factors which may be classified into three groups [4]-[6]:

- Intrinsic factors related to physical and chemical properties of polymers, chemical composition, electronic structure of macromolecules, structure, flaws, additives,

etc.

- Conditions in which the irradiation occurs: spectrum type and energy, absorbed dose and dose rate, dynamics of the irradiation action (permanently or in pulses), etc.
- Conditions in which polymer irradiation occurs: temperature, work environment, pressure, electric and magnetic fields, etc.

Interaction of ionizing radiation with the substance occurs at electronic level and is non-specific. An immediate consequence is the breakage of covalent bonds and occurrence of free radicals (transient chemical species), on the main chain (if lateral groups break) or from the main chain (if it breaks itself). The final effect is either crosslinking of the macromolecular ensemble, or the sectioning of the main chain of macromolecules (effect associated with macromolecule degradation) and the reduction of the average molecular weight. Actually the two effects, crosslinking and degradation, coexist and it is necessary to mention the prevalence of one of these. Crosslinking leads to an increase in the molecular weight and possibly the formation of a “closed network” system, while in the case of the degradation process, the molecular weight decreases. As both crosslinking and degradation are caused by the ionization and excitation processes, chemical changes caused by irradiation are therefore directly proportional with the dose of radiation and also depend on radiation intensity [5]-[7].

This article presents our studies on the behaviour of EPDM to irradiation with different electron beam doses. EPDM is known as a rubber with a very low content of non-polar –C=C– bonds, and with properties such as the type of balanced thermal stability, resistance to ageing and to the action of chemicals, good tensile strength [8]. Due to its non-polarity, EPDM elastomer has a good electrical resistivity, remarkable retention properties (even after ageing) as well as resistance to polar solvents such as water, acids, alkaline substances, phosphate esters, and ketones and alcohols [9], [10]. Due to remarkable electrical properties, as well as resistance to ageing and high temperatures, EPDM rubber found more and more applications in the cable insulation industry, in automotive and aerospace industries [8]-[10].

Electron beam irradiation of EPDM leads to both crosslinking and degradation reactions. In order to increase the share of crosslinking reactions to the detriment of degradation reactions, some studies have presented the effectiveness of adding polyfunctional monomers (MPF) into mixtures [10], [11]. This study examines the influence of the amount of multifunctional monomer TMPT on EPDM mixtures processed with electron beam at different irradiation doses in

M. D. Stelescu is with the National Research and Development Institute for Textile and Leather, Division: Leather and Footwear Research Institute, 93, Ion Minulescu St., 031215, Bucharest, Romania (e-mail: dmstelescu@yahoo.com).

E. Manaila, G. Craciun and D. Ighigeanu are with the National Institute for Lasers, Plasma and Radiation Physics, Accelerators Laboratory, 409, Atomistilor St., 077125 Magurele, Romania (e-mail: elena.manaila@infpr.ro, gabriela.craciun@infpr.ro, ighigeanu@yahoo.com).

the range of 22.6 kGy to 56.5 kGy, with a dose rate of 31.4 Gy/s, for 12 to 30 min. To evaluate the share of crosslinking reactions compared to degradation reactions, mixtures were analyzed by sol-gel analysis, crosslinking density measurements and Charlesby-Pinner parameter (p_0/q_0) calculations.

II. EXPERIMENTAL

A. EPDM/TMPT Sample Preparation

The following materials were used: EPDM, Nordel 4760 (Mooney viscosity is 70 ML₁₊₄ at 120 °C, 70% ethylene content, ENB 4.9 Wt %, density 0.88 g/cm³, 10% crystalline degree), antioxidant Irganox 1010 and polyfunctional monomer TMPT, Luvomaxx TMPT DL 75 (22% percentage of ash, pH 9.2, density 1.36 g/cm³, 75 ± 3% active ingredient). Blends were prepared on an electrically heated laboratory roller mill. The blend constituents were added in the following sequences and quantities: 100 phr EPDM, 3 phr TMPT (for EPDM/TMPT 3 phr samples), 9 phr TMPT (for EPDM/TMPT 9 phr samples) and 1 phr Irganox 1010. Process variables were temperature 60-80±5 °C, friction 1:1.1 and total blending time 7 min. Plates required for tests were obtained by compression molded using an electrically heated hydraulic press at a temperature of 120 °C, pressure of 150 MPa and time of 3 min in order to obtain sheets of 11.5x11.5x0.2 cm³.

B. Irradiation Facility

Electron beam (EB) irradiation experiments were carried out using the ALID 7 of 5.5 MeV electron linear accelerator. Mixtures were irradiated under the following conditions: kinetic energy E_c of EB was 5.5 MeV; $I_{EB} = 130$ mA; $P_{EB} = 670$ W (for fixed pulse duration $\tau_{EB} = 3.5$ μs and repetition frequency $f_{EB} = 50$ Hz). Rubber samples of 30x30x2 mm³ were covered with polyethylene foils to minimize the oxidation. The layers of ten sandwiched sheets were irradiated in atmospheric conditions and at room temperature of 25 °C. The dose rate was between 1.5 – 1.9 Gy/min.

C. EPDM/TMPT Sample Characterization

The sol-gel analyses were performed on cross-linked EPDM rubber to determine the mass fraction of insoluble EPDM samples. The samples were weighed and swollen in toluene for 72 h in order to remove any scissioned fragments and unreacted materials. Then they were dried in air for 6 days and in a laboratory oven at 80 °C for 12 h to completely remove the solvent and finally, reweighed. The gel fraction, G_F was calculated as follows:

$$G_F = \frac{W_3}{W_1} \times 100 \quad (1)$$

where, W_3 and W_1 are the weight of the dried sample after swollen and the weight of the sample before swollen, respectively [12], [13]. The reported results were the average of five specimens.

The cross-linking density was determined on the basis of equilibrium solvent-swelling measurements (in toluene at 23-

25 °C) by application of the modified Flory-Rehner equation, given by:

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

where $V_1 = 106.5$ cm³/mol is the molar volume of solvent (toluene), ν_{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 [13], [14]. The results reported were the average of five specimens.

Effect of electron beam radiation on EPDM/TMPT samples. In order to quantitatively evaluate crosslinking and chain scission yields of irradiated samples, we used Charlesby-Pinner equation [15]-[17]:

$$S + \sqrt{S} = \frac{p_0}{q_0} + \frac{1}{\alpha P_n D} \quad (3)$$

where S is the sol fraction ($s = 1$ -gel fraction), p_0 is the degradation density, average number of main chain scissions per monomer unit and per unit dose, q_0 is the crosslinking density, proportion of monomer units crosslinked per unit dose, P_n is the number averaged degree of polymerization, and D is the radiation dose in Gy.

FTIR spectroscopy - changes in the chemical structure of EPDM rubber samples having with different TMPT concentrations and subjected to EB at different irradiation doses were determined using a FTIR spectrophotometer – JASCO FT/IR 4200, by ATR measurement method. Samples spectra are the average of 30 scans realized in absorption in the range of 4,000–600 cm⁻¹, with a resolution of 4 cm⁻¹.

III. RESULTS AND DISCUSSION

A. The Crosslinking Mechanism with Electron Beam of EPDM/TMPT Rubber

The EB irradiation method, applied to EPDM/TMPT rubber, is based on our reported research results [12], [18]-[20] which demonstrated the efficiency of EB curing process. Ionizing radiation stands out by producing excited molecules directly by energy transfer or indirectly by neutralization of formed ions. The main processes in which ions and excited molecules take part have the important result of free radical formation. These processes prove highly effective in terms of chemical action because free radicals are atoms or molecules that contain one or more unpaired electrons, characterized by a high chemical reactivity, available for the formation of a new chemical bond. The chemistry of the process is based on macro-radicals formation from EPDM or TMPT chains (Figs. 1 and 2), which recombine (Fig. 3) causing the structuring [18]-[20].

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

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 [21].

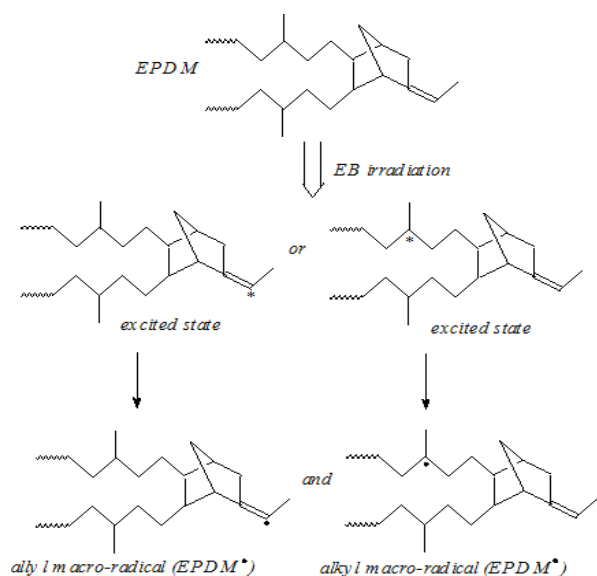


Fig. 1 The scheme of EPDM radicals obtaining by electron beam irradiation

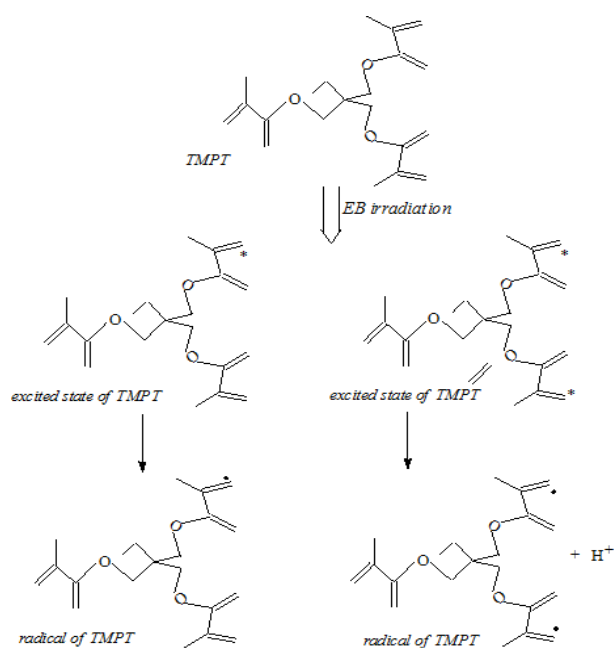


Fig. 2 The scheme of TMPT radicals obtaining by electron beam irradiation

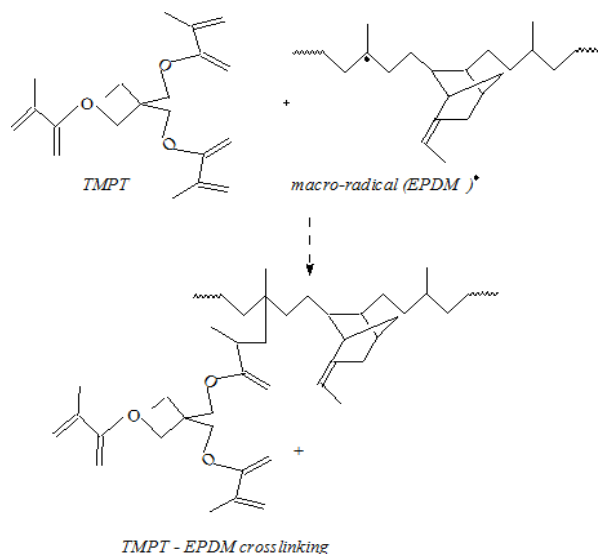


Fig. 3 The scheme of the final product based on EPDM/TMPT obtained by EB crosslinking

B. Sample Characterization

The rubber samples have been irradiated in air, at room temperature for 12, 18, 24 and 30 minutes, with a dose rate of 31.4 Gy/s. It means that irradiation doses were 22.6 kGy, 33.91 kGy, 45.21 kGy and 56.5 kGy, respectively. The crosslinking induced by EB irradiation was evaluated by analyzing the *gel fraction* (crosslinked polymer content) and *cross-link density* (number of crosslinks per unit volume in a polymer network).

For a more precise determination of the two parameters mentioned before, five determinations were achieved on each sample, from pieces cut from different parts of each rubber sample. The tests measurement uncertainty was of ± 0.04 . The results are presented in Table I.

The extent of the crosslinking may be estimated from sol-gel content determination. In our experiments, sol-gel studies revealed a high sensitivity of EPDM and EPDM/TMPT to EB irradiation. The gel content slowly increases with irradiation dose as a result of the induced cross-linking, which occurs through the formation of mainly carbon-carbon bonds [18]-[20]. Also, small differences were observed between the results obtained for EPDM / 3 phr TMPT series and EPDM / 9 phr TMPT series. Similar results were obtained for cross-linking degree.

When polymers are subjected to ionising radiation, crosslinking and main chain scission are usually observed. The processes ultimately cause the formation of an insoluble gel, if crosslinking predominates over scission. In order to evaluate the crosslinking and chain scission yields of irradiated EPDM samples, plots of $S + S^{1/2}$ vs. $1/\text{absorbed dose (D)}$ from the equation 3 (The Charlesby-Pinner equation) were drawn (Fig. 4) [15]-[17]. It is observed that EPDM and EPDM/TMPT blends present linear dependence of $S + S^{1/2}$ with $1/D$ as it was expected from the Charlesby-Pinner equation (3).

TABLE I
CHANGES OF GEL FRACTION (G_f) AND CROSS-LINK DENSITY, $\nu \times 10^{-4}$,
DEPENDING ON THE IRRADIATION DOSE, FOR DIFFERENT SAMPLES
COMPOSITION

| Irradiation time (min) | Absorbed dose* (kGy) | Gel fraction, G_f (%) | | |
|--|-------------------------|-------------------------|--------------------|--------------------|
| | | EPDM | EPDM/TMPT 3 phr | EPDM/TMPT 9 phr |
| 12 | 22.6 | 70.11 | 87.83 | 99.03 |
| 18 | 33.9 | 73.96 | 95.97 | 99.64 |
| 24 | 45.2 | 84.69 | 97.00 | 99.77 |
| 30 | 56.5 | 88.96 | 98.21 | 99.86 |
| Cross-link density, $\nu \times 10^{-4}$ | | | | |
| 12 | 22.6 | 0.3517 | 0.7352 | 1.2704 |
| 18 | 33.9 | 0.4433 | 1.1543 | 1.9378 |
| 24 | 45.2 | 0.5891 | 1.3694 | 2.1825 |
| 30 | 56.5 | 0.6126 | 2.2308 | 2.8444 |

*Note: The absorbed dose (kGy) was calculated as a function of dose rate of 31.4 Gy/s and the mentioned irradiation times

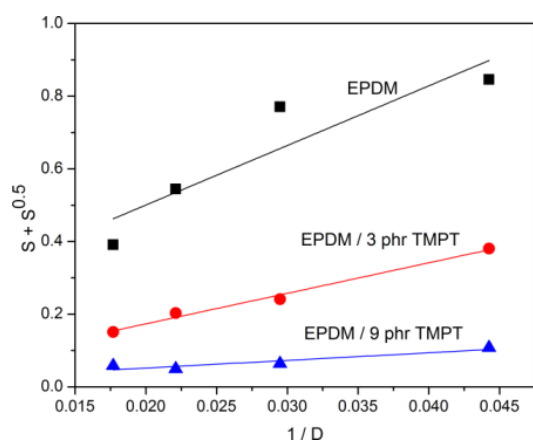


Fig. 4 The Charlesby-Pinner plots for EPDM/TMPT composites

In Table II, the values of p_0/q_0 ratio, involved in Charlesby-Pinner equation are presented. Lower values of p_0/q_0 are suggestive of relatively improved radical-radical interactions in polymers or elastomers, probably due to decrease in free-volume as reported by other workers for similar systems [15]-[17].

Radiation exposure of EPDM and EPDM/TMPT samples

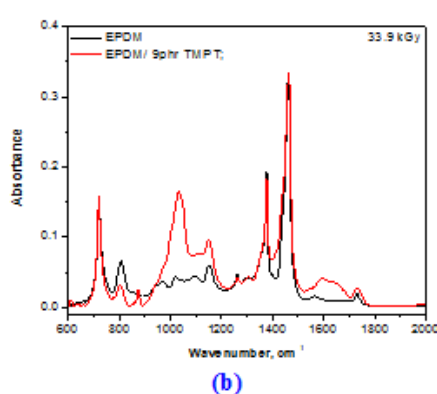
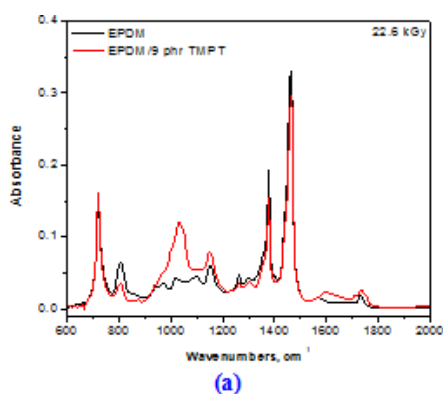
leads to different degree of crosslinking. The best results were obtained for samples of EPDM having 3 phr TMPT, followed by samples of EPDM having 9 phr TMPT and EPDM. During irradiation, it was a competition between the crosslink formation and chain scission in the polymer blend matrix and because p_0/q_0 ratio is very small we can conclude that crosslinking reaction predominates over the degradation reaction and that the irradiation conditions were proper established.

TABLE II
THE COMPOSITIONAL CHARACTERISTICS AND p_0/q_0 RATIO FOR EPDM AND
EPDM/TMPT SAMPLES

| Samples type | p_0/q_0 |
|-----------------|-----------|
| EPDM | 0.17 |
| EPDM/3 phr TMPT | 0.005 |
| EPDM/9 phr TMPT | 0.01 |

Figs. 5 (a)-(d) shows infrared absorption spectra for samples of EPDM and EPDM/ 9 phr TMPT irradiated at different irradiation doses, from 22.6 kGy to 56.5 kGy, with a dose range of 31.4 Gy/s.

ATR FTIR analysis showed that for EPDM, the spectrum is dominated by the specific strong bands at 2920 cm^{-1} , 2851 cm^{-1} which are due to the asymmetric and symmetric stretching frequency of the C-H group (which stems from $-\text{CH}_2-$ bonds in EPDM), a medium band located at 1463 cm^{-1} attributed to deformation frequency of the same methylene groups and a weak band at 720 cm^{-1} (also, for $-\text{CH}_2-$). The bands located in the region of $3000 - 2700\text{ cm}^{-1}$ have not been modified regardless of the presence or absence of polyfunctional monomer. Significant changes were recorded in the region of $1700 - 750\text{ cm}^{-1}$. More than that for EPDM/9 phr TMPT samples irradiated at the highest doses of 45.2 kGy and 55.6 kGy appears a new peak at 1640 cm^{-1} . This peak mainly resulting from C=C stretching of trans-vinylene present in TMPT. Also, IR studies indicate band absorbance in the regions $1750 - 1500\text{ cm}^{-1}$ and $1000 - 1260\text{ cm}^{-1}$ up to 100 kGy and hence increased C=O and C-O-C concentration, which may cause crosslinking as well as chain scission of the EPDM/TMPT rubber [12], [21]-[23].



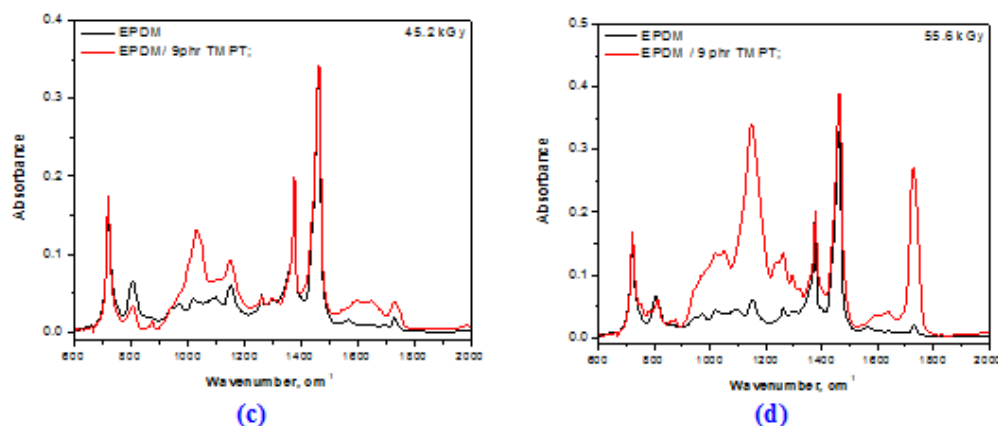


Fig. 5 The infrared spectra in a range of 600-2000 cm^{-1} for EPDM and EPDM / 9 phr TMPT: (a) irradiated at 22.6 kGy; (b) irradiated at 33.9 kGy; (c) irradiated at 45.2 kGy; (d) irradiated at 56.5 kGy

IV. CONCLUSIONS

The variation in gel content and crosslinking density, when different concentrations of TMPT (3 phr or 9 phr) were added to the blend and various irradiation doses (from 22.6 kGy to 56.5 kGy, with a dose range of 31.4 Gy/s) were used, showed increases because of the well-known reactivity of TMPT involved in this study. Its reactivity leads to the bridges formation by radiation-induced free radical mechanism and produces a three-dimensional network structure even at low doses. The best results were obtained for mixtures that contain 9 phr TMPT irradiated at the highest doses of 45.2 kGy and 55.6 kGy. ATR FTIR analysis showed modified and new bands caused by crosslinking and chain scission of the EPDM/TMPT rubber.

ACKNOWLEDGMENT

This work was supported by a grant of the Ministry of National Education and Scientific Research, RDI Programe for Space Technology and Avanced Research - STAR, project number 140/2017.

REFERENCES

- [1] Mondelaers W., "Low-energy electron accelerators in industry and applied research", Nuclear Instrument and Methods in Physics Research B, 1998, 139(1-4), 43-50
- [2] Berejka, A. J., and Cleland, M. R. "Industrial Radiation Processing With Electron Beams and X-rays", IAEA International Atomic Energy Agency, 1 May 2011 – Revision 6
- [3] Mehnert R., "Review of industrial applications of electron accelerators", Nuclear Instrument and Methods in Physics Research B, 1996, 113, 81-87
- [4] E Manaila, M D Stelescu, G Craciun, Chapter 1" Aspects Regarding Radiation Crosslinking of Elastomers", Advanced Elastomers – Technology, Properties and Applications, 2012, Ed. In Tech., Rijeka, Croatia, p. 3-34
- [5] Long Cheng, David R. Kerluke, Radiation for Modification of Polimers, The 2003 Annual Technical Conference of Society Engineering (ANTEC), 2003;
- [6] Milinchuk V.K., Klinshpont E.R., Tupikov V.I., Radiation Stability of Polymer. New Chain Reactions, Intern. Journal Polymeric Mater., 23(3-4), 197 – 206, 1994;
- [7] Milinchuk V.K., Klinshpont E.R., Khimiya vysokikh energij, 25, 483 – 492, 1991;
- [8] K Rajkumar, Chandresh Dwivedi, P Thavamani, P. Jeyanthi, P. Pazhanisamy, Effect Of Nanosilica On Ethylene Propylene Diene Monomer Rubber Nanocomposites, International Journal of Innovative Research & Development, Vol 2 Issue 5, May, 2013, pp. 831-841, www.ijird.com.
- [9] M. Homocianu, A. Airinei, D. M. Stelescu, D.Timpu, A. Ioanid, Morphological Structure and Surface Properties of Maleated Ethylene Propylene Diene Monomer/Organoclay Nanocomposites, *POLYMER COMPOSITES*—2012, DOI 10.1002/pc.22159, Vol 33, issue 3, march 2012, p.379-387
- [10] M. D. Stelescu, E. Manaila, G. Craciun, Vulcanization of ethylene-propylene-terpolymer-based rubber mixtures by radiation processing, *Journal of Applied Polymer Science*, Article first published online: 11 JUL 2012, DOI: 10.1002/app.38231, vol. 128, pp. 2325-2336
- [11] Datta S.K., Pradhan N.K., Chaki T.K., Aging and Chemical Resistance of Crosslinked Ethylene Vinyl Acetate Copolymer, *Kautschuk Gummi Kunststoffe*, 7-8, 554-559, 1997;
- [12] M.D. Stelescu, E. Manaila, D. Martin, G. Craciun, D. Ighigeanu, L. Alexandrescu, New Technologies of grafting and crosslinking rubber blends by electron beam and microwave irradiation, Performantica Publishing House, Iasi, 2011.
- [13] P.J. Flory, J. Rehner, Statistical mechanics of crosslinked polymer networks II. Swelling, *J. Chem. Phys.* 11 (1943) 521-526.
- [14] P. Anelli, S. Baccaro, M. Carenza, G. Palma, Radiation grafting of hydrophilic monomer onto ethylenepropylene rubber, *Rad. Phys. Chem.* 46 (1995) 1031-1035.
- [15] A. Charlesby, Gel formation and molecular weight distribution in long-chain polymers, *Proc. Royal Soc. London*, A222 (1954) 542-557.
- [16] A. Charlesby, S.H. Pinner, Analysis of the solubility behaviour of irradiated polyethylene and other polymers, *Proc. Royal Soc. London*, 249A (1959) 367-386.
- [17] Charlesby A.: Atomic radiation and polymers. Pergamon Press, New York (1960).
- [18] Banik I., Bhowmick A.K. Effect of Electron Beam Irradiation on the properties of cross-linked rubbers. *Radiation Physics and Chemistry*. 2000; 58:293-298.
- [19] Bhattacharya A. Radiation and Industrial Polymers. *Progress in Polymer Science*. 2000; 25:371-401.
- [20] Bhowmick A. K., Vijayabaskar V. Electron beam curing of elastomers. *Rubber Chemistry and Technology*. 2006; 79(3):402-428.
- [21] Stelescu M.D., Manaila E., Craciun G., Zuga N. Crosslinking and grafting ethylene vinyl acetate copolymer with accelerated electrons in the presence of polyfunctional monomers, *Polymer Bulletin*. 2012; 68(1):263-285.
- [22] Zaharescu T., Setnescu R., Jipa S., Setnescu T. Radiation processing of polyolefin blends. I. Crosslinking of EPDM-PP blends. *Journal of Applied Polymer Science*. 2000; 77(5):982-987.
- [23] Chowdhury R., Banerji M.S. Electron beam irradiation of ethylene-propylene terpolymer: Evaluation of trimethylol propane trimethacrylate as a crosslink promoter. *Journal of Applied Polymer Science*. 2005; 97(3):968-975.