

MODIFICATION OF UV CURED POLYACRYLATE RUBBER THROUGH ELECTRON BEAM IRRADIATION

Demetrio Jackson dos Santos, demetrio.santos@poli.usp.br

Lab. de Engenharia de Fabricação – Dept. Eng. Mecatronica e de Sistemas Mecânicos –EPUSP - Av. Prof. Mello Moraes, 2231 – Cidade Universitária – 05508.970 – São Paulo – SP – Brasil

Gilmar Ferreira Batalha, gilmar.batalha@poli.usp.br

Lab. de Engenharia de Fabricação – Dept. Eng. Mecatronica e de Sistemas Mecânicos –EPUSP - Av. Prof. Mello Moraes, 2231 – Cidade Universitária – 05508.970 – São Paulo – SP – Brasil

Abstract. *In this paper, the structural changes of an UV curing polyacrylate rubber (ACM), caused by different doses of electron beam irradiations, were investigated with the help of uniaxial stretching test and infrared spectroscopy in the attenuated total reflectance modes. The irradiation was carried out by the Institut of Energetic and Nuclear Researchs (IPEN) at three different irradiation levels: 20 kGy, 50 kGy and 100 kGy. The mechanical results shown an increase of the strenght and a decrease in the elongation by increasing the irradiation dose, the more relevant changes occurred with the 100 kGy dose. Variation of specific absorbance values indicated changes in the polymer structure. The rubber property improvements, through EB irradiation, indicated a possibility to use irradiation with the purpose to increase some rubber properties in industrial applications.*

Keywords: *polyacrylate, EB irradiation, acrylic rubber*

1. INTRODUCTION

Elastomers are applied in a wide range of industrial areas, like solid gaskets, seals, tires, hose and shock absorbers. Acrylic rubber (ACM) is a synthetic, non-crystalline elastomer, which presents high oil and heat resistance when vulcanized. Due its high performance in these conditions, ACM is largely used to produce solid gasket, applied on the automobile industry. ACM is usually vulcanized by thermo-chemical vulcanization methods.

Recently, a liquid acrylic rubber technology was developed, what contains an UV sensitive cure monomer. This new technology makes possible to apply the rubber, in a liquid form and to cure it after the application, using a traditional UV curing process, ideal for potting or special gasket applications.

Recently many authors have presented electron beam (EB) radiation as an alternative for rubber vulcanization, or for modification of vulcanized rubber properties, mainly in special applications. Banik et al. (2000) investigated the effects of EB radiation on vulcanized FKM, NR, EPDM and NBR, in all cases the modulus increased and the elongation at break decreased with an increase on the irradiation dose.

According to Zagórski (2004) the radiation chemistry of elastomer (HNBR) has common features to the radiation chemistry of PE: (i) Ionizing radiation interacts statistically with outer sphere electrons, no matter what compound in the system they belong to. (ii) Most of the energy appears as single ionization spurs, the remaining 20% is located in multi-ionization spurs.

In practice, the irradiated elastomer can present two different behaviors: (i) An increase in some mechanical properties, caused by an increase in the elastomer crosslinking level. (ii) A kind of elastomer degradation, caused by excessive multi-ionization spurs, or chain scission, in a specific small volume of material.

In this work the effects of EB radiation on the ACM material, cured by UV radiation, were investigated, in order to verify the mechanical and structural changes caused by such radiation. Uniaxial tension tests, infrared spectroscopy and scanning electron microscopy (SEM) were used to make this investigation possible.

The improvement of ACM mechanical properties through EB radiation can create some new industrial applications for this kind of radiation and solve some industrial application problems, due any possible limitation in the mechanical behavior of acrylic rubber, chemical or cured by UV.

2. EXPERIMENTAL

2.1. Materials

The UV cured ACM dumbbell specimens were obtained according to the ASTM 412 – 6a standard and were supplied by an european adhesive company. The shape and dimensions of these specimens conform to the Die C of the presented standard.

The samples were irradiated in air at room temperature of $25^{\circ} \pm 2^{\circ}\text{C}$ at the Instituto de Pesquisas Energéticas e Nucleares (Institut of Nuclear and Energetic Research), São Paulo. Irradiation doses of 20, 50 and 100 kGy were applied.

2.2. Mechanical properties

Tensile specimens were obtained from an UV cured sheet, conform to the ASTM Die C. The tests were carried out according to the same standard, using an universal testing machine (EMIC 5000), at a crosshead displacement of 500 mm/min and 25°C, at the Loctite Engineering Center Brazil.

2.2. Infrared spectroscopy - Attenuated total reflectance

ATR spectra of the ACM sheets in the different conditions, without irradiation and with three irradiation doses, were taken using a Spectrum One FT-IR Perkin Elmer spectroscope, the ATR method (Attenuated Total Reflectance) was used. Two different regions of the samples were analyzed, surface and the middle region, in order to verify the chemical groups present in both regions.

The spectra were obtained by absorbance, which offers a linear rate between the peaks and the functional group contents in the regions, according to the Lambert-Beer Law.

Table 1. Peak positions and assignment of peaks in the infrared spectra of ACM rubbers.

Wave number (cm ⁻¹)	Chemical Group
2980	-CH stretching vibration of O-CH ₂ -CH ₃
2926	-CH ₂ stretching vibration of O-CH ₂ -CH ₃
1740	>C=O
1632	>C=C<
1378	-CH ₃ deformation of O-CH ₂ -CH ₃
1160	C-O-C stretching
1153	R-CO-R symmetric deformation
851	C-O-C deformation

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Three samples of each condition were tested, below follow the strength x displacement curves of such conditions:

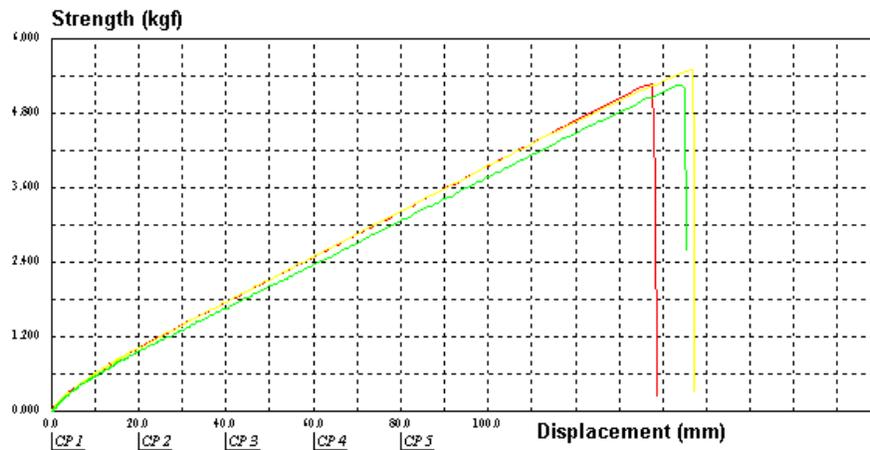


Figure 1. Strength x displacement curves of non EB irradiated samples.

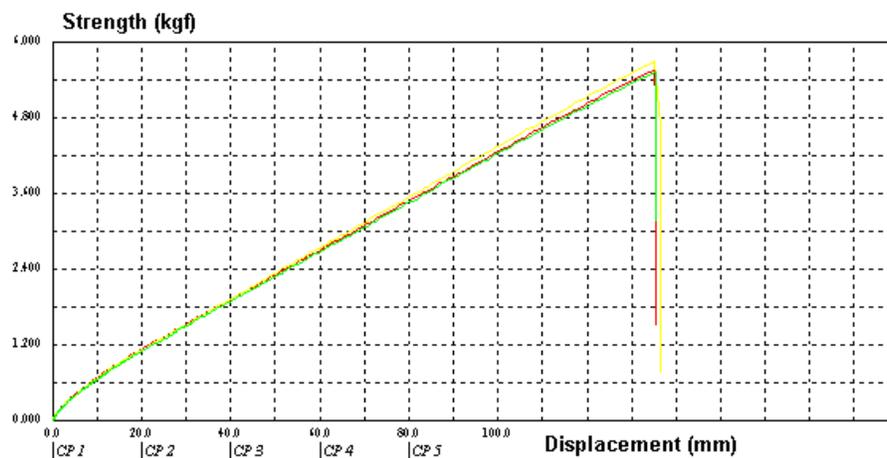


Figure 2. Strength x displacement curves of EB irradiated samples with dose of 20 kGy.

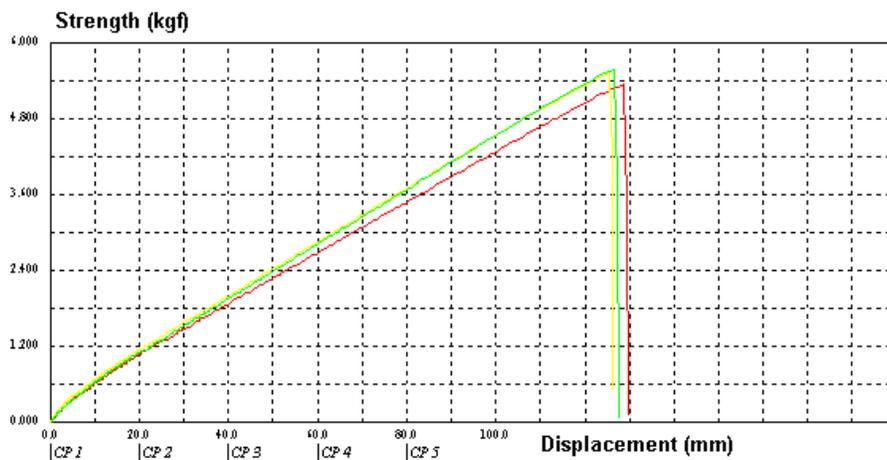


Figure 3. Strength x displacement curves of EB irradiated samples with dose of 50 kGy.

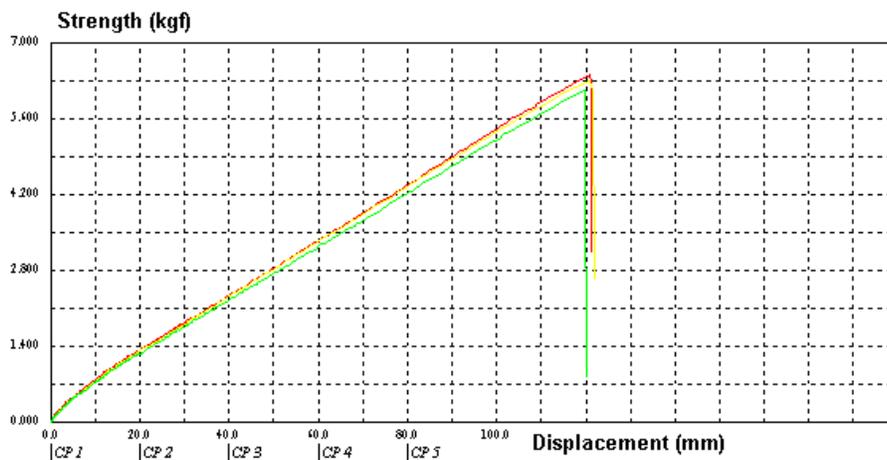


Figure 4. Strength x displacement curves of EB irradiated samples with dose of 100 kGy.

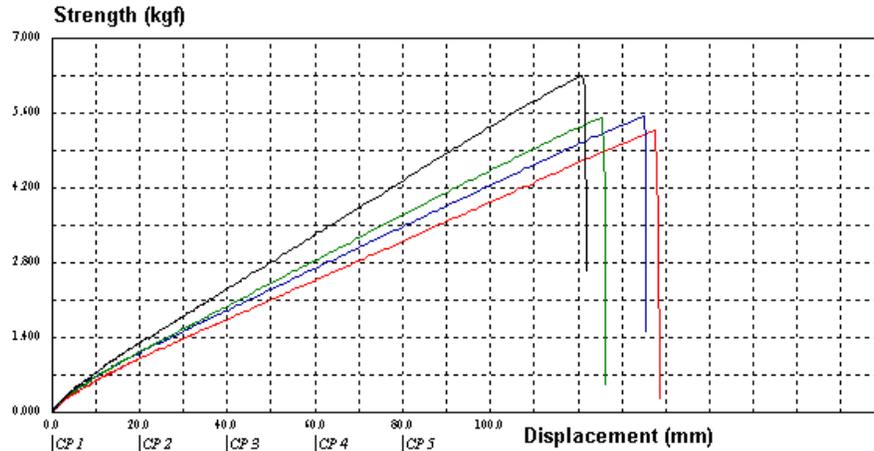


Figure 5. Average curve of each irradiation dose: 0 kGy (red), 20 kGy (blue), 50 kGy (green) and 100 kGy (black).

Figure 5 shows that the tensile strength increases with an increase in the irradiation dose. This change is mainly observed comparing the 0 kGy with 100 kGy conditions. The other two conditions show a light tensile strength at break increase in comparison to the non irradiated samples. According to the literature, there is a maximum level of tensile strength increase for ACM modified by EB. This indicates that can exist also a maximum level for the UV cured ACM, after that the tensile strength would decrease. Higher irradiation doses should to be applied to UV cured ACM in order to be able to determine this maximum level, in case it exists. In an opposite way, the elongation decreases with an increase in the irradiation dose. The decrease in the polymer elongation shows a network structure formation, it means, an increase in the polymer crosslinking level.

For small deformation, the traditional elasticity theory can be used to describe the mechanical behavior of elastomers, based on materials constants obtained through the equations below:

$$P = K \left(\frac{\Delta V}{V_0} \right) \quad (1)$$

$$\text{Where } G = \frac{\tau}{\gamma} \quad (2)$$

Where:

P: applied hydrostatic pressure;

K: module of compression;

V_0 : initial volume;

ΔV : volume variation.

For large deformations, elongations superior to 25%, non linear elasticity theories are applied to describe the mechanical behavior of elastomers. Many models are available to describe such behavior of elastomers, like Ogden, Gent and Arruda Boyce Models. A simple uniaxial test is not enough for characterizing the material properties, but if only this kind of test is available, the Arruda-Boyce Model is suggested. For an accurate characterizing of elastomer properties, three kind of mechanical tests are required, uniaxial, equibiaxial and pure shear tests, applying the results in the models like Gent or Ogden Model. The Equation 3 presents the Ogden Model.

$$W(\lambda_1, \lambda_2, \lambda_3) = \sum_{p=1}^{N_{\infty}} \frac{\mu_p}{\alpha_p} (\lambda_1^{\alpha_p} + \lambda_2^{\alpha_p} + \lambda_3^{\alpha_p} - 3) \quad (3)$$

Where:

W: Strain energy density;

λ_1, λ_2 and λ_3 : extension rates;

μ and α : material constants.

3.2. Infrared spectroscopy

The infrared spectroscopy shows different chemical group contents in the analyzed regions, surface and middle region. The main important changes were detected after to apply 100 kGy irradiation dose. The EB causes a decrease on the level of $>C=O$ (1740 cm^{-1}), $>C=C<$ (1632 cm^{-1}) and $C-O-C$ (1160 cm^{-1}) groups on the surface, by all applied doses. In the middle of the samples, the irradiation caused the opposite changes, all group intents increased with an increase in the irradiation dose. Such behavior may be explained by the differences cure schemes obtained through UV cure, it means, the polymer structure on the surface have some differences in comparison to the middle of the sample. The structure changes caused by the EB, are illustrated by the Figure 6, 7 and 8, were some chemical reactions are presented.

The Figure 7 shows the oxidation reaction, usually present on the material surface because of the presence of oxygen in the ambient during the irradiation. The Table 2 shows an increase in the $C=O$ group level in the middle of the samples after irradiation, it can be explained by the presence of small air bubbles in the analyzed materials. In this reaction, the radiation causes a hydrogen release, creating a radical which reacts with oxygen present in the air, generating a new $C=O$ group.

Table 2. Absorbance at 1160 , 1632 and 1740 cm^{-1} at surface and middle region.

Samples	1740 cm^{-1}	1632 cm^{-1}	1160 cm^{-1}
	H	H	H
No Irradiation _ Surface	0,3607	0,0531	0,1534
20 kGy _ Surface	0,3547	0,0557	0,1481
50 kGy _ Surface	0,3396	0,0582	0,1348
100 kGy _ Surface	0,3426	0,0429	0,1441
No Irradiation _ Middle	0,2638	0,0989	0,1057
20 kGy _ Middle	0,3002	0,1054	0,1193
50 kGy _ Middle	0,2942	0,1041	0,1168
100 kGy _ Middle	0,3068	0,1072	0,1198

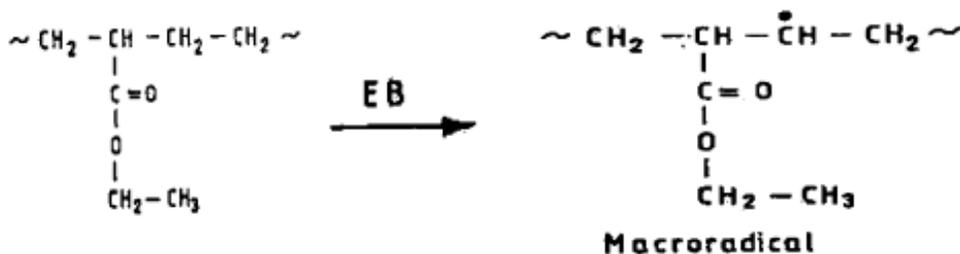


Figura 6 – Macroradical formation through EB (Vijayabaskar, 2004).

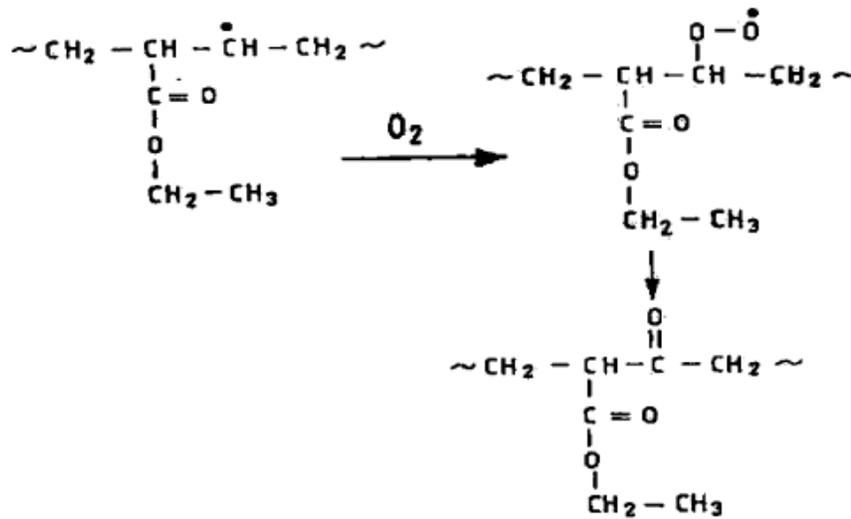


Figure 7 – ACM elastomer oxidation caused by EB radiation (Vijayabaskar, 2004).

The first part of Figure 8 presents a possible reaction, or chain scission, which can be responsible for polymer degradation if the formed macroradicals react with released hydrogen or other low molecular weight formed macroradical. In the reaction presented by the Figure 8, the formed macroradical reacts initially with oxygen, then with hydrogen and finally the two formed macroradicals react forming an C-O-C group. The Table 2 shows a decrease of this group level at the surface after irradiation and a increase in the level of such group in the middle of the irradiated material.

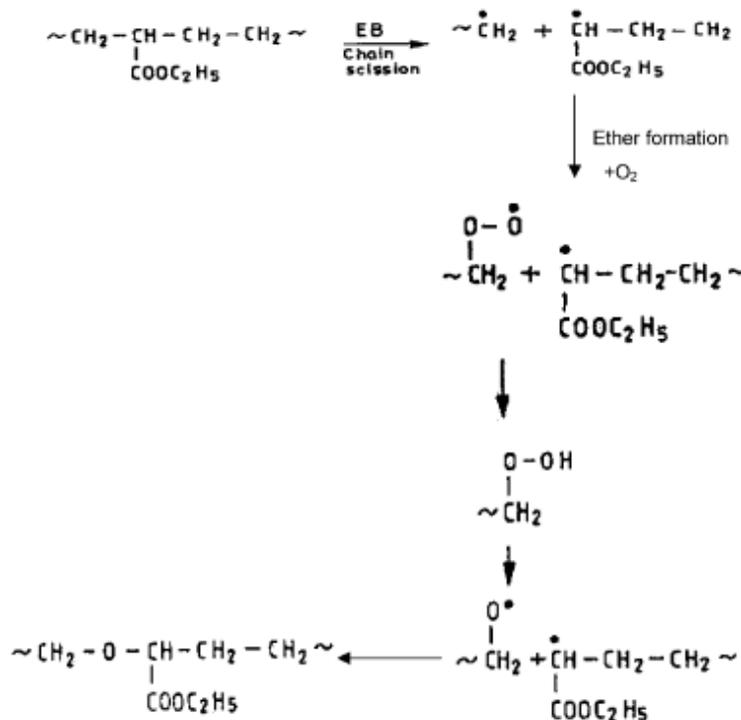


Figura 8 – Chemical group C-O-C obtained through EB in ACM (Vijayabaskar, 2004).

4. CONCLUSIONS

The EB radiation causes structural changes and consequently mechanical property changes on UV cured acrylic rubber.

Chemical group changes occur in different levels on surface and in the middle region of the sample. Many reaction types occurs at the same time, like oxidation, chain scission and recombination with C-O-C formation.

An increase of the irradiation dose results an increase of the tensile strength at break higher than 15%, for a 100 kGy dose. The increase of the irradiation dose causes a decrease of the elongation at break. The changes are valide for doses up to 100 kGy. The changes are not linear to the radiation dose.

Irradiation needs additional costs, but can be a solution for improvement of rubbers applied on special applications.

5. ACKNOWLEDGEMENTS

The authors are grateful to Instituto de Pesquisas Energéticas e Nucleares (IPEN), for experimental assistance with irradiation processing, mainly to Mr. José Mauro Vieira and Mr. Wilson Calvo.

We would like to thank Mr. Guilherme Andrade for believing on this project and for keeping us motivated during this process.

6. REFERENCES

- Banik, I. & Bhowmick, A. K. Effect of electron beam irradiation on the properties of crosslinked rubbers. *Radiation Physics and Chemistry*, v. 58, p. 293 – 298. 2000.
- Bernardi, B. A.; Langley, M. W. & MANLEY, P. E. An Introduction to Polycrylate Elastomers. In: Rubber Division Meeting of the American Chemical Society, April, 1999, Chicago. Paper n° PA0910.1.
- Bik, J.; Gluszewski, W.; Rzymiski, W. M.; & Zagórski, Z. K. EB radiation crosslinking of elastomer. *Radiation Physics and Chemistry*, v. 67, p. 421 – 423. 2003.
- Boulenouar, A. & Mazari, M. Characterization of Elastomer Fracture Behavior by Energetic Parameters. *Computational Materials Science*, 2008. No prelo.
- Chen, J.; Czayka, M.; & Uribe, R. M. Effects of electron beam irradiations on the struture and mechanical properties of polycarbonate. *Radiation Physics and Chemistry*, v. 74, p. 31 – 35. 2005.
- Estados Unidos. Vanderbilt Company, Inc. *The Vanderbilt Rubber Handbook*. 3rd ed. Vanderbilt Company, 1990. 832 p.
- Gent, A. N. Elastic Instabilities in Rubber. *International Journal of Non-Linear Mechanics*, v. 40, p. 165 – 175, 2005.
- Harper, C. A. *Handbook of Plastics, Elastomers, and Composites*. 4th ed. New York: McGraw Hill, 2002. 884 p.
- Hofmann, W. *Rubber Technology Handbook*. Muenchen: Hanser, 1996. 611 p.
- Koenig, J. L. *Microspectroscopic Imaging of Polymers*. Washington, DC: American Chemical Society, 1997. 411 p.
- Manas, D.; Manas, M.; Stanek, M.; & Danek, M. Improvement of Plastic Properties. *Archives of Materials Science and Engineering*, v. 32, p. 69 – 76, Aug. 2008.
- Mishra, J. K.; Chang, Y.W.; Lee, B. C & Ryu, S. H. Mechanical properties and heat shrinkability of electron beam crosslinked polyethylene-octene copolymer. *Radiation Physics and Chemistry*, v. 77, p. 675 – 679. 2008.
- Rosário, S. C. Estudo do efeito da radiação ionizante por feixe de elétrons sobre o polietileno de ultra alto peso molecular virgem e reciclado industrial. 2006. 62 p. Dissertação (mestrado). Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 2006.
- Salgueiro, W.; Somozaa, A.; Marzocca, A. J.; Consolati, G.; & Quasso, F. Evolution of crosslinking structure in the elastomer NR and SBR. *Radiation Physics and Chemistry*, v. 76, p. 142 – 145. 2007.
- Sengupta, R.; Tikku, V.K.; Somani, A. W.; Chaku, T. K.; & Bhowmick, A. K. Electron beam irradiated polyamide 6-6 films – I: characterization wide angle X-Ray scattering and Infrared spectroscopy. *Radiation Physics and Chemistry*, v. 72, p. 625 – 633. 2005.
- Vijayabaskar, V.; Bhattacharya, S.; Tikku, V.K & Bhowmick, A. K. Electron beam initiated modification of acrylic elastomer in presence of polyfunctional monomers. *Radiation Physics and Chemistry*, v. 71, p. 1045 – 1058. 2004.
- Zagórski, Z. P. EB – crosslinking of elastomers, how does it compare with radiation crosslinking of other polymers. *Radiation Physics and Chemistry*, v. 71, p. 261 – 265. 2004.

5. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.