

## CROSSLINKING AND GRAFTING THE NATURAL RUBBER BY MEANS OF ACCELERATED ELECTRONS IN THE PRESENCE OF TRIMETHYLOL-PROPANE TRIMETHACRYLATE (TMPT)

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*În această lucrare s-a studiat influența concentrației de trimetilolpropan trimetacrilat (TMPT) și a dozei de iradiere cu electroni accelerati, asupra proprietăților fizico-mecanice ale amestecului de cauciuc natural (NR). S-a observat că prin creșterea concentrației de TMPT și a dozei de iradiere, are loc creșterea durătății, a modulului de elasticitate 100%, a rezistenței la rupere și a rezistenței la sfâșiere, precum și scăderea alungirii la rupere și a alungirii remanente. Amestecurile de cauciuc natural care conțin 6 phr și respectiv 9 phr TMPT, iradiate la 15 Mrad și respectiv 20 Mrad, prezintă proprietăți fizico-mecanice superioare celor ale amestecului martor (obținut prin metoda de vulcanizare clasică).*

*In this work the influences of the trimethylol-propane trimethacrylate (TMPT) percentage and accelerated electron irradiation dose on the physical-mechanical characteristics of the natural rubber (NR) blend were investigated. The increase in the hardness, 100 % elastic modulus, tensile strength and tear strength, as well as decreases in elongation at break and elongation set with content TMPT and irradiation dose have been revealed. The NR blends containing 6 phr and 9 phr of TMPT, respectively, each irradiated with 20 Mrad, have physical-mechanical properties which are superior to the standard blend obtained by a classical crosslinking.*

**Keywords:** natural rubber, accelerated electron irradiation, trimethylol-propane trimethacrylate.

### 1. Introduction

The radiation induced grafting and crosslinking of polymers are new techniques applied in modifying polymers. The use of radiations as power source is justified by the limited classic resources, on the one hand, and by a number of specific benefits, on the other hand, such as: (1) removing the curing agents, (2)

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obtaining new high purity materials, (3) a fast process which enables an accurate monitoring, (4) an effective and uniform curing the whole rubber body because of the high penetrating ability of radiation, (5) lack of wastes [1-15].

Some recent studies [3,4,7] have revealed that the application of the multifunctional monomers in irradiation induced recycling of elastomers has led to an increased effectiveness of the irradiation induced crosslinking resulting in the shorter irradiation time and the lower dose. Also, the improved physical-mechanical characteristics, accelerated ageing resistance and fastness to chemicals and a minimization of macromolecular chain splitting reactions are performed.

In our experiments, the natural rubber blends were grafted and crosslinked by means of the accelerated electrons in the presence of a multifunctional monomer - trimethylol-propane trimethacrylate (TMPT). The influences of the trimethylol-propane trimethacrylate (TMPT) percentage and the accelerated electron irradiation dose on the physical-mechanical characteristics of the natural rubber (NR) blends were investigated.

## 2. Experimental Part

The used materials were: natural rubber Crep 1X (NR), trimethylol-propane trimethacrylate TMPT DL 75 (TMPT), precipitated silica Ultrasil VN3, zinc oxide, stearic acid, polyethylene glycol, antioxidantizing agent Irganox 1010, and benzoyl peroxide Perkadox 14-40B-GR as curing agent for the control blend.

Natural rubber blends containing 0, 3, 6 and 9 phr of TMPT were prepared by blending on a laboratory roller mill. From these, blends samples in a shape of plates were obtained by means of hydraulic press at 150 MPa and 100°C. The resulted plates were treated by irradiation.

The accelerated electrons exposure experiments were carried out using an experimental arrangement consisting mainly of the following units: an electron linear accelerator of 6.23 MeV and 75 mA (ALIN-10) and an irradiation chamber. The accelerated electrons dose rate was established to 2.4 kGy/min in order to accumulate 50 kGy, 100 kGy, 150 kGy and 200 kGy with a variety of accelerated electron doses (5, 10, 15 and 20 Mrad) by means of a betatron.

The control blend was obtained with benzoyl peroxide as curing agent. The blend was prepared on a laboratory roller mill and the control sample curing was accomplished on hydraulic press at 160°C. The best curing time (12'30") was determined using a Monsanto Rheometer.

The characteristics of samples were assessed by test methods according to standards in force in the field (SR ISO 7619/2001, SR ISO 37/1997, SR ISO 34-1/2000, 1817/2000).

### 3. Results and Discussions

Figs. 1-6 illustrate the changes in physical-mechanical characteristics depending on the TMPT percentage in the blend and irradiation dose. From these Figs. the following influences can be evidenced:

- Hardness (Fig. 1) increases as the irradiation dose and TMPT percentage increase; the hardness values for the blends with 6 and 9 phr of TMPT each irradiated at 15 and 20 Mrad are similar to those of the control blend (83°ShA);

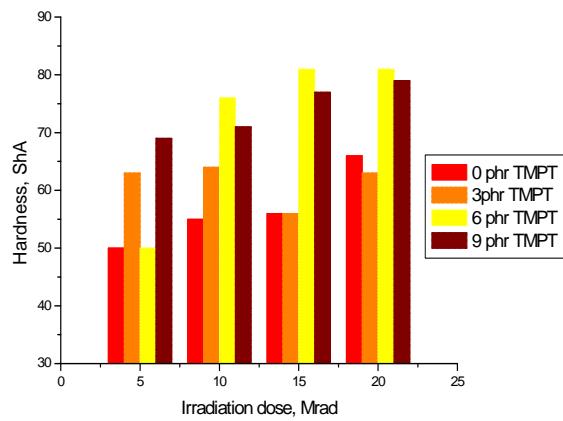


Figure 1 Changes in hardness versus the irradiation dose and TMPT percentage

- Elastic modulus at 100 % elongation (Fig. 2) for the blends with 6 and 9 phr TMPT at an irradiation dose of 20 Mrad shows a higher value than 100 % elastic modulus for the control sample (4,6 N/mm<sup>2</sup>);

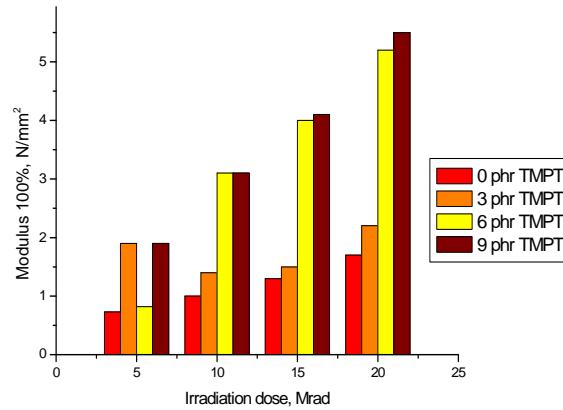


Figure 2 Changes in modulus 100% versus the irradiation dose and TMPT percentage

- Tensile strength (Fig. 3) for the samples from blends with 6 and 9 phr TMPT, irradiated by means of accelerated electrons shows higher values than for the control sample ( $10,3 \text{ N/mm}^2$ ), even at an irradiation dose of 10 Mrad;

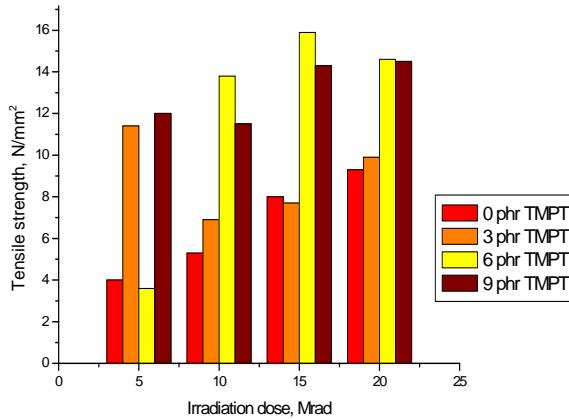


Figure 3 Changes in tensile strength versus the irradiation dose and TMPT percentage

- Values of the elongation at break (Fig. 4) for the samples irradiated with accelerated electrons are higher than those for the control sample (246 %). This aspect decreases as the irradiation dose and TMPT percentage increase;

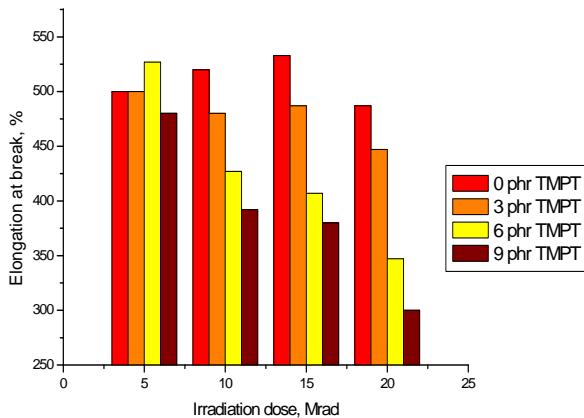


Figure 4 Changes in elongation at break versus the irradiation dose and TMPT percentage

- Elongation set (Fig. 5) decreases as the irradiation dose and TMPT percentage increases for the blends with 6 and 9 phr of TMPT irradiated with 15 and 20 Mrad, the elongation set values are lower than those for the control sample (14,6 %), revealing a high crosslinking level.

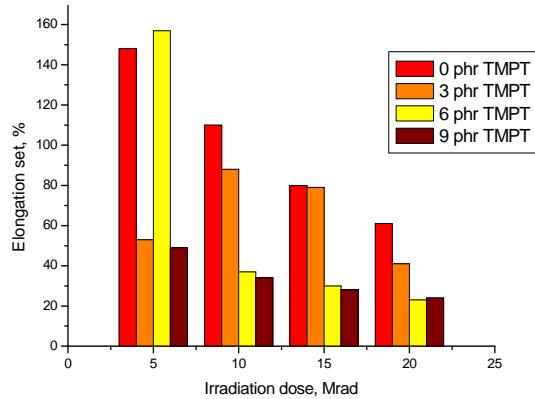


Figure 5 Changes in elongation set versus the irradiation dose and TMPT percentage

- Tear strength (Fig. 6) for the samples from the blends irradiated with accelerated electrons shows higher values than those for the control sample (14,6 N/mm);

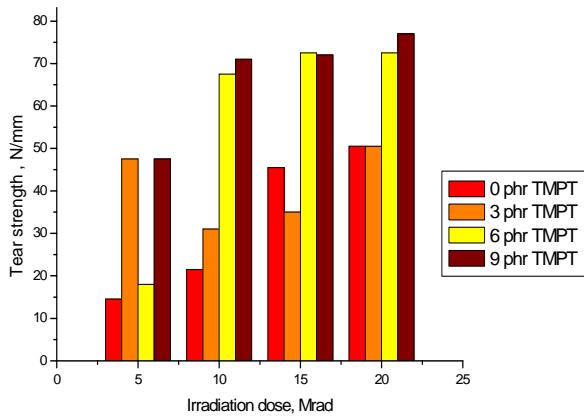


Figure 6 Changes in tear strength versus the irradiation dose and TMPT percentage

#### 4. Conclusions

As a conclusion, the natural rubber blends containing 6 and 9 phr of TMPT irradiated each of them at 20 Mrad have shown higher physical-mechanical characteristics than those for the control sample (obtained by curing with peroxide at 160°C). This proves the advantages of a new processing technique for the NR blends resulting in 10 times shorter curing time, removing the curing agents, and lack of wastes.

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