

RADIATION VULCANIZATION OF NATURAL RUBBER USING TMPT AS POLYFUNCTIONAL MONOMER

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In our study, the effect of trimethylpropane trimethacrylate (TMPT) as polyfunctional monomer on radiation vulcanization (electron beam, EA) of natural rubber (NR) was evaluated. Gel fraction, crosslink density and FTIR of the natural rubber/TMPT samples have been investigated as a function of absorbed dose. The dependence of gel fraction and crosslink density on irradiation dose was determined from in the dose range of 100 to 250 kGy. The results showed an increase in gel fraction and crosslink density due to the introduction of TMPT.

Keywords: natural rubber, electron beam, trimethylpropane trimethacrylate, gel fraction, crosslink density, FTIR

INTRODUCTION

Natural rubber is a high molecular weight polymer of isoprene in which essentially all the isoprene's have the cis 1-4 configuration. Since it is of biological origin, it is renewable, inexpensive and creates no health hazard problems. NR is an interesting material with commercial success due to its excellent physical properties, especially high mechanical strength, low heat build-up, excellent flexibility, and resistance to impact and tear, and above all its renewability (Daniel *et al.*, 2005). The most important stage in the rubber processing technology is vulcanization/crosslinking. During 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. This is normally done by sulphur and accelerator for general purpose rubbers. The vulcanisation of natural rubber (NR) by sulphur in presence of organic accelerator is a complicated process (Steleescu *et al.*, 2011, Gonzalez *et al.*, 2005). The mechanism of vulcanization and its acceleration depends on the structure of the rubber, type and concentration of accelerators and activators (zinc oxide and fatty acid) and on the thermodynamics of each particular reaction. Vulcanization with peroxides is done by radical mechanism when bonds are formed 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. Besides the conventional techniques, crosslinking of NR can also be achieved by means of *high energy radiation*. This technology has been studied for a long time. Radiation can produce crosslink densities like those obtained by sulfur curing, but the net effects, while similar, are not identical. The type of crosslink formed in this method (–C–C–) give rise to better mechanical properties at higher temperature. 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 (MGM Rubber Company-Research and Development, 2007). 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 (Vijayabaskar & Bhowmick, 2005; Yasin *et al.*, 2005) could be used to obtain desired rubber physical properties at lower irradiation doses (Hafezi *et al.*, 2006). Co-agents are multi-functional organic molecules which are highly reactive towards free radicals (Alvarez Grima, 2007). They are used as reactive additives to boost the vulcanization efficiency (Endstra, 1990).

In our study, the effect of trimethylopropane trimethacrylate (TMPT) as polyfunctional monomer in radiation vulcanization (electron beam, EB) of natural rubber (NR) was evaluated. Gel fraction, crosslink density and FTIR of the samples have been investigated as a function of absorbed dose. The dependence of gel fraction and crosslink density on irradiation dose was determined in a dose range of 100 to 250 kGy.

EXPERIMENTAL

Materials

All the raw materials: natural rubber Crep 1X (Mooney viscosity is 74 ML₁₊₄ at 100°C, 0.32% volatile materials content, 0.38% nitrogen content, 0.22% percentage of ash, 0.021% impurities content), pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate Irganox 1010, and polyfunctional monomer trimethylopropane-trimethacrylate Luvomaxx TMPT DL 75 (22% percentage of ash, pH 9.2, density 1.36 g /cm³, 75 ± 3 % active ingredient), were used directly without purification.

Sample Preparation

Blends were prepared on an electrically heated laboratory roller mill. For preparation of NR with TMPT, the blend constituents were added in the following sequence and amounts: 100 phr NR and 3 phr TMPT. Process variables: temperature 25-50 ±5°C, friction 1:1.1, and total blending time 5 min. Plates required for physico-chemical tests were obtained by pressing in a hydraulic press at 110 ±5°C and 150 MPa.

Experimental Installations and Sample Irradiation

EB irradiation experiments were carried out with an electron linear accelerator of 6.23 MeV and 75 mA (ALIN-10). The optimum values of the EB peak current I_{EB} and EB energy E_{EB} to produce maximum output power P_{EB} for a fixed pulse duration τ_{EB} and repetition frequency f_{EB} are as follows: $E_{EB} = 6.23$ MeV; $I_{EB} = 75$ mA; $P_{EB} = 164$ W ($f_{EB} = 100$ Hz, $\tau_{EB} = 3.5$ μ s). The EB effects are related to the absorbed dose (D) expressed in Gray or J kg⁻¹ and absorbed dose rate (D*) expressed in Gy s⁻¹ or J kg⁻¹ s⁻¹. For EB treatments, the rubber sheets were cut in rectangular shapes of 0.1 x 0.03 m² and

covered with polyethylene foils to minimize oxidation. Sandwiches consisting of ten layers of material were irradiated in atmospheric conditions and at room temperature of 25°C.

Laboratory Tests

The sol-gel analysis was performed on crosslinked NR/TMPT samples to determine the mass fraction of insoluble NR (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, then dried in an oven for 12 h at 80°C to completely remove the solvent 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 (Stelescu, 2010).

The crosslink density (ν) 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, then dried in an oven for 12 h at 80°C to completely remove the solvent and reweighed. Finally, the samples were weighed for the last time (m_s), and volume fractions of polymer in the samples at equilibrium swelling ν_{2m} were determined from swelling ratio G as follows:

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

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

where: ρ_e and ρ_s are the densities of elastomer samples and solvent (0.866 g/cm³ for toluene), respectively.

The samples crosslink densities, ν , were determined from measurements in a solvent, using the Flory-Rehner relationship:

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

where V_1 is the molar volume of solvent (106.5 cm³/mol for toluene), ν_{2m} is the volume fraction of polymer in the sample at equilibrium swelling, and χ_{12} is the Flory-Huggins polymer-solvent interaction term (the values of χ_{12} are 0.393 for toluene (Lopez-Manchado *et al.*, 2003; Arroyo *et al.*, 2003; Chenal *et al.*, 2007).

Fourier Transform Infrared (FTIR) Spectroscopy

Changes in the chemical structure of NR/TMPT samples 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 $4,000\text{--}600\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

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 (Tawney et al. 1964). The polyfunctional monomers can participate in a number of radical reaction mechanisms, including grafting and radical addition. So, 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 this paper the induced crosslinking was evaluated by 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 the crosslink density (number of crosslinks per unit volume in a polymer network) and the results are presented in Figure 1 and 2, respectively.

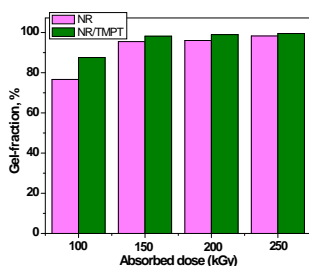


Figure 1. Gel fraction versus absorbed dose

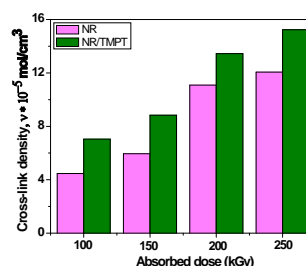


Figure 2. Cross-link density versus absorbed dose

The samples which were not subjected to crosslinking treatment (by irradiation with electron beam) were completely dissolved in toluene – in the same conditions as the irradiated samples. Sol-gel studies revealed higher sensitivity of NR and NR/TMPT to EB irradiation. Even at a low dose (100 kGy) gel fractions (Figure 1) was found to be 76.60% and 87.57% for NR and NR/TMPT respectively. A slow increase is observed for all samples when irradiation dose increases from 100 to 250 kGy. Similar results were obtained for crosslinking degree. Figure 2 shows that, for all samples the crosslinking degree increases with absorbed dose increasing. As expected the spectacular increase in the degree of crosslinking was obtained for NR/TMPT samples.

Thus, were obtained values of $7.04 \times 10^{-5} \text{ mol/cm}^3$ for the smallest irradiation dose (100 kGy) and $15.24 \times 10^{-5} \text{ mol/cm}^3$ for the biggest tested irradiation dose (250 kGy).

Figures 3 and 4 show the infrared spectra and characteristic infrared bands observed (in the region of $4,000\text{--}560 \text{ cm}^{-1}$) of NR/TMPT after irradiation. The main component of NR is cis-1,4-polyisoprene with a high degree of long chain branching generally associated with the presence of non-hydrocarbon groups distributed along the chains. The broad band in the region $3300\text{--}3270 \text{ cm}^{-1}$ were identified to the proteins and both mono-peptides and dipeptides present in natural rubber (Eng *et al.*, 1992; Manaila *et al.*, 2014). Absorption bands with a maxima at $3040\text{--}3030 \text{ cm}^{-1}$ corresponding to CH stretching in the $-\text{CH}=\text{CH}_2$ group, were observed. Vulcanization of the samples results in consumption of the double bonds in NR molecules, so that the intensities of these absorption bands decrease. The characteristic bands of the saturated aliphatic $\text{sp}^3 \text{ C-H}$ bonds are observed in the region $2980\text{--}2830 \text{ cm}^{-1}$ which are assigned to $\text{as}(\text{CH}_3)$, $\text{as}(\text{CH}_2)$, and $\text{s}(\text{CH}_2)$, respectively (as three corresponding bands) (Ali *et al.*, 2008; Manaila *et al.*, 2014).

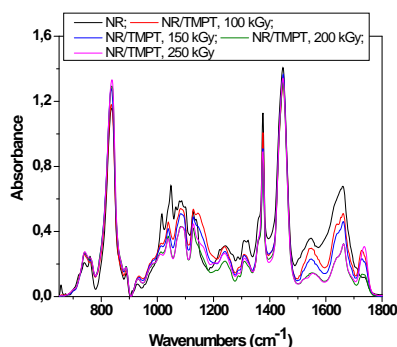


Figure 3. FTIR spectra of NR in range of $650\text{--}1800 \text{ cm}^{-1}$

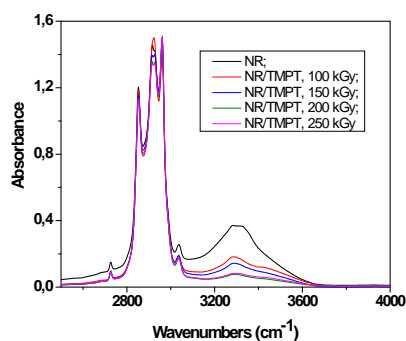


Figure 4. FTIR spectra of NR in range of $2500\text{--}4000 \text{ cm}^{-1}$

The presence of absorption bands in the spectral region located between $1670\text{--}1630 \text{ cm}^{-1}$, is due to valence vibration of homogeneous double bonds ($\text{C}=\text{C}$) in the NR structure. Their intensity decreases with the increasing of absorbed dose. The evidence for methylmethacrylate (MMA) group being present in TMPT, was observed at $1.730\text{--}1.720 \text{ cm}^{-1}$ for $\text{C}=\text{O}$ stretching and $1.130\text{--}1.120 \text{ cm}^{-1}$ for the $-\text{C}-\text{O}-$ moiety of the ester functional groups of MMA (Watcharakul *et al.*, 2011).

CONCLUSIONS

Radiation crosslinking has been promoted as a cleaner and more homogeneous cure process. This study demonstrated that chemical properties of NR can be improved as a function of irradiation absorbed dose. Sol-gel studies revealed higher sensitivity of NR and NR/TMPT to EB irradiation. Even at a low irradiation dose (100 kGy) the gel fraction was found to be 76.60% and 87.57% for NR and NR/TMPT respectively. A slowly increasing was observed for all samples when irradiation dose has increased from 250 kGy. Similar results were obtained for crosslinking degree. The obtained results demonstrated that gel fraction and crosslink density were improved as a function

of absorbed dose. When the EB dose increases, there is a increase of gel content (G %) and crosslink density () of samples, due to the formation of a three-dimensional network structure.

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