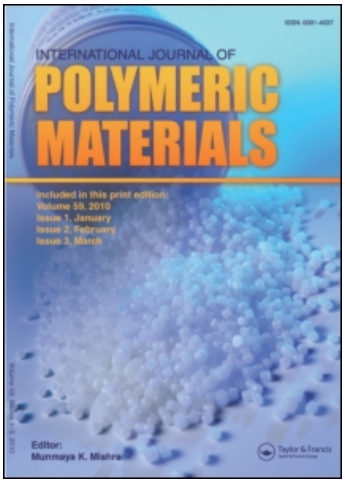

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CROSSLINKING OF HYDROXY-TERMINATED POLYBUTADIENE WITH ^{60}Co-γ-RAYS

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Crosslinking of hydroxy-terminated polybutadiene was carried out in the presence of functional reactive monomers like trimethylolpropane triacrylate and ditrimethylolpropane tetraacrylate, employing high-energy ^{60}Co-γ-rays. Specimens of the crosslinked material were then no longer soluble in organic compounds such as toluene, but swelled to an extent that inversely depended on the amount of radiation to which they have been exposed, that is on the degree of crosslinking. Not all molecules were, however, linked into the network, and appreciable amounts of soluble material could be removed, which allowed the gel fraction determination. The gel content and the swelling index were found to follow the progress of the reticulation reaction.

Keywords: hydroxy-terminated polybutadiene, HTPB, γ-irradiation, crosslinking, gel determination, swelling index

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INTRODUCTION

Liquid polybutadienes are presently the most important liquid elastomers gaining increasing importance in the world marketplace. Hydroxy-terminated polybutadiene (HTPB), synthesized via free radicals, has been an important polymer because of its specific characteristics that permit the production of elastomers with better physical properties and with a broader diversity of applications [1–4].

Polymers can be modified by means of light-induced chemical reactions initiated with the formation of reactive species whose nature will depend on the radiation type and on the reaction most probable to occur, either degradation or crosslinking [5].

The expansion in the use of radiation-reticulation technology truly occurred in the 1980s, due to a significant number of factors, such as need to reduce the emissions of volatile organic components, energy saving, clean energy (free of gases and vapor emissions), economic and highly productive processes, possibility to obtain new materials, and ability to reticulate on heat sensitive surfaces [6].

Few studies have been conducted on the radiation yields using HTPB and reactive monomers exposed to high-energy radiation, although some have been carried out employing systems of HTPB-based urethane polymers [7–8].

The present study was carried out to provide more information on the degree of crosslinking obtained when HTPB systems with reactive monomers like trimethylolpropane triacrylate and ditrimethylolpropane tetraacrylate are irradiated with ^{60}Co γ-radiation rays.

EXPERIMENTAL

Materials

The hydroxy-terminated polybutadiene (HTPB) used in this study is a commercial product of Petroflex Indústria e Comércio S.A., designated as LIQUIFLEX H ($M_n = 2800$, hydroxy value $= 0.775$ meq/g) used without treatment. The reactive monomers trimethylolpropane triacrylate (TMPTA) and ditrimethylolpropane tetraacrylate, named in this work as TETRA, were supplied by Sartomer Company and used as received. Toluene was used as solvent without further purification.

Irradiation Methods

The samples of HTPB in the presence of 5, 7, 15, and 30% (w/w) of trimethylolpropane triacrylate or ditrimethylolpropane tetraacrylate

reticulants were prepared in aluminum capsules covered with a lid, placed on an aluminum support and irradiated with a Gammacell 220 irradiator at temperatures between 30 and 35°C, in the absence of O_2. A ^{60}Co source having an activity of $3.34*10^{14}$ Bq (11750 Ci) was used for γ-irradiation. The samples were irradiated with doses of 5, 30, 75, 100, 130, and 200 kGy. The absorbed doses were determined by means of an alanine dosimeter with EPR (electron paramagnetic resonance) characterization [9].

Gel Content and Swelling Index

The irradiated samples were submitted to gel and swelling index determination using the modified ASTM method [10]. The samples were allowed to stand for 5 days in a dark place under a constant temperature of 24°C to guarantee complete solubility and to avoid degradation reactions. The test was carried out by dissolving 0.40 g of the sample in 100 ml of toluene, for periods of 5 days using the screen rack. After that, the solution was analyzed as to solids and gel contents, calculated as the difference in weight relative to the initial sample. The following equation was employed to determine the gel content:

$$\% \text{ gel} = (m_1 - 100/15^* m_2)/m_1{}^* 100$$

where m_1 is the mass of initial sample and $100/15*m_2$ is the mass of dry residue in the aliquot. The factor 100/15 corrects the aliquot to represent the entire amount of solution.

The gel-swelling index was calculated as the mass of solvent-swollen gel related to the mass of dry gel. To determine the swelling index the following equation was employed:

$$\text{Swelling index} = (m_3 - m_4)/(m_1 - 100/15^* m_2)$$

where m_1 is the mass of initial sample; $100/15*m_2$ is the mass of dry residue in the aliquot corrected by the factor 100/15 to represent the entire amount of solution; m_3 is the mass of the glass recipient with lid, containing the screen rack and the swollen sample; and m_4 is the mass of the glass recipient with the lid and the screen rack previously weighed.

RESULTS AND DISCUSSION

The HTPB/TMPTA and HTPB/TETRA systems irradiated with doses of up to 200 kGy were homogeneous and have been analyzed as to the

gel content, in order to evaluate the conversion of the reticulation reaction and the efficiency of reticulation for each irradiation dose.

Figure 1 shows that the gel content tends to increase as a function of the irradiation dose and of the TMPTA concentration. The systems containing 5 and 7% (w/w) of TMPTA behaved quite similarly, although the systems with 30% (w/w) of reactive monomer showed an anomalous behavior. Experimentally it was observed that this system was the only one to show phase separation upon irradiation. This may be the reason for the irregularity. It is verified that there is a general tendency to slow the reticulation rate around 75 kGy dose. This phenomenon can be related to the increases in the viscosity of the reaction medium, which is more rapid as the dose increases, hindering the diffusion of the active species. This would, at first, make the reaction rate slow down due to the difficulty of the reactive species to get close for the reaction to occur. As a consequence the gel content starts to level off. As the irradiation dose increases beyond a certain degree, the energy content in the system will be high enough to compensate for the statistically unfavorable condition.

The HTPB/TETRA system showed the same tendency as the HTPB/TMPTA system in relation to the gel content, the irradiation dose, and the concentration of reactive monomers, as shown in Figure 2. The sample containing 30% (w/w) of TETRA, in contrast with the system HTPB/30% TMPTA, showed uniformity in the gel results,

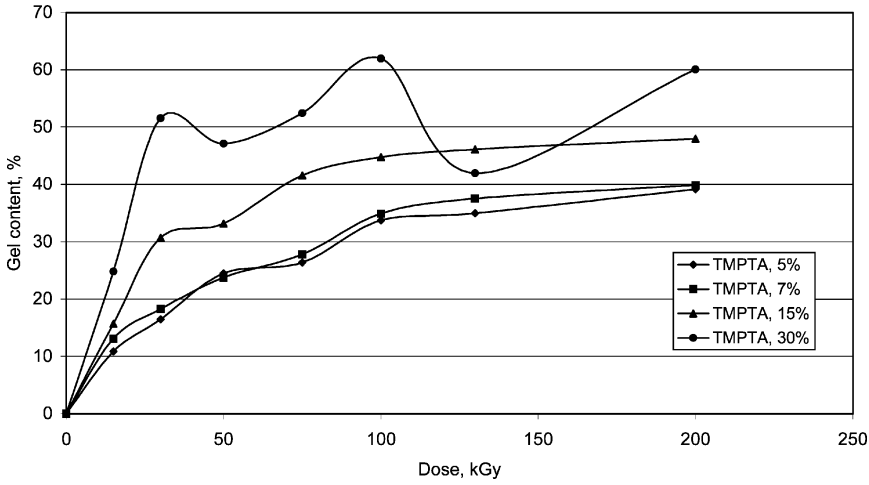

FIGURE 1 Effect on the gel content by the irradiation dose in the HTBP/TMPTA system.

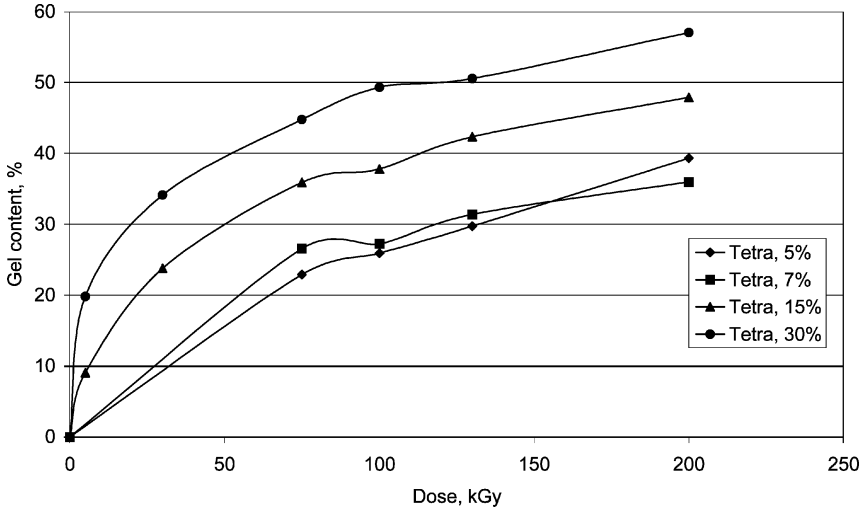

FIGURE 2 Effect on the gel content by the irradiation dose in the HTPB/TETRA system.

despite a little turbidity that appeared during the mixture with HTPB, indicating minor phase heterogeneity.

Comparing the two types of reactive monomers, it was observed that, for a given monomer concentration, TMPTA generated a higher gel content than TETRA, especially for doses below 50 kGy. This indicates that the functionality of the reactive monomer is not a prevailing factor for reticulation in this dose range. The gel contents for higher doses showed a tendency to become independent of the crosslinking agent type in all concentrations.

In Figure 3 it was verified that there exists a correlation between the gel content and the swelling index, which determines the type of reticulation network (reticulation density) and the average molecular weight between reticulations. The type of network is predominantly determined by the gel content, because specific changes do not take place with the irradiation dose or with the concentration of the reactive monomer. That is, similar reticulation networks can be obtained employing a certain combination of irradiation dose and of reactive monomer concentration, provided that similar gel contents are achieved. For the HTPB/TETRA system a correlation also exists between the gel content and the swelling index, as can be observed in Figure 4. Comparing Figures 3 and 4, a small difference is observed in the quality of the reticulation network with regard to the gel content, because it becomes a little tighter when the HTPB/TETRA system is employed.

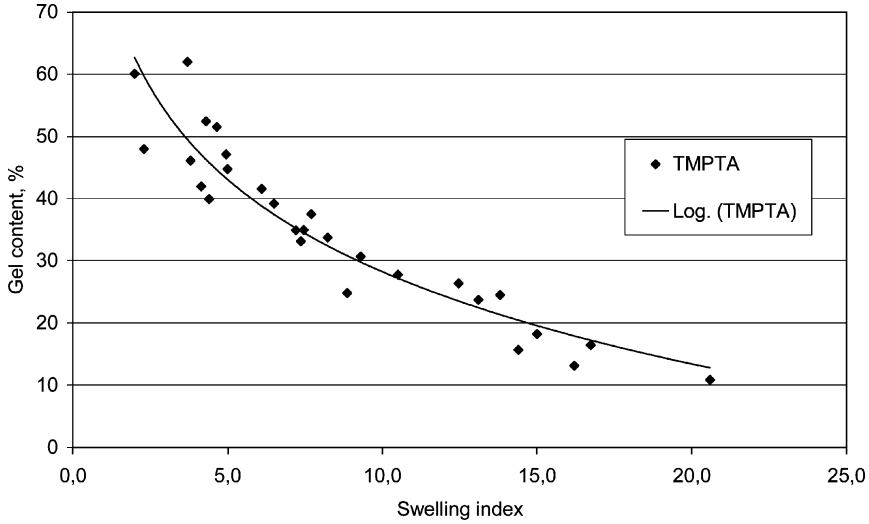

FIGURE 3 Relationship of the gel content and the swelling index for the system of HTPB/TMPTA.

CONCLUSIONS

The HTPB/TETRA and HTPB/TMPTA systems irradiated with ^{60}Co-γ-radiation rays show that the reticulation density and the gel content are functions of the irradiation dose and the concentration of reactive

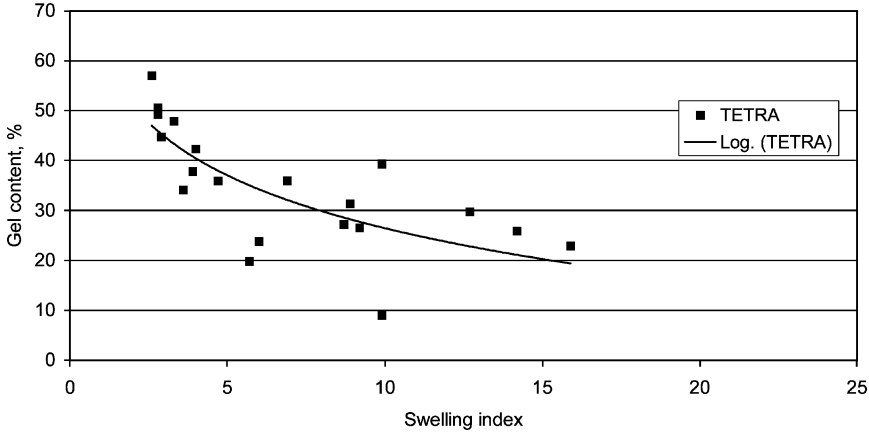

FIGURE 4 Relationship of the gel content and the swelling index for the system of HTPB/TETRA.

monomers. The reactive monomer TMPTA produced higher conversions for a given dose of irradiation than TETRA.

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