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Effect of Gamma Irradiation on Crosslinking of Polyester-Styrene Resin: Experimental Study and Glass Transition Temperature Analysis

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1. Introduction

Polymeric crosslinking is a process that occurs when linear or branched polymer chains are interconnected by covalent bonds, a process known as crosslinking, that is, bonds between linear molecules producing three-dimensional polymers with high molar mass. With increasing cross-linking, the structure becomes more rigid [1].

Because of cross-linking, the polymer chain loses its fluidity and, as a result, is no longer shaped. Such polymers are called thermosets. The increase in molecular weight makes these polymers insoluble in water and soluble in organic solvents. A thermoset polymer can be considered a macromolecule due to the network formed by the interconnection of polymer chains [1].

The cross-linking process can be carried out by irradiating polymers with a consequent increase in molecular weight, which can form an insoluble three-dimensional network. Crosslinking is the predominant reaction in the irradiation of polystyrene, polyethylene, natural and synthetic rubbers, among others. It has a beneficial effect on the mechanical properties of some polymers and is commercially used to produce polyethylene with increased stability and resistance to creeping at high temperatures, for example. Ionizing radiation, when interacting with polymers, transfers energy to the atoms of the polymer chain, causing permanent changes in their physical-chemical structure. Such modifications can result in the cross-linking or scission of polymer chains, which are simultaneous and competing processes, and the preponderance of one or the other depends mainly on the dose of radiation with which the material was treated. Some of the radiation interactions with the polymeric material can also directly result in energy transfer, which is not sufficient to cause ionization, but directly results in an electronically excited state. These molecules that are in the excited state decay to the ground state, emitting phosphorescence and fluorescence or through chemical reactions, by heterolytic bond breaking producing ions, or by homolytic bond breaking, favoring the formation of radicals, where the process of crosslinking. The degree of crosslinking is proportional to the absorbed dose, being independent of the radiation intensity [2].

In addition to irradiation, in the free-radical crosslinking copolymerization method, the polymerization is initiated by free radicals, which can be generated through various means such as thermal initiation, photoinitiation, or chemical initiation with initiators like peroxides. These free radicals react with monomers, causing them to polymerize and form polymer chains. Additionally, the presence of multifunctional monomers or crosslinking agents allows for the formation of crosslinks between polymer chains during the polymerization process [3].

The final product is a copolymer with a network structure formed by interconnected polymer chains through crosslinks. This network structure provides the copolymer with unique properties compared to linear polymers, such as increased mechanical strength, heat resistance, and solvent resistance.

2. Methodology

The REICHHOLD RESAPOL® LP 8847 is a non-promoted and low viscosity polyester resin for pipes, tanks and other applications submitted to chemicals manufactured by spray-up, hand lay-up and filament winding.

This resin is composed of a mixture of 50% polyester, 45% styrene and 5% other materials.

Radiation processing took place through irradiation with gamma radiation in the Cobalt-60 Multipurpose Irradiator at the CTR-IPEN Radiation Technology Center.

The samples were exposed to gamma radiation at absorbed doses of 1, 3, 5, 8, 15, 20, 25, 30 and 50 kGy, at rates of 1 kGy.h-1, to compare the effects on the resin.

For samples exposed to doses of gamma radiation, between 30 kGy and 50 kGy, polymethylmethacrylate (PMMA) dosimeters from Harwell (Amber and Red) were used and readings were taken on the Thermo Scientific Genesys 20 spectrophotometer, from the CETER Radiation Technology Center /IPEN, to ensure the measurement of the applied dose.

Using the differential scanning calorimetry (DSC) method, it was possible to obtain the Tg of each irradiated sample.

3. Results and Discussion

To establish the T_g of RESAPOL® LP 8847 resin, the Gordon-Taylor method was used, which assumes a linear relationship between Tg and the volumetric fraction of the components in the mixture. The basic formula of the Gordon-Taylor method is (1):

$$\frac{1}{T_{g,m}} = \chi_1 \cdot \frac{1}{T_{g,1}} + \chi_2 \cdot \frac{1}{T_{g,2}} \quad (1)$$

Where:

- $T_{g,m}$ is the T_g of the mixture.
- X1 and X2 are the volumetric fractions of components 1 and 2, respectively.
- $T_{g,1}$ and $T_{g,2}$ are the Tg of components 1 and 2, respectively.

To apply this formula, it is necessary to know the glass transition temperatures of the pure polymers (polyester and styrene) and their respective volume fractions in the mixture. Once you have this information, you can calculate the T_g of the mixture using the formula above [3].

4. Conclusions

The study carried out demonstrated the effect of gamma radiation irradiation on RESAPOL® LP 8847 resin, composed of 50% polyester, 45% styrene and 5% other materials. Using the differential scanning calorimetry (DSC) technique, it was possible to determine the glass transition temperature (Tg) of each irradiated sample. Using the Gordon-Taylor method, a relationship was established between the Tg of the mixture and the volumetric fractions of the components. This method allowed calculating the Tg of the mixture based on the Tg of the pure polymers and their fractions in the mixture.

The results indicated that irradiation with gamma radiation significantly affected the Tg of the resin, with variations observed depending on the dose of radiation applied. This study provides valuable information on the behavior of resin subjected to gamma irradiation, highlighting the importance of controlled dosage, and understanding the resulting properties.

In short, the results obtained contribute to the advancement of knowledge about the polymeric crosslinking process by gamma irradiation, offering important insights for the development of polymeric materials with specific properties, such as thermal resistance and chemical stability, relevant for a variety of industrial applications.

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