Mechanical and rheological properties of high molecular weight polypropylene modified by gamma irradiation

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The purpose of this work was to examine the effects of different concentrations of *Tri-allyl-isocyanurate* (TAIC) and gamma irradiation on mechanical and rheological properties of a high molecular weight isotactic polypropylene (iPP). It were studied two kinds of iPP, one with granular form and other without additive (spheric form). An attempt has been made to correlate the structure of the irradiated iPP to the properties. The modified polypropylenes were characterized by oscillatory rheology, tensile tests and morphology analyses by differential scanning calorimetry. The results showed improve in the mechanical properties for this condition of process.

Introduction

The mechanical and rheological properties of semicrystalline polymers depend on the chemical structure, molecular weight, molecular weight distribution, crosslinking, crystallinity and morphology. These factors also influence the crystallinity of these materials supported by the crystallization conditions[1-5]

When the polymer is submitted to high ionizing radiation (gamma rays, accelerated electrons and X-rays) there is the formation of very reactives intermediates, free radicals, ions and excited states. These intermediates can follow several reaction paths which conduct to the formation of new bonds and species. Radiation process is used efficiently for the production of newly modified polymers commonly called pos-reactor reactions[5].

In the present work, gamma radiation was used to modify the isotactic polypropylene (iPP) by producing radicals to evaluate the formation of short chain graft. For this purpose *Tri-allyl-isocyanurate* (TAIC) was mixed in to the polymer and then irradiated. On the other hand, the radiation also degradated the polymer by chain scission. This process and crosslinking are observed. How the crystalline structure and thermal memory of the iPP, as received, are influenced by gamma irradiation? This work will try answering the question. The structural modification of iPP was analyzed by the oscillatory rheology, tensile tests whereas their morphology was studied by calorimetric analysis.

Experimental

Material and sample preparation

The polypropylene used in this work obtained from Braskem. This material in the spheric and granular form has shown a melt flow index of 0.5 g/10 min, determined by using ASTM D 1238 (230°C and 2.16 kg). The polyfunctional monomer studied was *Tri-allyl-iso-cyanurate* (TAIC) at a concentration of 1.5 to 5.0 mmol/100g of polymer. The samples were gamma irradiated (^{60}Co) at a dose of 20 kGy under nitrogen gas atmosphere. Such irradiation was carried out in the Embrarad with a ^{60}Co source at dose rate of 10 kGy/h and the dosimetry performed with Harwell Red Perspex 4034.

Oscillatory test

As for rheological measurements they were conducted using Physica MCR300 rheometer equipment with an electrically heated temperature chamber. A plate/plate measuring system (25.0 mm disk) was used. Furthermore, 1.0 mm thick molded disk have been employed as frequency sweep varied between 0.1 to 200 s^{-1} at a constant strain (γ) of 5%. As regards temperature, all experiments were carried out at 200°C.

Tensile strength measurements

Tensile stress-strain measurements were made on an Emic model DL-300 instrument at room temperature. The dimensions of the test specimens were according to ASTM D 638. Moreover, a fixed value of 50 mm/min was used as constant strain rate. At least six measurements were made on each sample and whenever they presented discordant measurements they were repeated until at least six concordant results were obtained.

Thermal analysis

The experiments were carried out in a Mettler Toledo DSC 822^{e}. The samples were heated with a heating rate of 10°C/min from room temperature to 280°C, held at 280°C for 5 min, and then cooled from 280°C to –50 °C a cooling rate of –50°C/min. After that, the samples were heated again with the same condition.

Results and Discussion

It is acknowledged that the crosslinking and branching have dramatic effects in the rheological properties of molten polymer mostly at lower frequencies. In this region it is possible to analyse the distribution of molar mass of theses samples. In Fig. 1

one can see that granular form showed values of viscosity higher than spheric form due to the small degree of degradation. On the other hand, TAIC coagent shows higher efficiency, as a graffting or crosslinking promoter after the recombination of the radicals formed more commonly seen in spheric than granular cases. The values of η_o (zero shear viscosity) of iPP spheric modified increase with monomer concentration in comparison with pure resin. Yet, in the case of granular form no change was observed.

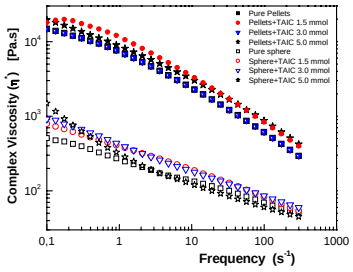

Figure 1 – Evolution of the complex viscosity curves as a function of angular frequency for all samples, at 200°C.

The presence of crosslinking and short graffting will influence the level of entanglement in the bulk and will most likely change the degree of crystallinity. The sample's percentages of crystallinity were determined by the integration of the area under the DSC curves obtained in the first scanning. Besides, the melting enthalpy of 100% crystalline iPP used was 190J/g[1]. It was observed a slight rise in the degree of crystallinity for all samples with monomer concentration, see Fig. 2.

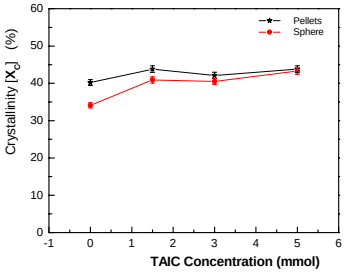

Figure 2- Crystallinity degree as a function of monomer concentration. Gamma irradiation dose was 20 kGy.

As it can be seen, the variation of the mechanical properties due to the structural modification of the high molecular weight iPP is really relevant (See Figs. 3-4).

Monomer concentration increase eventually lead to high values of breaking stress corresponding to more than the double of the of pure resin value. Nevertheless, the elongation diminished for all iPP modified according to monomer concentration degree.

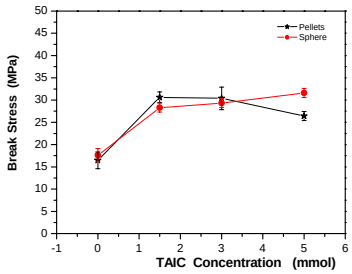

Figure 3 – Break stress as a function of monomer concentration. Gamma irradiation dose was 20 kGy.

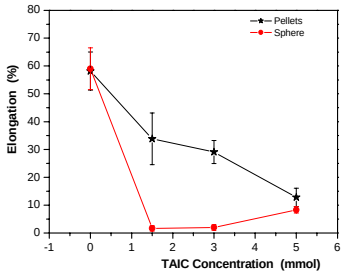

Figure 4 – Elongation as a function of monomer concentration. Gamma irradiation dose was 20 kGy.

Conclusion

To sum up: gamma irradiation and the concentration of TAIC modifies the structure of high molecular weight iPP. Theses conditions improve their mechanical properties probably due to the degradation occurred during processing and to the presence of monomer concentration that change the morphology. However, the difference observed in the elongation data for both polymers is probably due to the presence of crosslinking. Finally, it was observed that both geometry and the presence of additive also influence iPP mechanical and rheological properties.

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