STUDY OF RHEOLOGICAL PROPERTIES IN MODIFIED RANDOM PROPYLENE-ETHYLENE COPOLYMER.

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ABSTRACT

The random copolymer of propylene and ethylene (RP) presents exceptional transparency and brightness; possess low transference of odor and flavor showing better relation of rigidity/impact than homopolymer of polypropylene (PP). Due to the existence of units of ethylene this copolymer has distinct characteristics than PP of the same melt flow rate, improving its processability and allowing the use in processes such as: injection and blow molding and thermoforming of the plates. In the case of the thermoforming, the melt conventional polypropylene has the tendency to collapse during the process. It's well known, that the incorporation of a second monomer diminishes drastically the melting point of the sample up to 5°C changing its rheological characteristic and processing conditions. Therefore, the aim of the present work is to modify the random copolymer of propylene-ethylene with melt flow of 10g/10min and check its properties. In this process gamma irradiation technique was used to induce chemical changes in RP in the presence of *Tri-allyl-cianurate* (TAC), with concentration ranging from 0 to 5.0 mmol/100g of the pure resin. All samples had been characterized adequately with respect to rheological properties as: viscosity at low shear rate, storage and loss modulus, as well as, the evaluation of molecular mass distribution from zero shear viscosity value (η_0). The improvements in the rheological properties and processability had been evaluated in term of its performance during the thermoforming vacuum process. The modified samples showed a good performance during the thermoforming process. This behavior was observed exactly when the monomer concentration increase, except in the case of 5.0 mmol, where the sample tores during thermoforming, probably due to the high degree of ramification and branching in polymer chain.

1. INTRODUCTION

Modification in polymeric structure of plastic material can be brought by conventional chemical means or by exposure to ionizing radiation from either radioactive sources or highly accelerated electrons. The radiation technology is widely used to produce polypropylene (PP) with controlled rheology characteristic [1-4].

Isotatic polypropylene (iPP) is difficult to crosslinking by ionizing radiation, because the crosslinking reaction and degradation reactions proceed at almost same rate leading to deterioration of its physical properties. In generally high energy and thermal treatment leads to chain scission rather than crosslinking. PP along with a number of valuable properties exhibits intrinsically brittle behavior under impact loading, especially at low temperatures and high deformation speeds. To overcome this disadvantage the melt blending with other polymers, as well as, copolymers is most commonly performed for example the propylene-ethylene random copolymer (RP).

The propylene-ethylene random copolymer have excellent characteristic of processability and mechanical resistence at room temperature, allied to a relatively low price when compared

with other copolymers that could be used in the same applications. However, for applications where the mechanical resistence at low temperatures is demanded, the material cannot be used, therefore its glass transition temperature is not so low to allow the use in these applications.

Therefore, the aim of the present work is to modify the random copolymer of propylene-ethylene with melt flow of 10g/10min and check its properties. In this process gamma irradiation technique was used to induce chemical changes in RP in the presence of *Tri-allyl-cianurate* (TAC), with concentration ranging from 0 to 5.0 mmol/100g of the pure resin.

2. EXPERIMENTAL

2.1. Material and sample preparation

The RP with melt flow index of 10 g/10 min was used to evaluate the rheological behavior under irradiation process. This material was supplied by Braskem. Samples contain respectively monomer concentration were processed in the chamber of twin screw rheometer from Haake, with temperature zone of 175, 180, 185 and 190°C and the screw speed maintained constant in 40 rpm for all samples. After extrusion these samples were irradiated with a ^{60}Co source from Embrarad at dose of 20 kGy with dose rate of 10 kGy/h. Finished the radiation process they were heated for 60 minutes at 100°C to erase residual radicals. In this work only results to 20 kGy will be analyzed others doses will bee discussed elsewhere.

2.1.1. Gel fraction

Gel content of the modified RP was determined by extracting the soluble components in boiling xylene containing antioxidant Irganox 1010 for a total of 24 h at 135°C. After that, the residue was dried at 150°C to constant weight for 24 hours. Three samples were used to determine the average gel content for each modified RP (ASTM D 2765-01).

2.1.2. Melt flow index

The melt flow index (MFI) of the modified RP was measured in a Melt Flow Equipment Mod.09237 of Ceast in which the samples were flowed through an orifice of 2.0 mm diameter during 1.0 min under loading of 2.16 Kg at 230°C (ASTM D 1238-04c).

2.1.3. Rheological measurements

The characterization in shear flow was performed at a temperature of 200°C using rotational Physica rheometer (MCR300) with parallel-plate geometry of 25mm in diameter. The amplitude oscillatory was performed in the frequency range 0.01 – 100 s^{-1} with strain of 5% and a gap of 1.0 mm.

2.1.4. Dynamic mechanical analyse

The glass transition temperature (T_g) was determined in a equipment DMA of Netzsch using the three point bending mode. The range of temperature was of –40 to 40 °C with heating rate of 2 °C/min and the amplitude of measure of 60 µm. The samples dimensions were 50x8x2mm³ and had been prepared by thermopressing at 190°C in a Hidralmac thermopress during 15 minutes, being 10 for melting and 5 minutes with pressure of 80 bar.


3. RESULTS AND DISCUSSION

Changes in the melt flow index may be related to the modification in the random copolymer by degradation during the radiation process. As can be see in the table 1, when de RP was irradiated with 20 kGy in the inert atmosphere the value of MFI was three times the pure one, showing in this case the chain scission predominantly corroborated by the gel fraction result. Thereafter, when the TAC concentration increase a significant enhancement in MFI was seen and the gel fraction does not change in comparison with pure RP, except for the 5.0 mmol in which degradation process overlap the crosslinking phenomenon. From data of gel fraction and MFI it is well known that TAC don't graft in the polymer chain.

Table 1. Results of gel fraction and melt flow index of pure RP and samples irradiated and modified with TAC at different concentrations with 20 kGy.

| Samples	Gel Fraction (%)	Melt Flow Index (g/10min)
Pure RP	1.62 ± 0.5%	9.2 ±3%
RP/Irradiated	0.26 ±0.5%	27.8 ±1%
RP/0.5	1.13 ±0.5%	47.0 ±2.7%
RP/1.0	1.67 ± 0.5%	31.0 ±1.4%
RP/1.5	1.69 ± 0.5%	47.6 ±4.5%
RP/3.0	1.72 ± 0.5%	31.2 ±1%
RP/5.0	0.60 ± 0.5%	25.0 ±5%

Linear viscoelastic properties are very sensitive to the structural change in the material. The complex viscosity curves of the pure RP and modified RPs are shown in Fig. 1(a). When only radiation was used, complex viscosity decreased severely at low frequency and Newtonian-zone became broader, indicating that there was only degradation reaction and the molecular weight decreased. With the addition of TAC, the complex viscosity curves changes lightly than irradiated sample at low frequency, indicating that the additions of TAC reduced the degradation, but no variation has been see in comparison with the pure RP. Moreover, no changes were observed in the zero-shear viscosity (η_0) of RPs modified. Beside η_0, the storage modulus is sensitive to presence of low amounts of long chain branching in this process. The storage modulus (G') plotted as a function of frequency of all samples exhibited the typical terminal behavior indicating that they are linear polymers. Similar behavior was

obtained from the *tanδ- ω* curves shown in Fig 1(b). For the case of RP only irradiated and 5.0 mmol of TAC, the curves were ascending with the frequency decreasing, which is a typical terminal behavior of degradated material.
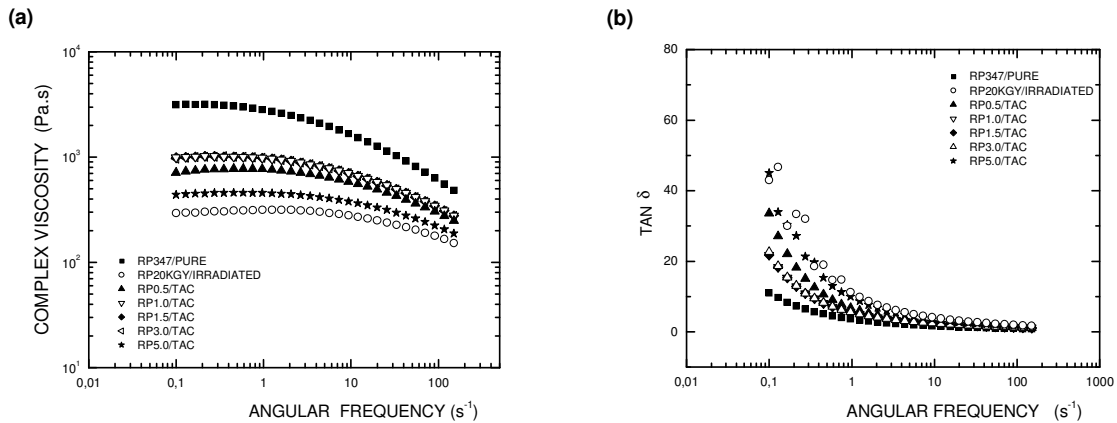
Figure 1 – Complex viscosity (a) and Tan δ (b) vs angular frequency for the pure RP and samples irradiated and modified with TAC at different concentrations with 20 kGy.

The mechanical loss factor, tan δ, can be see in Fig 2 (a) for the pure RP, irradiated and modified RP. The loss peak maximum is assigned to the glass temperature, T_g, of the amorphous phase and was observed that the peak maximum shift to the lower temperature with the increase of TAC concentration to 1,5mmol and then it decreaes with the concentration, see Fig. 2 (b).
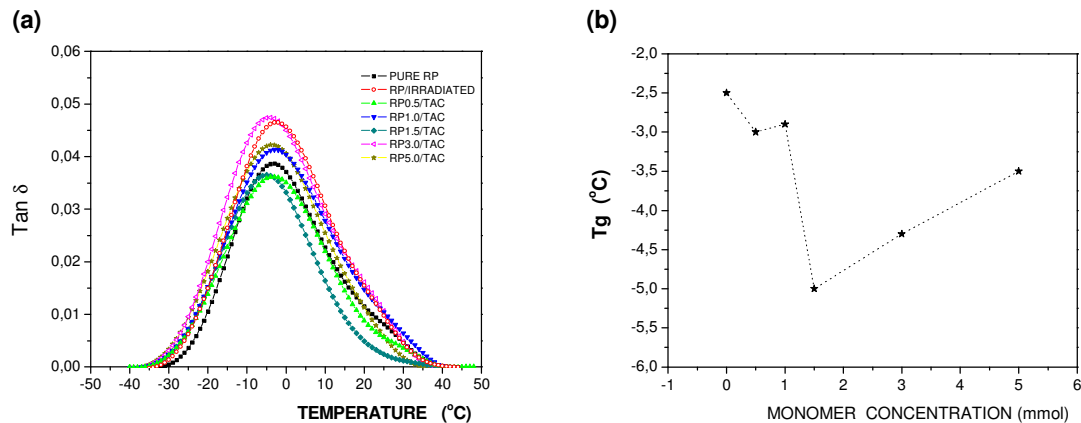

Figure 2 – DMA curves showing tan δ as a function of temperature at frequency of 1 Hz (a); Glass transition temperature T_g plotted against the monomer concentration (b).

Finally, it's currently recognized that for a material to have good thermoformability, it must exhibit high melt strength. Polypropylene homopolymer typically do not have sufficient melt strength or sag resistance to be used in industrial processes such as thermoforming [5]. In this

process, deformations in the sheet caused by sagging may in turn lead to irregularities in final products, such as unacceptable variations in weight and thickness, which may even result in tearing of the sheet. In the case of ethylene-propylene random copolymer, see Fig. 3(a) and (b), it was observed that the extruded samples show the uniformity on their surfaces and they didn't break up during the vacuum process, except for the sample 5.0/TAC. The modified and irradiated RP shown to be useful in such industrial process, the modified PP must exhibit sufficient elastic behavior to resist sagging, but remain viscous enough to flow into the mold under stress.

It is know that there a lot of factors that influences the behaviour of samples submitted to thermoforming testes like those presented in the fugure 3, in comparison with the PP homopolymer that is not adequate to this process. The modified samples, with exception of the highest TAC concentration, supported the thermomechanical conditions. This result is difficult to explain with the experiments done in melt state (see table 1 and figure 1) because the samples, RP irradiated and 5,0mmol/TAC, presented the similar behaviour.
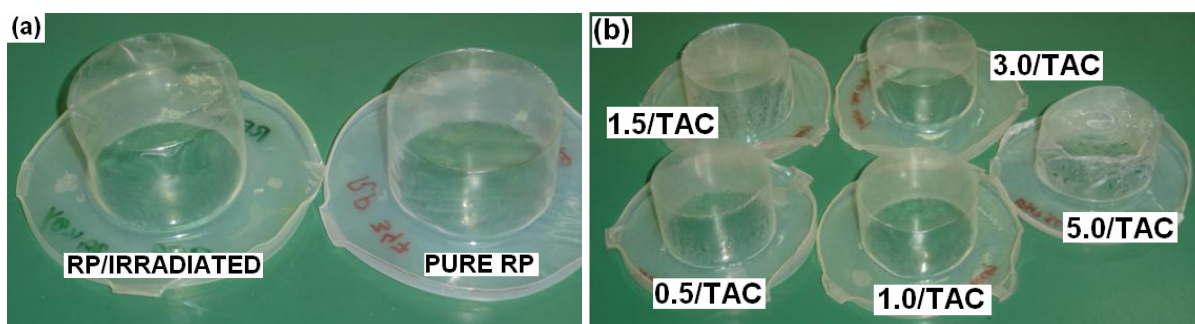
Figure 3 – Thermoforming tests under vacuum (a) pure RP and pure RP irradiated (b) RP modified with TAC at dose of 20 kGy.

4. CONCLUSIONS

The irradiation process at dose of 20 kGy of propylene-ethylene random copolymer with different concentration of TAC changes the rheological properties in comparison to the pure resin. The addiction of TAC monomer in pure random polypropylene with thermal treatment and irradiation process brought modifications in the polymer structure, as observed in the results of the realized tests, melt flow index, gel fraction and rheological properties. These results denotes that degradation process by chain scission overcome the branching process. In despite the intense degradative process, fact that can be evidenced through the increase of melt flow index in all samples, the processability of copolymer in the thermoforming process was improved. The modified samples presented good performance during the thermoforming simulation, the only exception was the sample contends 5mmol of TAC that didn't show a good resistance during the application of the vacuum, generating an irregular product, when compared with the others.

ACKNOWLEDGMENTS

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