

EVALUATION OF THE DEGRADATION EFFECT ON THE PROCESSABILITY OF HIGH MOLECULAR WEIGHT POLYPROPYLENE

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ABSTRACT

One way to improve the processability of high molecular weight and melt strength of Polypropylene (PP) is reducing its molecular weight by chain scission with increase of flow index. Nevertheless, the more significant occurrence of chain scission in its structure, further improved its processability is at expense of physical properties. It is well known that the high energy radiation creates free radicals in the polymer chains that subsequently stabilize forming structures. These structures composed by low molecular weight chains and by grafted, branched and crosslinked chains modify the physical and chemical properties of the polymer, depending of their distribution. The low molecular weight chains become from the degradation process by high energy irradiation, which decreases the melt strength and improves its processability. So, this work has the objective to evaluate the degradation of the high molecular weight PP using different irradiation doses. Two kinds of PP samples were utilized. The first one, without additive, presented a flow index of 1.9 g/10 min, and the second, additivated with 0.2 wt % of antioxidant phenolic, Irganox 1010, with a flow index of 0.9 g/10 min. These samples were irradiated with doses of 12.5 and 20.0 kGy. The results of flow index and melt strength obtained with these two kinds of samples showed the antioxidant and the radiation action.

1. INTRODUCTION

There are many technologies to produce polypropylene (PP) with controlled rheological behavior especially in the case of elongational flow [1-8]. Modification of polypropylene can be made through *in situ* polymerization using metallocene catalysts through electron or gamma irradiation in the presence of polyfunctional monomers or by different methods of degradation. One of prominent methods of degradation is to use distinct peroxides to promote degradation of polypropylene during extrusion, also termed vis-breaking, as a well recognized manufacturing process [1-4, 7]. Degradation of PP with peroxides is believed to occur by a series of free-radical reactions involving steps as initiation, scission, transfer and termination. These steps processes have been observed when polymers were irradiated with high energy radiation [9]. Chain scission generally converts the low melt flow index (MFI) commodity resins into high MFI resins with superior processing properties. However, because of viscosity and elasticity reduction, this final material will eventually have poor melt tensile properties.

The objective of this work was to evaluate the degradation process due to the irradiation of a resin of low MFI, with and without an antioxidant, Irganox 1010, and its influence on the rheological properties of this resin.

2. EXPERIMENTAL

2.1. Material and Sample Preparation

The two polypropylene used in this work were obtained from Braskem Petroquímica as spheres and presented MFI of 1.9 g/10 min and 0.9 g/10 min, respectively, determined using ASTM D 1238 (230°C and 2.16 kg). The second was additivated with 0.2 wt % of antioxidant phenolic, Irganox 1010 supplied as spheres by Ciba Especialidades Químicas Brasil, with aim to avoid the thermo-oxidative degradation. The additivation was carried out with the solubilization of the Irganox with acetone followed by the mixture with the resin during 10 minutes at room temperature.

After that, all samples were irradiated with gamma radiation (^{60}Co) at doses of 12.5 and 20 kGy under nitrogen atmosphere.

2.2. Gamma Irradiation

The samples were irradiated at Embrarad with a ^{60}Co source, at a dose rate of 10 kGy/h and the dosimetry was performed with Harwell Red Perspex 4034.

2.3. Gel Content Measurements

Gel content was measured using a standard method ASTM D2765. Samples of iPP modified were weighed, placed in bags and extracted with xylene as solvent (i.e. refluxing) for 24 hours at temperature of 135°C. After that, the extracts were removed, dried under vacuum for 24 hours to constant weight and weighed to determine the gel fraction according to equation 1

$$\text{Gel fraction (\%)} = (W/W_0) \cdot 100 \quad (1)$$

Where W and W_0 are the weights of the dried samples after and before the extractions procedure, respectively.

2.4. Melt Flow Index

The MFI of the modified polypropylenes was measured in a Melt Flow Junior equipment Mod 09237 in which the samples were flowed through an orifice of 2.00mm diameter during 10 min under loading of 2.16 kg at 230°C (ASTM D 1238).

2.5. Rheological Characterization in Shear Flow

The rheological measurements in shear were performed at a temperature of 200°C using rotational Physica MCR 300 rheometer with plate-plate geometry of 25mm in diameter and a gap of 1.0mm. The frequency sweeps were carried out between 0.1 and 250.0 s⁻¹ and at a constant strain (γ) of 5%. Samples of a thickness of 1.2 and diameter of 25mm were prepared from the irradiated and stabilized pellets in a hot press at a temperature of 190°C.

3. RESULTS AND DISCUSSION

The results presented in Table 1 showed a decrease of the gel fraction and an increase of the MFI of the samples irradiated in comparison with the pure and pure plus Irganox samples, respectively. The higher values of the gel fraction and lower values of the MFI of these two samples are due probably to the entanglement of the chains that have a high molecular mass. The changes due to the irradiation with gamma rays can be explained by the chain scission that diminishes the molar mass and consequently the entanglements. Nevertheless, the significant difference between the MFI values of the pure and irradiated samples, with and without Irganox, shows the effect of the antioxidant to prevent the thermo-oxidative degradation.

Table 1. Gel fraction (%) and MFI of the pure and modified samples.

Sample	Gel Fraction (%)	MFI (g/10min)
iPP pure	8.12	1.5
iPP + Irganox	8.41	1.0
iPP 12.5 kGy	0.94	25.0
iPP + Irganox 12.5 kGy	1.07	11.5
iPP 20 kGy	3.13	24.6
iPP + Irganox 20 kGy	1.04	14.3

In the Figures 1 and 2 are presented the curves of complex viscosity and $\tan \delta$ as a function of angular frequency, respectively, for the pure and modified samples. In Figure 1 it can be seen that the complex viscosity of the irradiated samples is lower than that of the pure and pure with Irganox samples, which presented practically no difference. This decrease of the viscosity can be associated to the chain scission. In Figure 2 the effect of this phenomenon is observed by the increase of the $\tan \delta$ of the modified samples except of the pure with Irganox sample in the angular frequency range analyzed. Concerning the modified samples it can be observed that the influence of the irradiation with and without antioxidant is quiet different. In the first case there is a clear difference between the sample irradiated with 20 kGy that shows a degradation behavior (lower viscosity and higher $\tan \delta$). In the second case the difference is not so important, but the degradation is higher for the sample irradiated with 12.5 kGy.

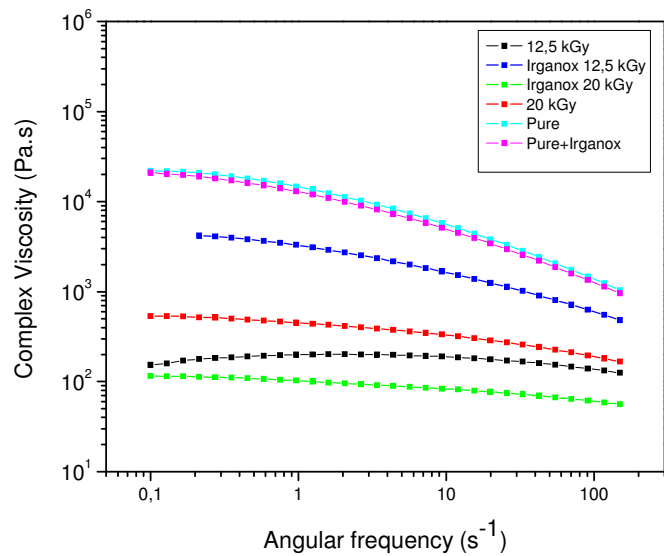


Figure 1. Complex viscosity as a function of angular frequency for the pure and modified samples.

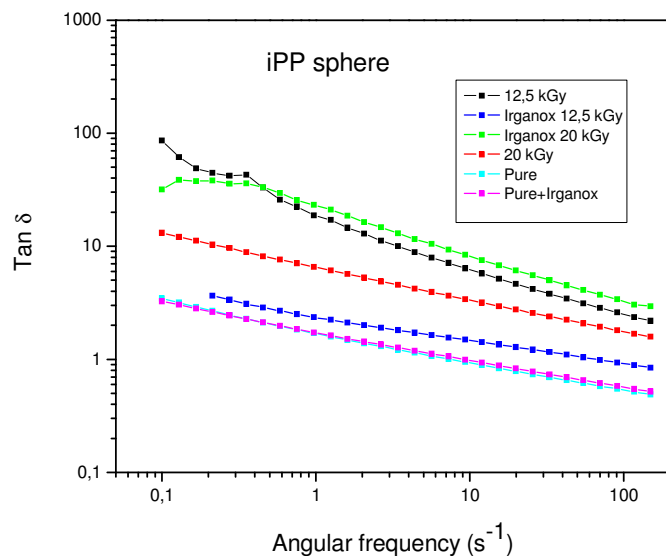


Figure 2. Tan δ as a function of angular frequency for the pure and modified samples.

4. CONCLUSIONS

The polypropylene with high molecular weight submitted to an irradiation process with and without antioxidant showed a degradation phenomenon, mainly due to the radiation. The antioxidant effect is more pronounced in the case of the dose of 12.5kGy. On the other hand, this dose provokes a degradation effect on the sample without antioxidant.

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