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RADIATION-INDUCED GRAFTING OF STYRENE ON POLYPROPYLENE PELLETS

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ABSTRACT

The changes of radiation-induced in polypropylene (PP) pellets exposed to gamma irradiation in inert atmosphere were investigated in correlation with the applied doses (10 and 50 kGy). Also, results from the grafting of styrene onto PP pellets using simultaneous irradiation at the same doses are presented. The grafting reaction was carried out using toluene as solvent, under nitrogen atmosphere and at room temperature. The properties of the irradiated and grafted PP pellets were studied using Melt Flow Index, thermal analysis (TG and DSC), and ATR-IR. The degree of grafting (DOG) for the grafted pellets was gravimetrically determined. The results showed that radiation-induced graft polymerization on pellets were successfully obtained and the influence of dose irradiated didn't change the thermal properties in spite of the increase in the MFI and consequently this increase in the viscosity results an decrease the molecular mass. The MFI for grafted pellets was not achievable because the high degree of viscosity of polymer, even arising the test temperature, the polymer was not flow enough.

1. INTRODUCTION

Nowadays polymer is one of the most materials used in industries. Polypropylene is one of these polymers used in numerous applications. The not polar nature of PP confers low water absorption property but this polymer has good chemical and thermal resistance, in spite of suffers degradation when is exposed at ultraviolet light and oxidation agents. Tertiarycarbons, present in the isotactic polypropylene polymer matrix, enhance its oxidation possibility that affects the physical and mechanical properties [1].

The melt flow index is an important tool to quality control in industry. This value is proportional inverse to viscosity and molar mass of polymer. In the case of PP if no crosslinking occurs and degradation overcomes, this behaviour leads to a decrease in molecular weight, reflected by the increasing melt-flow rate [2].

Ionizing radiation is a simple process which is used to modified polymer. The effects of this process consist in scission [3], crosslinking or grafting polymerization of chain polymer. There are numerous consequences for these polymers with new characteristics like: improves

adhesion, tensile strength, abrasion resistance, dying compatibility, thermal and photochemical stability.

In the case of grafting polymerization there are two methods for the polymer matrix modification: one is pre-irradiation method, which means the base polymer is irradiated and then monomer is added and grafted. The other is simultaneous irradiation method, i. e., the base polymer is soaked in the grafting solution and then irradiated together.

In this work, the effects of irradiation dose of 10 and 50 kGy and grafting polymerization by simultaneous irradiation method were studied. The samples were characterized by TG, DSC, ATR-IR, MFI and degree of grafting (DOG) was calculated.

2. EXPERIMENTAL

2.1. Materials

In this study pellets purchased by Braskem Ltda. were used as received with melt flow index (MFI) 3.4 g $10min^{-1}$ for pellet A. The value was determined using ASTM D-1238-L index.

In order to evaluate the influence of total absorbed dose in these samples, they were submitted at 10 and 50 kGy under inert atmosphere and at room temperature. The simultaneous irradiation method was used to carry out the grafting polymerization in both samples and at the same doses.

The grafting solution consists in styrene and toluene (1:1, v/v) and nitrogen gas was bubbled to guarantee oxygen free atmosphere during irradiation process. After irradiation the samples were washed with hot acetone to remove homopolymer and impurities, in the sequence were dried in the vacuum oven at 100 °C until constant mass.

2.2. Characterization techniques

The grafting degree was determined as the following equation (1):

$$\% \text{ DOG} = [(w_f - w_i)/w_i] \times 100 \qquad \text{eq. (1)}$$

where w_i and w_f are the masses of the PP samples before and after grafting, respectively.

The properties of all samples pure, irradiated and grafted were studied. Thermogravimetric (TG) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in nitrogen atmosphere of 50 mL min^{-1}, in the range from 25 up to 650 °C at a heating rate of 10 °C min^{-1}. Samples at about 10 mg were placed at alumina pans.

Differential Scanning Calorimeter (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere of 50 mL min^{-1} at a heating rate of 10 °C min^{-1}, in the temperature range of 30 to 250 °C. The polymer samples at about 10 mg were placed in closed aluminum pans.

Infrared spectroscopy (ATR-IR) was performed at Nexus FTIR of Thermo Nicolet. S.A with pellets analyzed directly without KBr. The pellets were put between the machine base and the probe of ATR.

Melt Flow Index (MFI) was determined at 230 °C / 2.16 kg and the degree of grafting of styrene onto PP pellets was determined gravimetrically.

3. RESULTS AND DISCUSSION

For pellet A the infrared spectra were made in all samples in order to analyze the effect of irradiation and the grafting process. In Fig. 1 is revealed that only the irradiation does not cause any change in the structural polypropylene, but in the grafted spectrum is indentified news peak related to styrene grafted: the benzene ring at 698 cm^{-1}, this peak is absent in the pure PP spectrum [4].

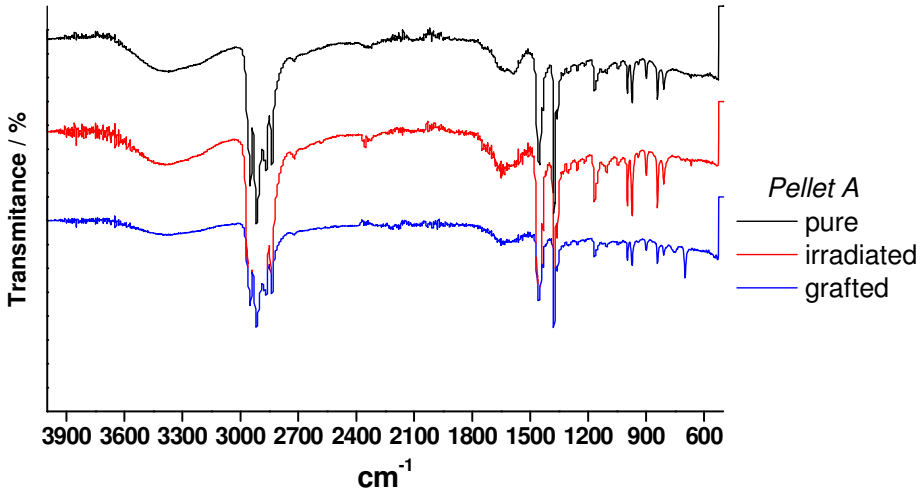

Figure 1. Infrared Spectra (ATR-IR) for pellets A pure, irradiated and grafted.

Thermal properties were verified for all samples studied and the degree of grafting was determined gravimetrically. In Table 1 is showed the results of DSC analysis and DOG calculated. At 50 kGy in pellet A is observed that the melting temperature had a decrease in this value as consequence of irradiation and grafted reaction [5]; and the crystallinity degree (W_c) had the same behaviour in this dose which confirms that higher irradiated dose causes

more degradation than low dose. The value for PP homopolymer 100% crystallinity is 209 J g^{-1} [6]. For grafted samples was not calculated the W_c because the grafted styrene causes interference in the polymer.

The highest degree of grafting was obtained for the highest dose which was expected because high dose leads to more radical formation and consequently leads to more grafting reactions. The degree of grafting was calculated as average of 3 (three) samples for each dose.

Table 1. Values of degree of grafting, melting temperature and crystallinity degree

Pellet A	DOG / %	T_m / °C	W_c / %
Pure	--	170	39.2
10 kGy	--	166	40.9
Styrene 10 kGy	9	166	---
50 kGy	--	167	37.2
Styrene 50 kGy	24	161	---

The degradation in pellet A after irradiation and grafting processes was confirmed by thermogravimetric measurement (Fig 2). For the initial degradation temperature is possible to verify at 50 kGy a decrease in this value for pure sample from 440 °C to 413 °C for irradiated and grafted sample, this fact is related directly to the grafted length which is less stable than the polypropylene. Although this, all curves present the same profile: only one step degradation, the styrene and the PP matrix are decomposing on the same temperature range.

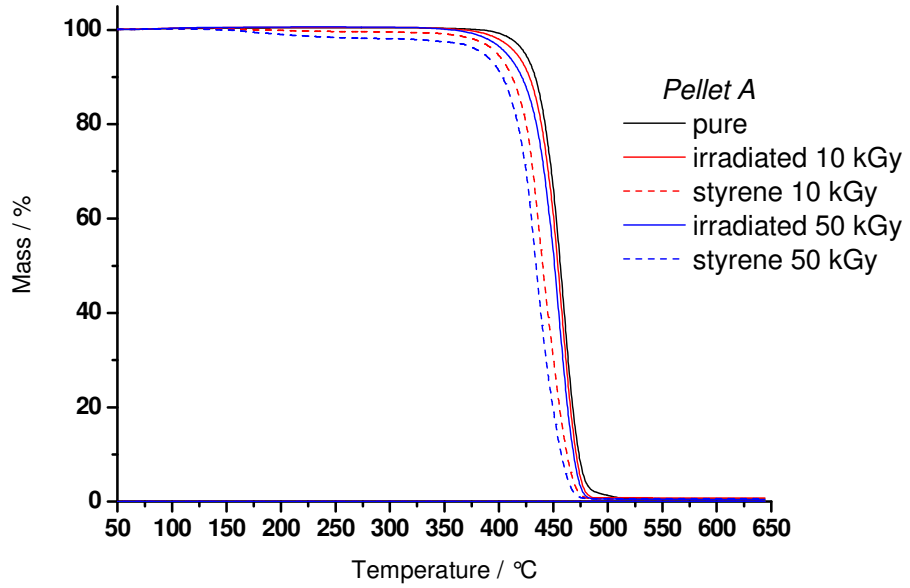

Figure 2. Thermogravimetric curves for pellets A pure, irradiated and grafted.

This decrease in the initial degradation temperature and in the melting temperature for these pellets are directly related with the irradiation process, which causes chain scission indicating more structural heterogeneity in degraded backbone polymer.

The melt flow index (MFI) is related with polymer molar mass. When the polymer has low MFI this indicates that it has high molar mass, due to the size of polymeric chains. The increase in values of MFI are demonstrated in Table 2 and confirm that increasing the irradiated dose more degradation in the polymer is caused. The grafted samples were degraded but possible due to the grafted styrene it was not possible to measure the melt flow index, the polymer didn't flow enough to permit to complete the test.

Table 2. Experimental Melt flow index values

Sample	MFI / g 10 min^{-1}
Pure	3.33
10 kGy	9.2
50 kGy	70.6

4. CONCLUSIONS

The TG curves for all samples present only one degradation step and the decrease in the initial degradation temperature were expected with the increase of dose irradiated and grafting yield. The irradiated samples show an increase in the MFI measurement when compared with the pure samples, suggesting that the degradation effect was caused by radiation. This fact is confirmed by DSC analysis due to the decrease in the melting temperatures of the irradiated samples in relation to the pure pellet.

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