Production of high melt strength polypropylene by gamma irradiation.

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Abstract

High melt strength polypropylene (HMS-PP) have been recently developed and introduced in the market by the major international producers of polypropylene. Therefore, BRASKEM the leading Brazilian PP producer together with EMBRARAD the leading Brazilian gamma-irradiator and the IPEN´s polymer group worked to developed a national technology for the production of HMS-PP. One of the effective approaches to improve melt strength and extensibility is to add chain branches onto polypropylene backbone using gamma radiation. Branching and grafting result from the radical combinations during irradiation process. Crosslinking and main chain scission in the polymer structure are also obtained during this process. In this work gamma irradiation technique was used to induce chemical changes in commercial polypropylene with two different monomers, Tri-allyl-isocyanurate (TAIC) and Tri-methylol-propane-trimethacrylate (TMPTMA), with concentration ranging from 1.5 to 5.0 mmol/100g of polypropylene. These samples were irradiated with a ^{60}Co source at dose of 20kGy. It were used two different routes of HMS-PP processing. The crosslinking of modified polymers was studied by measuring gel content; melt flow rate and rheological properties like melt strength and drawability. It was observed that the reaction route and the monomers type have influenced the properties; however the concentration variation of monomer has no effect.

***Keywords**: Polypropylene; gamma radiation; crosslinking and melt strength.*

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Introduction

There are many techonologies to produce polypropylene (PP) with controlled rheological behavior especially in the case of elongational flow[1-6]. The modification of polypropylene can be made through *in situ* polimerization, using metallocene catalysts, electron or gamma irradiation in the presence of polyfunctional monomers or by different methods of degradation. In the last case, the more proeminent method is used the distints peroxides to promote degradation of polypropylene during extrusion, also termed vis-breaking, as a well recognized manufacturing process [1-4]. 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[7]. Degradation process, generally converts the low melt flow index (MFI) commodity resins to high MFI resins with superior processing properties, but reducing viscosity and elasticity this final material has poor mechanical properties.

The isotactic polypropylene (iPP) is a typical thermoplastic with a number of desirable basic properties that make it a versatile material among thermoplastics. These properties coupled with its low specific gravity and low cost are the primary reason for this popularity as a commodity resin. However, its linear structure leads to poor processability involving elontional flow. It's known that the molecular weight and molecular weight distribution (MWD) determine the rheological properties of polypropylene melts. These parameters must be controlled to get better material response during processing and to achieve the diversity in polymer grades suitable for the different applications. To improve the processability of iPP and to have various grades, the molecular weight and the MWD can be modified in a post-reactor operation by means of different methods[1-7]. In the case of iPP the presence of long chain branching or grafting strongly affect the molar weight and MWD.

The radiation process has played an important role to produced polymers with these controlled rheological properties. The irradiation of polymeric materials with ionizing radiation (accelerated electrons, X-rays, ion beams, gamma rays) leads to the formation of very reactive free radicals intermediate, ions and excited states. These intermediates can follow several reaction paths results in the new bonds formation, as well as in the case of peroxide degradation process. The transformation degree (extension) depends on the structure of the polymer and the conditions of pre treatment, during and after irradiation as well as dose rate. The modification of polymers by irradiation cover crosslinking, induced polymerization (graft polymerization and curing) and degradation. The success of radiation technology for the processing of synthetic polymers can be attributed to two reasons, namely the easiness of processing in various shapes and sizes and, secondly, most of these polymers undergo crosslinking reaction upon exposure to radiation. A significant difference exists between electron beam and gamma processing of polymers, which is related to dose rate and often to oxidative degradation of material at or near the surface for reactions conducted at low dose-rates [1,5-7].

Actually, there are different interests for development of polypropylene with long branching or grafting, the new family of polypropylene called high melt strength polypropylene (HMS-PP). First of all, the transient elongational viscosity is very important for a description of process involving elongacional deformation such as film blowing, blow molding or thermoforming. On the other hand, elongational behavior is a sensitive indicator of properties concerning the molecular structure such as high molecular weight tails or long-chain branching and in some cases were influenced the existence of crosslinking and degradation. The influence of molecular structure of the melt on the spinning (Rheotens tests) and uniaxial elongational viscosity were described and studied by many authors [1,4,5,8-10]. Branching and crosslinking have strong effects on the rheological properties of the material in the molten state. In order to measure these effects the Rheotens tests has been used. In this test an extruded filament was subjected to elongational deformation under the action of a tensile force and the drawdown force need for extension of an extruded melt strand was measured as a function of drawdown velocity. The melt strength was considered as the drawdown force required to break the melt strand [8-10].

In the present work it were studied two routes to produce branching and grafting polypropylene (with rheological behavior controlled) using gamma irradiation and multifunctional monomers. In this case two kind of monomers were investigated: Tri-allyl-iso-cyanurate (TAIC) and Tri-methylolpropane-trimethacrylate (TMPTMA) with concentration ranging from 1.5 to 5.0 mmol/100g of polypropylene. These samples were irradiated at dose of 20kGy. The gel fraction, MFI and rheological analysis (elongational flow and drawability) have been performed, trying to extrapolate from these data the differences between the various monomers, their concentration routes of process.

Experimental

Material and Sample Preparation

The polypropylene used in this work was obtained from Braskem. This material showed a melt flow index of 1.5 g/10 min, determined using ASTM D 1238 (230°C and 2.16 kg). The polyfunctional monomers studied were *Tri-allyl-iso-cyanurate* (TAIC) and *Tri-methylolpropane-trimetacrylate* (TMPTMA), supplied by *Cytec* and *Sartomer Industries*, respectively. Both monomers are trifunctional and were used as received.

Monomers at a concentration of 1.5 to 5.0 mmol/100g of iPP were mixed at room temperature (route 1) and in the second case submitted to higher temperature mixing (route 2). After that, all samples were irradiated with gamma radiation (^{60}Co) at dose of 20 kGy under nitrogen gas atmosphere.

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.

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 130°C. After that, the extracts were removed, dried under vacuum for 24 hours until to constant weight and weighed to determine the gel fraction according to equation 1:

$$\text{Gel fraction (\%)} = (W/W_o) \,.\, 100 \qquad (1)$$

where W and W_o are the weights of the dried samples after and before the extraction procedure respectively.

Melt flow index

The melt flow rate of the modified polypropylenes by two routes of process was measured in a Melt flow Junior equipment Mod 09237 in which the samples were flowed through an orifice of 2.00 mm diameter during 10 min under a loading of 2.16 Kg at 230°C (ASTM D 1238).

Rheotens test

In the Rheotens test the tensile force needed for elongation of an extruder polymer filament was measured as a function of the draw ratio. The polymer was extruded in a Haake rheometer (screw diameter of the 2.0 mm) in combination with a Rheotens Mod.

71.97 apparatus manufactured by Göttfert. The extrusion melt temperature was 190°C and the die velocity varied between 40.0 at 575.0 mm.s^{-1}. It can be assumed that cooling of the extruded strand in the spinline is small, so the polymer melt is elongated under isothermal conditions.

Results and discussion.

The crosslinking degree, during the process of modification of iPP was estimated by gel content. In the Figure 1 is possible observed the gel fraction behavior of two sets of samples starting from two routes of process for TAIC and TMPTMA monomers in a large range of concentrations. These data were compared with the date for the pure polymer. It can be seen that, there was no change in the gel fraction of the samples produced by the route 1 in comparison with the pure iPP and the samples obtained by route 2. On the other hand, the increases of monomers concentration increase the gel fraction obtained by the route 2, except in the case of TAIC at 5.0 mmol. Probably, in this case the chain scissions occur preferentially to the other reactions, for example, grafting or crosslinking. In the route 2, the TAIC strongly react with the iPP chains modifying the structure in comparison with TMPTMA, showed by high values of gel fraction.

Insert Figure 1

In general, the increase of entanglement in the melt state from the introduction of branching or crosslinking carry out a decrease of melt flow rate. The values of MFI of the samples as a function of monomer concentration at each process route is showed in the Figure 2. The samples obtained by route 2 showed the smaller MFI value than that of the route 1 corroborating with the gel fraction value, high gel fraction lead to low MFI. But, the rise in the monomer concentration led to a decrease in the MFI for route 1 and practically no change was observed for samples obtained by route 2 (except for case of TMPTMA 3.0 mmol).

Insert Figure 2

Figures 3 shows the force at which the melt polymer breaks that corresponds to the melt strength for all the samples of modified polypropylene as a function of monomer concentration. Polypropylene modified via route 2 exhibit high values of melt strength for TAIC and TMPTMA. The measurement of the melt strength was not possible in the case of iPP with TAIC 5.0 mmol due to the high crosslinking degree of the material. On the other hand, route 1 showed lower values of melt strength and smaller than pure iPP. In this routes the degradation process (chain scission) may be dominant over grafting or branching phenomenon.

Insert Figure 3

The extensibility of iPP modified melt has been determined by the rheotens testes and can be defined as the drawdown force needed for elongation of an extruded strand and is measured as a function of slowly increasing drawdown speed. In the Figure 4 it can be observed the maximum drawdown velocity until the break of polymer filament for all samples as a function of monomer concentration. It was observed that samples with high values of melt strength show small drawdown velocity (route 2). However, samples produced by the route 1 the drawability is higher when compared with pure iPP and the samples prepared by the route 2. This behavior may be ascribed to the dependence of iPP melt strength on its molecular weight, polydispersivity, degree of branches and entanglement density. However, the melt extensibility probably depends on the existence of a high level of molecule entanglements. In other words, drawability arises from higher degradation process (see Figure 2).

Insert Figure 4

Conclusion.

Gamma-irradiation was successfully used to alter the molecular structure of linear polypropylene. The utilization of polyfunctional monomers TAIC and TMPTMA as a crosslinking agents lead to modification of iPP structure in the two applied routes of process. Evidence of this was found in the form of insoluble gel contents in the samples, as well as a variation on the melt flow rates. Higher concentration of monomers led to samples with a greater melt strength, especially in the route 2 in comparison to the route 1. But the drawability was dropped for all cases with the variation of monomer concentration. Different steps during process to obtain modified linear polypropylene pos-reactor influence the rheological properties of final product. In the irradiation of a polymer there is always a balance between crosslinking, branching and degradation reactions mechanisms influenced by chemicals presence. Modifications on the molecular structure area a result of these chemicals and reaction mechanisms.

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Figure 1 – Dependence of gel fraction of the modified polypropylene on the monomer content for two routes of synthese. Radiation dose of 20 kGy.

Figure 2 – Dependence of MFR of the modified polypropylene on the monomer content for two routes of synthese. Radiation dose of 20 kGy.

Figure 3 – Melt strength of modified polypropylene in dependence of the monomer concentration at 190°C. Radiation dose of 20 kGy.

Figure 4 – Draw down velocity at 190°C as a function of monomer concentration of modified polypropylene. Radiation dose of 20 kGy.

Fig. 1

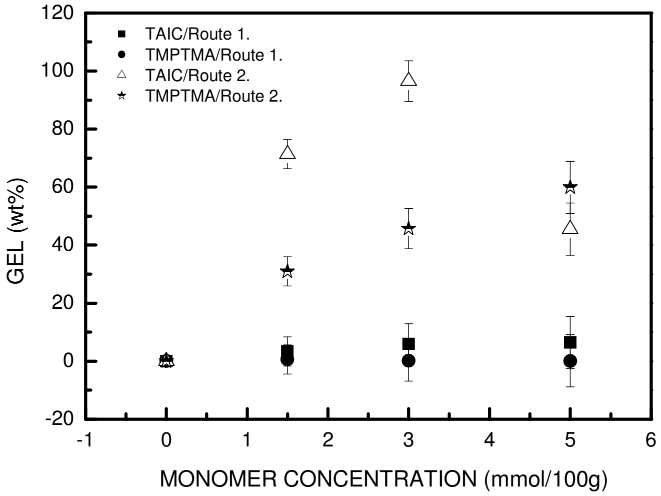


Fig.2

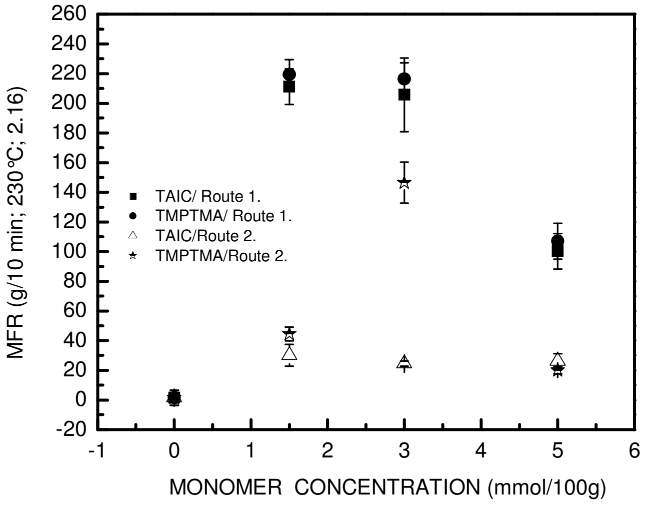


Fig. 3

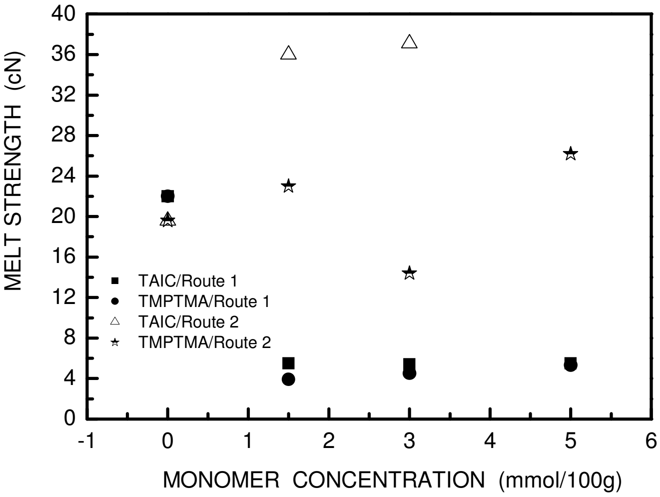
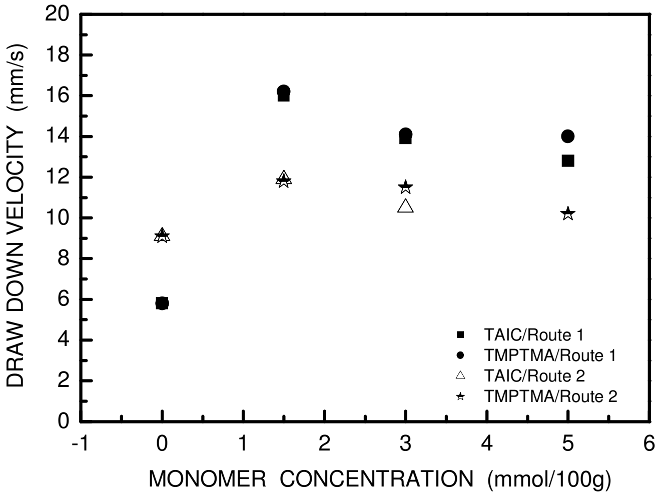

MELT STRENGTH (cN)
0
4
8
12
16
20
24
28
32
36
40
-1
0
1
2
3
4
5
6
MONOMER CONCENTRATION (mmol/100g)
■ TAIC/Route 1
● TMPTMA/Route 1
△ TAIC/Route 2
☆ TMPTMA/Route 2

Fig.4


DRAW DOWN VELOCITY (mm/s)
0
2
4
6
8
10
12
14
16
18
20
-1
0
1
2
3
4
5
6
MONOMER CONCENTRATION (mmol/100g)
■ TAIC/Route 1
● TMPTMA/Route 1
△ TAIC/Route 2
☆ TMPTMA/Route 2