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ScienceDirect
Radiation Physics and Chemistry 76 (2007) 1691–1695
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Production of high melt strength polypropylene by gamma irradiation

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Received 26 December 2006; accepted 12 March 2007

Abstract

High melt strength polypropylene (HMS-PP) has 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 (Institute of Nuclear Energy and Research) worked to develop 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-methylolpropane-trimethacrylate (TMPTMA), with concentration ranging from 1.5 to 5.0 mmol/100 g of polypropylene. These samples were irradiated with a ^{60}Co source at dose of 20 kGy. It used two different methods 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 method and the monomer type have influenced the properties. However, the concentration variation of monomer has no effect.

Keywords: Polypropylene; Gamma radiation; Crosslinking and melt strength

1. Introduction

There are many technologies to produce polypropylene (PP) with controlled rheological behavior especially in the case of elongational flow (Azizi and Ghasemi, 2004; He et al., 2003; Kurzbeck et al., 1999; Lagendijk et al., 2001; Lugão et al., 2000, 2002; Rätzsch et al., 2002; Romani et al., 2002). Modification of polypropylene can be made through in situ polimerization using metallocene catalysts through electron or gamma irradiation in the presence of polyfunctional monomers or by different methods of degradation. In the case, the prominent method is to use the distinct peroxides to promote degradation of polypropylene during extrusion, also termed vis-breaking, as a well-recognized manufacturing process (Azizi and Ghasemi, 2004; He et al., 2003; Kurzbeck et al., 1999; Lagendijk et al., 2001; Rätzsch et al., 2002). 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 (Chmielewski et al., 2005). 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 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

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0969-806X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radphyschem.2007.03.013

are the primary reason for this popularity as a commodity resin. However, its linear structure leads to poor processability under elongational flow. It is 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 (Azizi and Ghasemi, 2004; Chmielewski et al., 2005; He et al., 2003; Kurzbeck et al., 1999; Lagendijk et al., 2001; Lugão et al., 2000, 2002; Rätzsch et al., 2002; Romani et al., 2002). In the case of iPP, the presence of long-chain branching or grafting strongly affects the molar weight and MWD.

The radiation process has played an important role to produce polymers with these controlled rheological properties. The irradiation of polymeric materials with ionizing radiation (accelerated electrons, X-rays, ion beams, gamma rays) creates very energetic ions and excited states, which decay to reactive free radicals. These intermediate species can follow several reaction paths, resulting in the new bonds formation, as well as in the case of peroxide degradation process. The degree of transformation 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 encompasses 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 the fact that these polymers can 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 (Chmielewski et al., 2005; He et al., 2003; Rätzsch et al., 2002; Romani et al., 2002).

Actually, there are different interests developing 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 to understand processes involving elongational 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 was dependent on the existence of crosslinking and degradation. The role of molecular structure of the melt on the spinning (Rheotens tests) and uniaxial elongational viscosity were described and studied by many authors (Lagendijk et al., 2001; Lau et al., 1998; Lee et al., 2000; Muke et al., 2001; Rätzsch et al., 2002). 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 test 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 its 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 (Lau et al., 1998; Lee et al., 2000; Muke et al., 2001).

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

2. Experimental

2.1. Materials and sample preparation

The polypropylene used in this work was obtained from Braskem in the pellets form. This material has shown 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 1.5–5.0 mmol/100 g of iPP were mixed at room temperature (method 1) and in the second case submitted to higher temperature mixing at 190 °C in a Haake rheometer, screw diameter (method 2). After that, all samples were irradiated with gamma radiation (^{60}Co) at dose of 20 kGy under nitrogen gas 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 h at temperature of 130 °C. After

that, the extracts were removed, dried under vacuum for 24 h to constant weight, and weighed to determine the gel fraction according to

$$\text{Gel fraction (\%)} = \left(\frac{W}{W_o}\right) \times 100, \quad (1)$$

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

2.4. Melt flow index

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

2.5. Rheotens test

In the Rheotens test, the tensile force needed for elongation of an extruded polymer filament was measured as a function of the draw ratio. The polymer was extruded in a Haake rheometer (screw diameter of 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 and 575.0 mm s^{-1}. It can be assumed that the temperature variation of the extruded strand in the spinline is small, so the polymer melt is elongated under quasi-isothermal conditions.

3. Results and discussion

The crosslinking degree, during the process of modification of iPP, was estimated by gel content. The gel fraction behavior of two sets of samples starting from two different methods for TAIC and TMPTMA monomers in a large range of concentration is shown in Fig. 1. These data were compared with the data for the pure polymer. It can be seen that, there was no change in the gel fraction of the samples produced by the method 1 in comparison with the pure iPP and the samples obtained by method 2. On the other hand, the increase in monomer concentration enhances the gel fraction obtained by the method 2, except in the case of TAIC at 5.0 mmol. Probably, in this case chain scission occurs preferentially to other reactions, grafting or crosslinking. In method 2, the TAIC strongly reacts with the iPP chains modifying the structure. In comparison with TMPTMA showed higher values of gel fraction.

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 method are shown in Fig. 2. The samples obtained by method 2 showed smaller MFI value than method1 agreeing with the gel fraction value, high gel fractions lead to low MFI. But, the rise in the monomer concentration led to a decrease in the MFI for method 1 and practically no change was observed for samples obtained by route 2 (except for the case of TMPTMA 3.0 mmol).

Fig. 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. Polypropylenes modified via method 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 because the extruded strand in the spinline crystallized quickly and the force applied to the strand related to the beginning speed was not zero. On the other hand, method 1 showed lower values of melt strength even smaller than pure iPP. In this method,

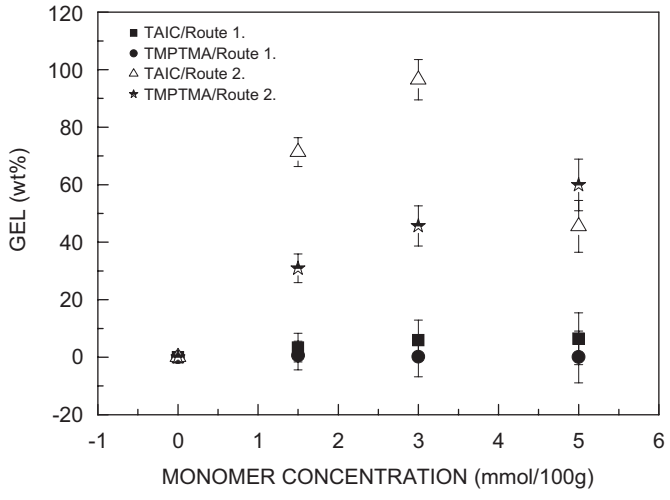

Fig. 1. Dependence of gel fraction of the modified polypropylene on the monomer content for two routes of synthese. Radiation dose of 20 kGy.

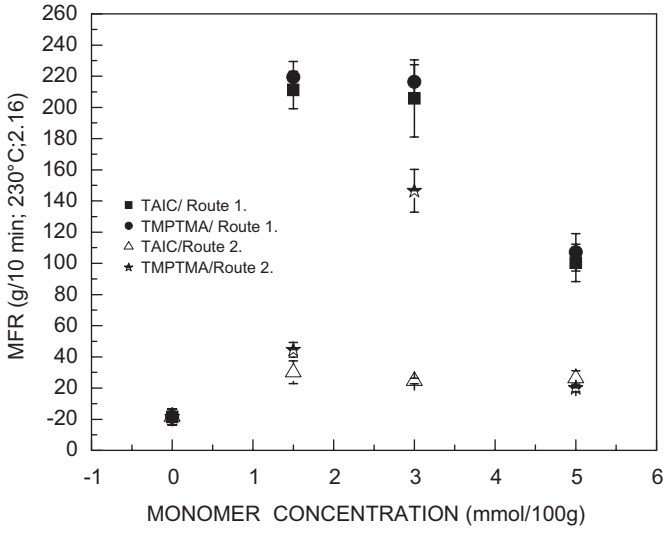

Fig. 2. Dependence of MFR of the modified polypropylene on the monomer content for two routes of synthese. Radiation dose of 20 kGy.

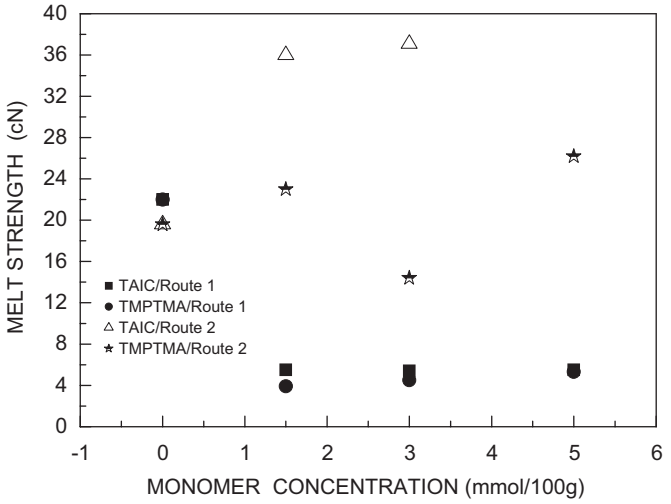

Fig. 3. Melt strength of modified polypropylene in dependence of the monomer concentration at 190 °C. Radiation dose of 20 kGy.

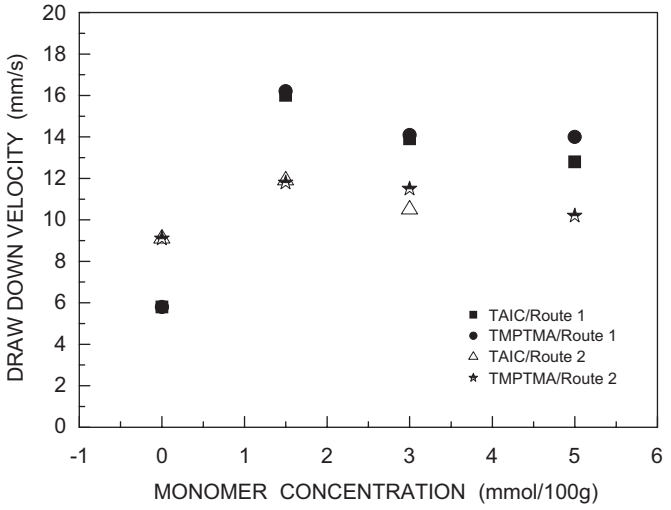

Fig. 4. Draw down velocity at 190 °C as a function of monomer concentration of modified polypropylene. Radiation dose of 20 kGy.

the degradation process (chain scission) may be dominant over grafting or branching phenomenon.

The extensibility of iPP-modified melt has been determined by Rheotens 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 Fig. 4, the maximum drawdown velocity can be observed 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, in samples produced by the method 1, the drawability is higher when compared with pure iPP and the samples prepared by the method 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 entanglement. In other words, drawability increases with chain scission (see Fig. 2).

4. Conclusion

Gamma-irradiation was successfully used to modify the molecular structure of linear polypropylene. The utilization of polyfunctional monomers TAIC and TMPTMA as crosslinking agents promoted the modification of iPP structure in the two applied methods. 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 higher melt strength, especially in method 2 in comparison to method 1. But the drawability decreases with monomer concentration after a sharp increase from 0 to 1.5 mmol/100 g. In the case of sample correspondent to 0 mmol/100 g of monomer has not been irradiated. The application of different methods of pos-reactor processing to obtain modified linear polypropylene changed the rheological properties of final product. In these processes, there is a balance between reactions of crosslinking, branching, and degradation controlled by the presence of multifunctional monomers.

Acknowledgments

FAPESP for the financial support and grants (process number: 02-13070-2 and 04-00383-8) and FINEP (process number: 0104034400 and 0105062300).

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