Production of high melt strength polypropylene by gamma irradiation


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 60Co 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 polymerization 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
are the primary reason for this popularity as a commodity resin. However, its linear structure leads to poor process-
sability under elongational flow. It is known that the
molecular weight and molecular weight distribution
(MWD) determine the rheological properties of polyprop-
ylene 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 prop-
ties. 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
encourages crosslinking, induced polymerization (graft
polymerization and curing), and degradation. The success
of radiation technology for the processing of synthetic
copolymers 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 poly-
propylene 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, elonga-
tional 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 degrada-
tion. The role of molecular structure of the melt on the
spinning (Rheotens tests) and uniaxial elongational vis-
cosity 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 prop-
ties 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 deforma-
tion 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 rheo-
logical behavior controlled) using gamma irradiation
and multifunctional monomers. In this case, two kinds
of monomers were investigated: 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 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-isocyanurate (TAIC) and Tri-
methylolpropane-trimethacrylate (TMPTMA), supplied by
Cytec and Sartomer Industries, respectively. Both mono-
nomers 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 (60Co) at dose of 20 kGy under nitrogen gas
atmosphere.

2.2. Gamma irradiation

The samples were irradiated at Embrarad with a 60Co
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 method 1 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,
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.

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References


