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Review on the production process and uses of controlled rheology polypropylene—Gamma radiation versus electron beam processing

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Abstract

Controlled rheology polypropylene grades are established commodities in the polymer processing market. However, new types, mainly the so-called high melt strength polypropylene (HMSPP) grades, are being introduced in the last two decades and radiation processing has played an important role. The melt strength properties of a polymer increases with molecular weight and with long-chain branching due to the increase in the entanglement level. As polypropylene (PP) is a linear polymer, the way to improve its elongational viscosity is by the production of a bi-modal polymer. Basell's patents claim the production of long-chain branching on PP by irradiating with electrons under oxygen free atmosphere, followed by two heating steps to allow radical recombination and annihilation reaction. Some other companies have issued patents using electron beam processing, but so far there is no actual production other than the Basell one. As a result of a research joint effort, IPEN, BRASKEM (the biggest Brazilian polymer producer) and EMBRARAD (the major Brazilian radiation processing center) developed a new process to produce HMSPP based on gamma processing. This paper will address some characteristics of each technology and the main industrial opportunities.

Keywords: Polypropylene; Gamma radiation; Electron beam; Crosslinking

1. Introduction

The consumption of isotactic polypropylene (PP) is growing fast as it is the polymer of choice for many industrial applications due to properties such as high tensile strength, high modulus, hardness, chemical resistance and excellent heat resistance. However, PP is a linear polymer with a non-polar polymeric structure which produces no strain-hardening under flow.

The elongational viscosity of polymer melts plays an important role in many processing operations like film blowing, blow molding, foam expansion, fiber spinning and thermoforming. A polymer melt under expansion undergoes shear and strong elongational deformation, so this property is at least as important as shear viscosity and for processes such as film blowing or blow molding they even prevail over shear deformation. It is known that most polyolefins show strain hardening effect under melt expansion. This effect induces a so-called self healing effect which contributes to avoid necking, sagging and other shape deformations under intense flow, as it promotes homogeneous thickness on overall dimensions. The appearance of strain hardening in uniaxial elongation of polyolefins at high deformation rates is related to the degree of long-chain branching as it was clearly established for low-density polyethylene (LDPE) as compared with polypropylene or other linear or short-chain branched polyethylenes. LDPE can be easily processed at comparatively very high take-up velocities in extrusion and blowing operations. The strain hardening is a very sensitive indicator of the influence of structural properties on the nonlinear behavior in elongational flow (Kurzbeck et al., 1999). The growing importance of PP stirred the study of

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their tensile properties in the melt, i.e., PP melt strength (MS).

Radiation processing was first proposed by Scheeve et al. (1995) to produce PP with improved melt strength and draw ability. These properties were achieved by radiation-induced chain scissioning of PP, followed by the introduction of these fragments in PP main chain to form long-chain branches in PP backbone. Electron beam processing of PP under nitrogen atmosphere is actually used in a continuous operation for large-scale production.

2. Objective

There is a need to study an alternative process with economic sense for regional markets. As a result of a research joint effort, Institute for Energy and Nuclear Research (IPEN), BRASKEM (the biggest Brazilian polymer producer) and EMBRARAD (the major Brazilian radiation processing center) developed a new process to produce high melt strength polypropylene (HMSPP) based on gamma processing (Lugão et al., 2000). This paper will address some characteristics of each technology.

3. High melt strength polypropylene

PP irradiation has been used to produce commercial grades of PP with improved tensile properties in the melt, based on the fragile behavior of PP molecules towards radiation. Montell now Basell, in the beginning of the 1990s, introduced in the market a recently developed high–melt strength polypropylene with high extensional viscosity, claiming that the new HMSPP enables foaming on conventional tandem extrusion equipment. Its rheological properties in the melt are unsuitable for a number of polymer transformation operations such as:

- high speed extrusion of coatings on paper or other substrates due to the formation of onset edge weave;
- profile extrusion due to flow instability in the co-extrusion of laminated structures;
- thermoforming due to sheet sagging and local thinning during melt thermoforming;
- foam formation due to bubble instability of melted PP;
- high tenacity fiber extrusion due to low extensibility of usual grades.

The analysis of the impressive series of Basell's patents, mostly authored by Dr. De Nicola and Dr. Scheeve and some others authors, indicate as the main original patent the US patent 4,916, 198 (Scheeve et al., 1995). Basell claims that the high melt strength is made by introducing long-chain branches into propylene polymers in a post-reactor modification process at room temperature and low dose irradiation of high molecular weight PP under N_2 atmosphere. Radicals are likely to decay very fast in amorphous phase, but under annealing, the radicals entrapped in the crystal phase are likely to move to the boundary and react. So the well-known reactions would be mostly chain scission followed by grafting and some minor crosslinking. Chain scission, however, is supposed to be the first and more intense reaction followed by grafting of PP fragments of degraded molecules onto PP main chain producing branching and competing with the creation of crosslinking. Their branched structures provide its combination of melt strength and melt extensibility. The post-reactor process comprises of two steps, high-energy electron beam irradiation under oxygen free atmosphere (very pure nitrogen flow) to create free radicals followed by heating to allow recombination of migrating radicals from crystals. Irradiation is conducted under N_2 to decrease as much as possible chain scission. The irradiation is supposed to be performed preferentially by accelerated electrons due to setting up of a continuous process. In this patent, a fluidized bed of PP travels under the beam, consequently, high energy (3–10 MeV) electrons are mandatory to promote a homogeneous reaction. Another interesting point is the promotion of branching or crosslinking by the use of free radical generated into the crystals. The free radicals move to the interface of crystalline regions under moderated heating conditions, where they react with neighbor radical, creating very large branched molecules.

A few radiation processes, using electron beam irradiation, were proposed to produce HMSPP:

- Yoshii et al. (1986) proposed the use of liquid acrylic multifunctional monomers ;
- Rätzsch et al. (1999) proposed the use of low-energy electron beams. This group also proposed other solid state methods to graft PP;
- Lucas et al. (1995) proposed the use of high content of antioxidants irradiating with gamma or electrons;
- Debras et al. (2004) proposed the irradiation of PP with electrons of at least 5 MeV, using 10 kGy. It looks like just a particular case of Basel's technology;

but the only known actual application is Basell's one.

IPEN developed an alternative production process of HMSPP in cooperation with BRASKEM. The process is based on the gamma irradiation of PP under acetylene atmosphere followed by a heating step to terminate the

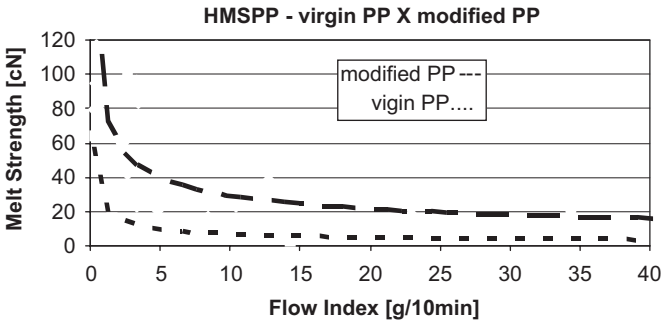

Fig. 1. MS of virgin and modified PP as a function of MFI.

reaction (Lugão et al., 2000). Fig. 1 shows the relation of melt strength (rheothens data) of virgin and modified resins (HMSPP) versus its melt flow index (MFI).

It is possible to see in Fig. 1 that the MS of the virgin resin increased considerably with the decrease of MFI. This behavior is the expected one and is explained by the increase in molecular weight. The MS of the irradiated PP in the presence of acetylene showed a much higher increase in MS over the entire range of MFI as compared with the virgin resin. The process of IPEN/BRASKEM takes the advantage of the use of acetylene to decrease degradation to promote crosslinking without leaving any residual monomer. Also the IPEN/BRASKEM process uses enhanced stabilization system to decrease degradation as much as possible, even with prejudice of crosslinking. The Basell process is advantageously conducted with accelerated electrons due to the need of high density of excited species to promote enhanced combination and termination reactions. The IPEN/BRASKEM process, on the other hand, is controlled by the diffusion of acetylene; consequently, the low dose rate typical of gamma irradiation allows the necessary recombination and termination reactions. Fig. 2 shows rheotens graph of PP irradiated with gamma under acetylene atmosphere against PP irradiated with electrons under N_2 atmosphere.

Fig. 2 shows an example comparing gamma irradiation of PP under acetylene atmosphere and electron-beam irradiation of PP under nitrogen atmosphere, against the rheological properties of virgin PP evaluated using a rheothen. It is possible to see that irradiation increased the drawn down velocity due to extensive chain scission for all samples, but only the samples irradiated by gamma under acetylene produced considerable higher melt strength. The main characteristic of the production process

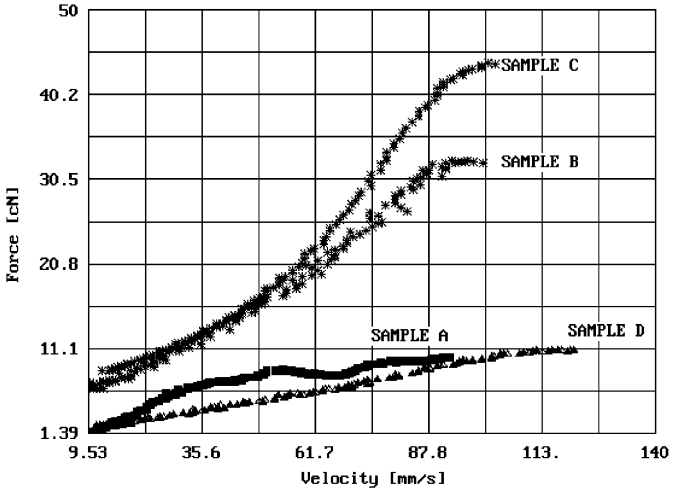

Fig. 2. MS evolution as function of drawn-down velocity for PP processed by different dose, atmosphere and dose rate.

of HMSPP using electron beam (Scheeve et al., 1995) and gamma (Lugão et al., 2000) are discussed as follows:

- Electron beam irradiation is performed under flow of pure N_2, producing basically chain scission followed by grafting. As a result it is easy to control the gel content, as almost only degraded PP and long-chain branching is generated. However, due to the limitations of electron penetration, the operation has to be conducted with medium to high energy electron beam machines. Therefore, the investment is only compatible with high production capacity.
- Gamma irradiation is performed under acetylene atmosphere, a bi-functional monomer. As a result, degraded and crosslinked PP are formed. Special care has to be applied to control crosslinking to avoid high gel formation and the cost of acetylene. On the other hand, it is possible to project small containers to fit the conveyor system of most gamma industrial irradiators. Therefore, the investment is minimum and the flexibility is high.

4. Conclusion

Gamma irradiation of PP under acetylene showed to be a competitive technology due to its process flexibility and almost absence of investment for small production.

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