STUDY OF THE POLYPROPYLENE MODIFICATION TO PRODUCTION OF MONOFILAMENT

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Isotactic polypropylene is an important polymer to produce synthetic filaments. It may exhibit a wide variety of mechanical properties. By suitable processing, it can used to produce tensile strength ropes with large elastic recovery. However in mooring systems, the polyesters have been used for production of ropes due to the fact that polypropylene presents low tenacity. There are various technologies that are utilized to improve this property, amongst them the polymer irradiation with the addition of polyfunctional monomers. Therein, three polypropylene homopolymers with different melt flow indexes (0.5; 3.5; 24 g/10 min) have been studied. The homopolymers were mixed with 5 mmol of EGDMA monomer and irradiated with a ^{60}Co source with a dose of 20 kGy. Tests of melt flow index, melt strength, drawability and dynamic viscoelastic properties were realized (DMA). The melt strength decreased for samples obtained by modification of resins with 0.5 and 3.5 g/10min. The drawability is a very important property for spinning the monofilament and it increased for all modified samples, the increase was very significant for sample obtained by modification of resin with 0.5 g/10min. This preliminary study demonstrates that concerning the melt strength and drawability, the more appropriate would be the sample obtained by modification of resin with melt flow index of 0.5 g/10min, nevertheless the low melt flow index can difficult the monofilament processing.

1.Introduction

The major part of the polypropylene (PP) applications depends of transformation processes that produce extensional deformation of the melt. The melt strength of a polymer is defined as the maximum force at which a molten thread can be drawn under standard conditions before it breaks. The melt deformations, known as shear-free flows, occur during extrusion of films, fibers, coatings, in thermoforming and in foaming, and are extremely sensible to the high molecular weight fraction and to the long chain branches of the polymer [1]. In extensional-

free flow it is necessary high melt strength to avoid the draw down propagation to rupture under the high velocities process. Even this limit is not attained it can occur a phenomenon known as draw resonance, that manifests by cyclic variations of the extruded thickness, with rupture possibility [2, 3]. If, from one side, the high molecular weight fractions are necessary to give elasticity and extensional strength to the melt, by the other, they can create heterogeneities in the normal stress distribution, causing draw resonance or other undesirable elastic effects. In certain situations, it seems to exist an "adequate" amount of high molecular weight, in which the entanglement density and the relaxation times contribute to an ideal rheological behavior for a specific application. In the specific case of platforms mooring systems, it is necessary filaments of PP with enhanced tenacity and creep properties.

Due to the Ziegler-Natta catalyst characteristics, the structure of the polymer obtained is constituted from linear chains and the essays to improve the PP melt strength under extensional deformation are limited in operational terms and/or in changes in catalytic system. One way to improve the extensional strength is the production of long chain branches (LCB) by means of a pos-reactor treatment. The introduction of these branches occurs by the formation of free radicals (via accelerated electrons, gamma radiation or peroxide) and its recombination under controlled conditions [4, 5, 6]. Structures with lateral chains with length higher than a determined minimum value present a strain hardening under extensional deformation. Nevertheless, crosslinking and main chain scission also occur in the polymer structure. Due to the chemical nature of PP it has a tendency to undergo β-scission which competes with grafting and crosslinking reactions. In order to decrease the degradation of PP and improve the degree of branching various polyfunctional monomers had been used to obtain chain branching.

The main objective of this work was to prepare three modified PP resins of different melt flow indexes by grafting of EGDMA using gamma irradiation, and then characterize these samples by mechanical and rheological tests.

2. Experimental

Materials

The commercial isotactic polypropylenes were supplied in a granular form by BRASKEM and their melt flow indexes obtained at 230^{o}C are listed in Table 1.

Modified polypropylene preparation

The homopolymers were mixed with 5 mmol of Ethylene Glycol Dimethacrylate (EGDMA) monomer and irradiated in a ^{60}Co source with a dose of 20 kGy at a dose rate of 5 kGy/hr. The dosimetry was performed with a Harwell Red Perspex

4034 dosimeter. After irradiation the samples were submitted to a thermal treatment at 100 ^{o}C during one hour and then compression moulded at 190 ^{o}C, in a Hidral-Mac press.

Analysis

Melt flow index

The melt flow index of the homopolymers and modified homopolymers was measured in a Melt Flow Junior Equipment Mod. 09237 of CEAST in which the samples were flowed through an orifice of 2.0 mm diameter during 1.0 min under loading of 2.16 kg at 230 ^{o}C (ASTM D 128-04c). The swelling ratio was calculated by diameter ratio of the extruded material to 2.0 mm.

Melt strength and drawability

In the Rheotens test the tensile force needed for elongation of an extruded polymer 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 ^{o}C and the die velocity varied between 40.0 and 575.0 mms^{-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.

Rheological measurement

The characterization in shear flow was performed at a temperature of 200 ^{o}C using rotational Physica rheometer (MCR 300) with parallel-plate geometry of 25 mm in diameter. The amplitude oscillatory was performed in the frequency range 0.01 – 100 1/s with a strain of 5% and a gap of 1.0 mm. Samples with 1.2 mm of thickness and 25 mm of diameter were produced by compression moulding at 190 ^{o}C.

3. Results and discussion

Table 1 – Results of melt flow index, swelling, melt strength and drawability of pure and modified samples.

Sample	Melt flow index (g/10min)	Swelling (%)	Melt strength (cN)	Drawability (mm)
A	24.4		0.9	8.2
A/EGDMA/20 kGy	34.8	48.4	1.0	8.9
B	3.3		8.2	9.4
B/EGDMA/20 kGy	18.8	69.5	2.9	12.2
C	0.3		91.2	4.4
C/EGDMA/20 kGy	0.9	83.1	10.8	12.0

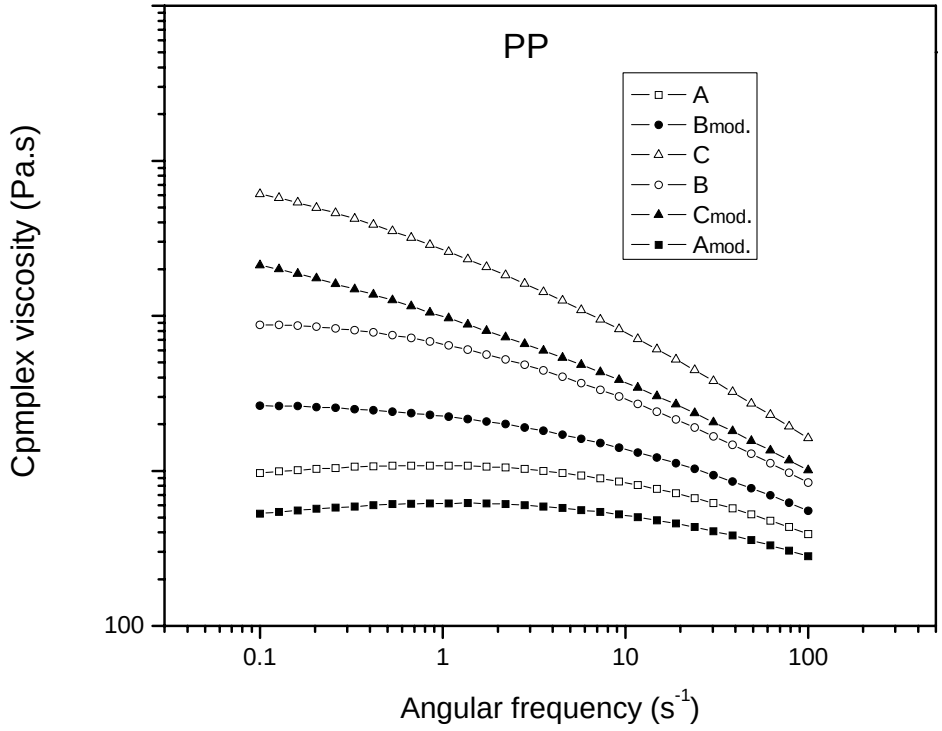

Figure 1. Complex viscosity as a function of angular frequency of the pure and modified samples.

In Table 1 it can be seen that there was an increase of the melt flow index for the three samples modified by the irradiation in the presence of the EGDMA with respect to the pure ones. Probably, in these cases chain scission occurs preferentially to other reactions, grafting or crosslinking. The values of swelling presented a …

Concerning the melt strength and the drawability the sample A showed an increase of approximatively 10 % in these two variables. Já nas amostras B e C houve uma diminuição da resistência do fundido e um aumento da extensibilidade, mais importantes no caso da amostra C. The drawability is a very important property for spinning the monofilament and its greater improvement has been observed for the sample C.

Na Figura 1 estão apresentadas as curvas da viscosidade complexa em função da freqüência angular para as amostras puras e modificadas. As amostras modificadas apresentaram valores da viscosidade complexa inferiores aos das respectivas amostras puras em todo o intervalo de medida. Este resultado confirma o aumento do índice de fluidez, denotando uma diminuição do peso molecular, provocado provavelmente pela cisão de cadeias.