



# **MONOFILAMENTS PRODUCED BY MODIFICATION OF ISOTACTIC POLYPROPYLENE WITH GAMMA IRRADIATION.**

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One of the effective approaches to achieve high melt strength polymers (HMS) is to add long chain branches onto backbone species using gamma radiation. Grafting and branching result from macroradicals combinations during the irradiation process. Nonetheless, crosslinking and main chain scission in the polymer structure are also obtained. Due to the chemical nature of polypropylene (PP), it has a tendency to undergo  $\beta$ -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 with lower doses. In this work, commercial polypropylene (iPP) with melt flow index of 10g/10min was irradiated with a <sup>60</sup>Co source at doses of 12.5 and 20 kGy under acetylene to improve melt strength and drawability. The results of mechanical and rheological tests demonstrate that in the sample modified with dose of 20 kGy the predominant phenomena was degradation by chain scission and in the sample modified with dose of 12.5 kGy were branching and crosslinking. So the monofilament of this sample was produced and it was observed an increase of tenacity in relation to the PP pure.

## **Introduction**

Synthetic ropes have undergone a development phase over the last five years. Due to their high performance, polyester ropes have been used in mooring systems<sup>1</sup>. Although polypropylene (PP) has not yet been established itself, it has steadily and surely gained acceptance due to properties such as cheapness, high stiffness, chemical resistance, no environmental pollution when incinerated, good mechanical properties and low specific density (floating)<sup>1-8</sup>. However, the isotactic polypropylene (iPP) is a linear polymer which exhibits low melt strength and poor processing characteristics in extensional flow-dominated processes. These characteristics difficult its processability into filaments for production of ropes. In the specific case of platforms mooring systems, it is necessary filaments of PP with enhanced tenacity and creep properties. In order to use PP in extensional flow-dominated processes, modifications are needed to enhance its strain hardening. It is often assumed that short chain branching (SCB) has little or no effect on the rheological behavior of polypropylene. Even though a very broad molecular weight distribution (e.g. bimodal) can achieve this, it is most efficiently done by the addition of long chain branches (LCB).

High melt strength polypropylene (HMS-PP), name used for the commercial long chain branched PP, has been recently developed and introduced in the market by the major international polypropylene producers. 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. As a consequence different methods have been applied to modify polypropylene by adding long chain branches (LCB) onto backbone<sup>9-14</sup>. The constrained geometry catalyst (CGC) has been found to be very useful for preparing LCB polyolefin, however this method is often used in laboratory. The methods that have been applied in industry to prepare LCB PP are postreactor chemical modifications and ionizing radiation. The Himont process irradiated PP with dose of 10-40 kGy under nitrogen atmosphere (inert) and then the modified PP was submitted to a thermal treatment at 80°C for recombination and 130°C for termination. BRASKEM, brazilian PP producer, together with EMBRARAD, brazilian gamma-irradiator, and the Nuclear and Energy Research Institute (IPEN) polymer group jointed forces to develop a national technology for the production of HMS-PP. The technology obtained comprises the addition of chain branches onto backbone polymer using gamma radiation from a <sup>60</sup>Co source<sup>16,17</sup>. Such irradiation is very convenient in order to improve polymer materials by crosslinking, grafting and chain scission. These reactions occur on account of the rearrangement of radicals formed in the polymer. It is well known that the main effect of gamma rays and polymers interactions is the creation of free radicals, which may further evolve into chain scission with molecular weight decrease, and chain branching with molecular weight increase up to crosslinking. Generally, although all these phenomena coexist, the dominance of each one depends on many factors, such as the initial molecular structure, polymer morphology and experimental irradiation conditions. The balance of branching, grafting crosslinking and scission reactions in polymeric chains exposed to high-energy radiation may result in enhance of properties and new applications. Grafting and branching improve the melt strength of polymers. The formation of a crosslinked network between the polymer chains may enhance thermal and chemical resistance as well as stress cracking. Pp is difficult to crosslink by radiation, because the crosslinking and chain scission reactions proceed at almost the same rate. However,

the efficiency of branching and crosslinking can be improved by adding functional monomers like acetylene, which have carbon-carbon double bond in its molecule<sup>11,12-18</sup>.

Generally, three techniques are used to quantify the level of LCB: C NMR, GPC and Rheology. For NMR, LCB corresponds to chain lengths of six carbon atoms or greater. GPC is insensitive to the high molecular weight species in the molecular weight distribution (MWD), whereas the branched species reside at the high molecular weight species, which makes the GPC inappropriate for very low LCB. So, rheology technique is very prevalent to detect the existence of LCB although it is an indirect method<sup>19-21</sup>.

The main objective of this work was to prepare modified PP by grafting of acetylene in PP with 10g/10min of melt flow index using gamma radiation, and then characterize the modified PP by mechanical, rheological and thermal tests. The linear viscoelastic behavior of these samples was investigated by an oscillatory rheometer. Rheological plots were used to differentiate modified PP qualitatively from linear PP. Melt strength and drawability were determined by Rheotens equipment and the influence of modified PP in fusion and crystallization processes was studied by differential scanning calorimetry.

## **Experimental**

### *Materials*

The commercial isotactic polypropylene was supplied in a granular form by BRASKEM and its melt flow index at 230°C is listed in Table 1.

### *Modified polypropylene preparation*

Acetylene was injected in bags of polyethylene containing the polypropylene. These samples were irradiated with a <sup>60</sup>Co Source from Embrarad, at dose of 12.5 and 20 kGy. After irradiation, the samples were heated for 60 min at 100°C to react residual radicals.

### *Melt flow index*

The melt flow index of the modified polypropylene was measured in a melt flow equipment 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°C (ASTM D 1238-04c).

### *Gel content*

Gel content of the modified polypropylene was determined by extracting the soluble components in boiling xylene containing antioxidant Irganox 1010 for a total of 24 h at 135°C. After that, the residue was dried at 150°C to constant weight for 24 hours. Three samples were used to determine the average gel content for each modified polypropylene (ASTM D 2765-01).

### *Mechanical properties*

The samples were injection molded on a DEMAG Ergotech pro injection molding machine. Table 2 shows the specification, set parameters of the machine and the molding conditions. The tensile samples were dumbbell-shaped with dimensions of 165x13x3 mm<sup>3</sup>, complying with ASTM D 638-03 standard. An EMIC DL 300 universal tensile/compression testing machine equipped with a data acquisition system was utilized to carry out the tensile tests. The speed velocity of testing was 50 mm/min and the tests carried out at a temperature of 23°C. At least six specimens were tested from each condition.

### *Differential scanning calorimetry (DSC)*

The thermal behavior of pure and irradiated polypropylenes was examined in a DSC Metler Toledo apparatus. Samples (10-15 mg) were melted at a heating rate of 10°C/min from -50°C to 200°C under nitrogen atmosphere. After 10 min at 200°C, the polypropylenes samples were crystallized by cooling at a rate of 50°C/min to -50°C and then reheated to 200°C, in accordance to ASTM D-3417.

### *Melt strength and drawability*

In the Rheotens test, the tensile force needed for elongation of an extruded filament was measured as a function of the draw ratio. The Rheotens consists of a pair of rollers rotating in opposite directions. The polymer melt strand

downwards from a capillary die and is drawn by the rotating rollers whose velocity increases at a constant acceleration rate. The polymer melt being stretched undergoes uniaxial extension. The samples were extruded at 190°C in a Haake rheometer (screw diameter) and were tested in a Rheotens Mod. 71.97 Gottfert at 190°C with acceleration of 6 mm/s<sup>2</sup>.

### Rheological measurements

The characterization in shear flow was performed at a temperature of 200°C using rotational Physica rheometer (MCR 300) with parallel-plate geometry of 25mm 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 molding at a temperature of 190°C.

## Results and Discussion

### Melt flow index and gel fraction

**Table 1** – Results of melt flow index and gel fraction

	Melt flow index (g/10min)	Gel fraction
A (pure)	10.0	0
B (12.5 kGy)	15.5	2.0
C (20 kGy)	19.5	1.1

**Table 1** illustrates the influence of radiation process and presence of acetylene monomer on phenomena like chain scission, grafting and crosslinking, expressed by melt flow index and gel fraction. The increase of melt flow index of samples B and C may be attributed to the dominance of chain scission. The gel fraction presented a very low increase for the two doses. Han<sup>18</sup> obtained gel fraction of approximately 60% with doses between 5 and 20 kGy for electron beam irradiated homopolymer with triallylisocyanurate (TAIC) and trimethylolpropane triacrylate (TMPTA). Uenoyama<sup>17</sup> produced crosslinked PP (TAIC and trimethylolpropane trimethacrylate – TMPTMA) with values of gel fraction higher than 55% with high doses. Schulze<sup>19</sup> also produced crosslinked PP with TAIC and high doses. Tian<sup>20</sup> didn't observe gel fraction in samples produced by extrusion of PP with 2,5-dimethyl-2,5(tert-butylperoxy) hexane peroxide and pentaerythritol triacrylate (PETA), but showed that long chains branched were presented. In this study high values of gel fraction were not desired too because the high degree of crosslinking could decrease the drawability and difficult the monofilament process.

### Mechanical properties

**Table 2** – Results of mechanical properties at yield and at rupture

	Tensile strength at yield (MPa)	Elongation at yield (%)	Tensile strength at yield (MPa)	Elongation at yield (%)
A (pure)	27.7 ± 1.4	10.2 ± 1.6	18.5 ± 3.7	576.9 ± 53.8
B (12.5 kGy)	29.4 ± 0.6	8.8 ± 1.1	15.4 ± 1.5	379.8 ± 10.2
C (20 kGy)	26.6 ± 0.7	10.8 ± 1.0	9.0 ± 0.8	443.0 ± 29.4

For iPP, ductile behavior occurs when the polymer is deformed at temperature above  $T_{g,am}$ , and is related with a significant plastic deformation that can be roughly described as a two-step process. The first includes phenomena that are controlled by the mobile macromolecules of the amorphous phase, and the second involves the reorientation and plastic deformation of the crystalline material. Due to the fact that the glass transition temperature of the amorphous phase of iPP is relatively close to the room temperature, the material is more sensitive to external parameters that may have impact on the mobility of the amorphous portion. It is well known that grafting reactions lead to branching and crosslinking preferentially in the amorphous area because the radicals generated in crystalline area cannot encounter with others to react. PP homopolymer is a material that difficult these reactions by gamma radiation due to the high crystallinity. The crosslinking and degradation reactions proceed at almost same rate that can lead to a deterioration of physical properties. The irradiation of PP leads to a greater degree of scission of macromolecules unless an effective co-agent is present. Scission results in a substantial drop in molecular weight and a consequent drop in tensile strength. It was not observed significant modification in yield tensile and elongation of modified samples, **Table 2**, however significant decrease of tensile strength and elongation was observed at rupture that denotes degradation by chain scission. This degradation was verified by increase of melt flow index and crystallization temperature (**Table 3**) and decrease of complex viscosity (**figure 1**) in spite of the increase of melt strength (**Table 4**).

**Table 3** – Results of melt temperature, crystallization temperature and crystallinity by DSC.

	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	Crystallinity (%)
A (pure)	167	110	45.3
B (12.5 kGy)	164	116	43.1
C (20 kGy)	165	110	41.4

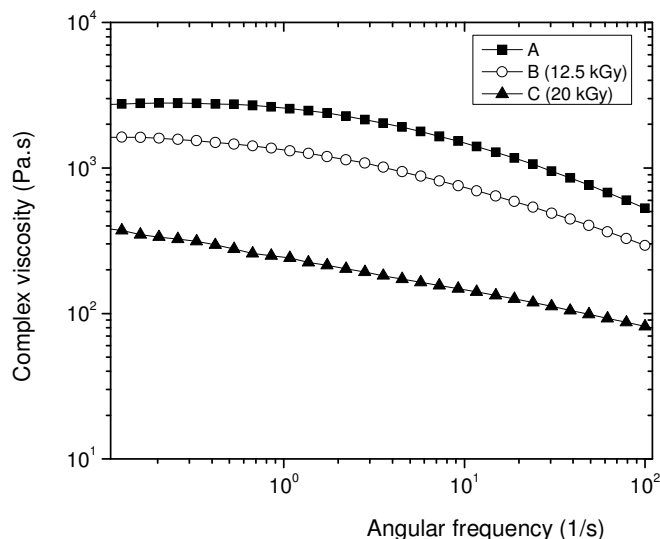
The DSC behavior of the pure resin was almost the same as the modified ones, so only melt temperature (T<sub>m</sub>), crystallization temperature (T<sub>c</sub>) and crystallinity are presented in **Table 3**. The melt temperature decrease with dose but only three degrees for the lower dose, but the crystallization temperature presented an increase of six degrees only for this dose. The thermal behavior didn't show significant modification of crystallinity which denotes that radiation has little effect on the change of crystallinity, as mentioned in other works<sup>22,23-25</sup>, but the variation between the sample C and the pure resin was 10%.

**Table 4** – Results of melt strength and drawability

	Melt strength (cN)	Drawability (cm/min)
A (pure)	3.3	9.2
B (12.5 kGy)	16.7	17.2
C (20 kGy)	6.4	16.2

It was expected that the acetylene added to PP would induce enhancement of the melt strength and drawability by the formation of a branched structure once that there weren't enough crosslinking reactions to promote significant increase of gel content. From results of **Table 4**, the samples B and C showed increase of melt strength and drawability, however the melt strength increase of sample B was more significant. Yoshii<sup>10</sup> modified PP with polyfunctional monomers and 5 kGy of electron beam irradiation and observed that bifunctional monomers with relatively shorter chains were better than longer chain monomers for improve melt strength of PP. The shorter chain monomers such as EGDMA, BBDA and HDDA had more mobility and penetrated into PP, so it could be considered that these monomers reacted effectively with the PP chain upon irradiation. In this work, the short chain monomer acetylene enhanced the melt strength of PP.

#### Rheological measurements

**Figure 1** – Complex viscosity as a function of frequency angular.

The complex viscosity plotted as a function of frequency angular is shown in **Figure 1**. At low shear rates sample A shows a Newtonian behavior with constant viscosity (plateau). The viscosity in the Newtonian regime is called the zero shear viscosity,  $\eta_0$ , which gives valuable information of molar mass. The samples B e C didn't show Newtonian behavior in the frequency range studied but the sample C presented a higher decrease of the viscosity denoting a more

important chain scission. So the rheological properties are dependent of reactions occurred during irradiation process: degradation by chain scission, branching and crosslinking. Due to this, different behaviors were observed by other authors. Lee<sup>21</sup> observed a shear thinning for branched PP compared to the linear polypropylene. The modified PP studied by Sugimoto<sup>22</sup> showed only a decrease of complex viscosity in relation to the unmodified PP. In the samples studied by Tian<sup>20</sup>, the effect of branches on viscosity was clear once there was no evident Newtonian plateau at low frequency and the shear thinning started at lower frequency than that of pure resin. The samples B and C didn't show a Newtonian plateau too, but they presented a lower viscosity which denotes a chain scission and not a branching.

## Conclusion

In this work the results about the molecular modifications induced by gamma irradiation of isotactic polypropylene under acetylene atmosphere were reported, however all the realized tests only proved the existence of branching and chain scission in a qualitative manner. Although the modified samples didn't show significant values of gel fraction, the results of mechanical and rheological tests confirmed the existence of branching. In this study the radiation had little effect on the change of crystallinity, only the crystallinity of sample C decreased 10%.

The molecular structure of irradiated polymers is a result of branching, crosslinking and degradation reactions. For chosen parameters of 12.5 and 20 kGy under acetylene the sample that showed significant increase of melt strength and drawability was that irradiated with the lower dose. These parameters favored the formation of branching and chain scission structures that increased the melt strength and drawability properties.

Monofilaments with sample B were already produced and initial tests determined that there was a significant increase of tenacity.

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