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ORIGINAL PAPER

Controlled degradation and crosslinking of polypropylene induced by gamma radiation and acetylene

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Abstract Isotactic polypropylene (iPP) undergoes crosslinking and extensive main chain scissions when submitted to irradiation. The simultaneous irradiation of PP and acetylene is able to control chain scission and produce grafting. The grafted PP further reacts with PP radicals resulting in branching and crosslinking. In this work, commercial polypropylenes (iPP) of different molecular weights were irradiated with a ^{60}Co source at dose of 12.5 kGy in the presence of acetylene in order to promote the crosslinking. The mechanical and rheological tests showed a significant increase in melt strength and drawability of the modified samples obtained from resins with high melt flow index. The characterization of the molecular modifications induced by gamma irradiation of isotactic polypropylenes under acetylene atmosphere proved the existence of branching, crosslinking and chain scission in a qualitative way. The G' and G'' indicated the presence of LCB in all samples. Therefore, PP irradiation under acetylene was proved to be an effective approach to achieve high melt strength polypropylene (HMSPP).

Keywords Melt strength · Drawability · iPP · Acetylene · Gamma irradiation

Introduction

As described by Clough [1] and by Lugão [2], polymer processing by ionizing radiation leads, essentially, to main chain scission and crosslinking. Both phenomena are known to induce changes in the polymer properties which may be

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used in various applications at distinct process conditions. Such scissons and crosslinking also take place when a polymer is exposed to ultraviolet irradiation (UV) and its rate changes during exposition time [3].

Generally, scission and crosslinking coexist, although the prevalence of each relies on many factors, such as the initial molecular structure, polymer morphology and the experimental irradiation conditions [4]. These factors influence the equilibrium between radiation induced crosslinking and scission reactions. The irradiation process carried out in presence of oxygen at low dose rates results in oxidative scission reactions. In acetylene atmosphere, radicals of irradiated PP react with acetylene to produce the grafting. This graft radical can react with another PP radical creating a crosslinked giant molecule. If the reaction proceeds in large extension, a network of crosslinked molecules shall be formed [5]. On the other hand, if degradation takes place simultaneously with crosslinking in a controlled way, no network will be formed. This partially crosslinked structure may hold very interesting rheological properties. Isotactic polypropylene (iPP) is a non-polar and linear polymer which presents low melt strength and poor processing characteristics, when submitted to processes dominated by extensional flow. Whereas irradiation of iPP under reactive atmosphere causes grafting, under inert atmosphere it promotes chain-scission and long chain branching resulting in enhanced melt strength material [4, 5]. In addition, while grafting may improve the melt strength of polymers; crosslinking may enhances thermal and chemical stability as well as stress cracking resistance. As a consequence, PP producers and laboratories are using the mentioned modifications to enhance strain hardening under extensional flows [4, 6–9].

High melt strength polypropylene (HMSPP) is the name used for the commercial long chain branched iPP, recently developed and introduced in the market by major international polypropylene producers. The polymer melt strength (maximum force at which a molten thread can be drawn under standard conditions before it breaks) is more efficiently achieved by the addition of long chain branches (LCB) [5, 10]. It is often assumed that short chain branching (SCB) has little or no effect on the rheological behavior of polypropylenes.

As a consequence, different methods have been applied in an attempt to modify polypropylenes by adding LCB onto the backbone. HMSPP obtained with constrained geometry catalyst has been recently introduced in the market by Dow Chemical under the trade name of Inspire® [11]. Chisso has introduced in the market their HMSPP grades (Newfoamer® and Newstren®) produced through additions of small amounts of very high molecular-weight polyethylene (PE) to PP via heterogeneous catalysis [12]. Another strategy to add LCB on PPs is the postreactor processing based on chemical and ionizing radiation modifications [13–18]. Twenty-five years ago, Himont, currently part of Basell, developed an ingenious process for HMSPP synthesis based on electron-beam irradiation of PP at dose range of 10–40 kGy under nitrogen atmosphere, thermal post-treatment at 80 °C for recombination and 130 °C for annihilation of residual radicals [18]. IPEN has developed a similar technology for the production of HMSPP which is based on gamma irradiation of iPP at dose range of 5–20 kGy in acetylene (or other conventional multifunctional monomer) atmosphere with the same thermal post-treatment [19, 20].

PP is difficult to crosslink by radiation due to the fact that crosslinking and chain scission reactions do proceed at almost the same rate. However, the branching and crosslinking efficiency can be improved by adding multifunctional monomers like acetylene, which are equivalent to 2 carbon-carbon double bond in its molecule [13, 14, 20, 21]. Uenoyama et al. [22] produced crosslinked PP with (triallyl-isocyanurate –(TAIC) and trimethylol-propane-trimethacrylate –(TMPTMA) with gel fraction values higher than 55% at high doses. They also observed that a rapid cooling from the molten state which reduces the crystallinity had favored the crosslinking of polypropylene copolymers with TAIC under gamma irradiation. On their turn, Han et al. [23] obtained gel fraction of approximately 60% at doses between 5 and 20 kGy for electron beam irradiated homopolymer with triallylcyanurate (TAC) and trimethylol-propane-triacrylate (TMPTA). Schulze et al. [24] also managed to produce crosslinked PP with TAIC by using high doses. The groups mentioned above have indeed developed a technology to create fully crosslinked network as thermoset shaped products. Otherwise there is radiation technology to produce partially crosslinked network understood as LCB based structure that confers thermoplastic behavior to the polymer.

Three techniques are in general used to quantify the level of LCB: ^{13}C nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and rheology. For NMR, LCB corresponds to chain lengths of six carbon atoms or more, but NMR is not a sensitive method for low concentration of long-branches. GPC is used with limitations to detect high molecular weight species in the molecular weight distribution (MWD). Long-branched species reside also at high molecular weight species, which makes the GPC not the best choice for very low LCB content. Considering those facts, rheology technique is the most likely to detect the existence of LCB, although it is an indirect method [24–26].

The main objective of this paper was to study the role of radiation and acetylene on the LCB formation of iPP with distinct molar masses (Mw) related to different values of melt flow index (MFI). The linear viscoelastic behavior of these samples was investigated by an oscillatory rheometer. Various rheological plots were used to differentiate qualitatively modified iPPs from linear iPP. Melt strength and drawability were determined by Rheotens equipment and differential scanning calorimetry (DSC) was employed to study the influence of controlled radiation degradation of iPP in its fusion and crystallization processes.

Experimental

Materials

The commercial isotactic polypropylenes were supplied in a granular form by Braskem, which melt flow indexes at 230 °C and Mw are listed in Table 1. According to the producer, resin A is visbreaking type, so it had a narrow molecular weight distribution. Resins B, C, D and E are conventional iPP with broad molecular weight distribution.

Table 1 Melt flow index, molecular mass average (Mw) and molar mass distribution (MWD) of resins

Resin	MFI (g 10^{-1} min^{-1}) (±0.5%)	M_w (g mol^{-1})	MWD (M_w/M_n)
A	24.0	223,183	4.02
B	10.0	228,105	4.95
C	3.5	303,000	4.66
D	1.5	338,000	5.30
E	0.5	340,000	5.01

M_w weight-average molecular weight, M_n number-average molecular weight

Modified polypropylene preparation and gel fraction

Isotactic polypropylene (iPP) was placed in thermal resistant bags with acetylene under pressure of 110 kPa, for irradiation procedure. These samples were irradiated with a ^{60}Co source from Embrarad, at dose of 12.5 kGy and 5.72 kGy h^{-1} dose rate. After irradiation, the samples were heated for 60 min at 130 °C to promote the recombination and annihilation of residual radicals. In the following text, the samples modified by γ-irradiation in acetylene are denoted as HMS-PPs.

The gel content of the modified polypropylenes was determined by extraction of soluble components in boiling xylene containing antioxidant Irganox 1010 for period of 12 h at 135 °C. After that, the residue was dried for 24 h at 150 °C or until constant weight. 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 in a DEMAG Ergotech pro injection molding machine. The set of parameters for the machine and the molding conditions were as follows: screw diameter = 35 mm; L/D screw = 3.3; injection pressure = 100 bar; nozzle temperature = 213 °C and 50–60 °C for the mold surface temperature. The tensile test samples were dumbbell-shaped with dimensions of $165 \times 13 \times 3$ mm^3, complying with ASTM D 638-03 standard.

Tensile tests were carried out at EMIC DL 300 universal tensile/compression testing machine equipped with a data acquisition system, and the speed velocity of testing was 50 mm/min at room temperature; at least six specimens were tested from each sample.

Differential scanning calorimetry (DSC)

The thermal behavior of pure and irradiated polypropylenes was examined in a DSC Mettler Toledo apparatus. The samples (10–15 mg) were heated from −50 to 200 °C under nitrogen atmosphere at heating rate of 10 °C min^{-1}. After 10 min at 200 °C, the polypropylene samples were crystallized by cooling at a rate of 50 °C min^{-1} to −50 °C and then reheated to 200 °C, according to ASTM D-3417. DSC apparatus was calibrated with Indium (m.p. 156.61 °C; $\Delta H = 28.54$ kJ kg^{-1}). Crystallinity was calculated according to Eq. 1:

$$Xc(\%) = \frac{\Delta H_f \times 100}{\Delta Ho} \tag{1}$$

$\Delta H_f =$ melting enthalpy of the sample, $\Delta Ho =$ melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1}.

Melt strength and drawability

In the Rheotens test performed, the tensile force needed for elongation of an extruded filament was measured as a function of the draw ratio, while the polymer melt has been stretched underwent uniaxial extension. The Rheotens test consists of a pair of rollers rotating in opposite directions. The polymer melt strand downwards from a capillary die is drawn by the rotating rollers, whose velocity increases at a constant acceleration rate. The samples were extruded at 190 °C in a Haake rheometer and then tested in a Rheotens Mod. 71.97 (Göttfert) at 190 °C with an acceleration of 6 mm s^{-2}.

Rheological measurements

The analysis of melt flow index of the samples was accomplished in a MFI apparatus CEAST according to ASTM D 1238-04c.

Samples 1.2 mm thick and 25 mm disk were produced by compression moulding at 190 °C and fast cooled by a water bath. The characterization in shear flow was performed at 200 °C using rotational Physica rheometer (MCR 300) with parallel-plate geometry of 25 mm in diameter and 1.0 mm gap. The test was performed in the frequency range 0.1–100(1/s) with a strain of 5%.

Gel permeation chromatography measurements

GPC measurements were performed in HPLC Waters 150CV using 1,2,4 trichlorobenzene as solvent and styragel column HT-6E :5,000–1,0000000 Daltons. Injection temperature was 140 °C and detector was RI. Calibration curve was performed within PS standards from Shodex Standard.

Results and discussion

Melt flow index and gel fraction

Table 2 illustrates the influence of irradiation process, in presence of acetylene monomer, on melt flow index and gel fraction.

Samples A, C and E revealed an increase in gel fraction, although MFI remained constant or even decreased. Therefore one can assume that there was competition between grafting, crosslinking and chain scission. The HMSPP sample from resin E was the only one showing a marked decrease in MFI. Considering the difficulties in having homogeneous flow of very high molecular weight resins, the difference

Table 2 Results of melt flow index and gel fraction

Resin	MFI (g 10^{-1} min^{-1}) (±1%)		Gel fraction (%) (±0.1)	
	PP	HMSPP	PP	HMSPP
A	24.0	19.9	0	2.0
B	10.0	15.5	0	2.0
C	3.5	3.5	0	1.5
D	1.5	2.5	0	1.9
E	0.5	0.1	0	1.5

should be attributed to experimental error. On the other hand, samples B and D confirmed main chain scission is a dominating process owing to significant increase in their MFI values in spite of gel fraction enhancement.

In contrast to the absent gel fraction in the virgin resins, all HMS samples were quite similar in low gel content. In terms of PP processing and drawability, resins of near zero values of gel fraction are advantageous. These results were in accordance with Tian et al. [26] work, in which similar gel fraction results were observed in samples produced by extrusion of PP with 2,5-dimethyl-2,5(tert-butylperoxy) hexane peroxide and pentaerythritol triacrylate (PETA), i.e. at conditions that confirmed the presence of long branched chains.

Mechanical properties and DSC

The tensile strength at yield is not affected significantly according to Table 3 except for HMS-E, even though the yield elongation decreased for all modified samples. It was not possible to obtain the mechanical properties at rupture for sample A due to the very high elongation up to the rupture (>500%).

Sample A was similar to B and D due to stable values of tensile strength at yield and the same pattern of decrease in elongation at yield after modification. Yet, while HMS A presented a huge decrease in elongation at break, HMS B and D presented a small increase. The small decrease in elongation at yield of all samples could be explained by some rupture in tie molecules after irradiation, as the mechanical properties at yield are mostly related with crystallinity. On the other hand, the significant plastic deformation means that happened a ductile rupture which can be roughly described in a two-step process. One step includes phenomena that are controlled by the mobile macromolecules of the amorphous phase and the other step involves the reorientation and plastic deformation of the crystalline material. Due to the fact that the glass transition temperature of iPP is relatively close to the room temperature, the material is more sensitive to structural or morphological modifications induced by radiation; for example, the presence of small number of crosslinked molecules can dramatically reduce the elongation and increase the tensile strength at break. HMS B and D displayed opposite behaviors which agree with the increase in the results of MFI in consequence of dominant main chain scission for these samples.

Table 3 Mean values and standard deviations of mechanical properties at yield and rupture

	Tensile strength at yield (MPa)	Elongation at yield (%)	Tensile strength at rupture (MPa)	Elongation at rupture (%)
A	30.0 ± 0.7	9.4 ± 0.8	Does not break	>500%
HMS-A	30.4 ± 0.3	7.4 ± 0.4	16 ± 1	250 ± 17
B	31.8 ± 0.5	8.8 ± 0.7	14 ± 1	82 ± 14
HMS-B	31.6 ± 0.3	6.9 ± 0.2	13 ± 1	112 ± 9
C	29.9 ± 0.5	8.9 ± 0.2	15 ± 1	59 ± 6
HMS-C	32.6 ± 0.9	6.1 ± 0.5	20 ± 2	31 ± 6
D	30.5 ± 0.4	9.9 ± 0.7	17 ± 1	52 ± 12
HMS-D	30.0 ± 0.9	7.2 ± 0.4	13 ± 1	85 ± 4
E	31.0 ± 0.4	8.8 ± 0.6	13 ± 3	63 ± 6
HMS-E	35.0 ± 0.4	6.3 ± 0.5	28 ± 2	16 ± 3

The DSC results of the studied samples were almost the same and although they had different molecular mass and molecular weight distribution, all pure resins had similar values of melting temperature and crystallinity (Table 4). HMS-B, HMS-C and HMS-D presented little decrease on crystallinity in relation to the respective pure resins, HMS-A was the more significant difference, 42–38%. The decrease in crystallinity was attributed to branching and crosslinking. Samples HMS-B and HMS-D showed a decrease in tensile strength and increase in elongation that denotes degradation by chain scission confirmed by an increase in the crystallization temperature. For instance, the increase in tensile strength and decrease in elongation at rupture were observed for HMS-C and HMS-E, although not confirmed by the MFI values. DSC results show small changes in crystallinity and no significant modifications in melting or crystallization temperature. In agreement with this, the morphology is only affected in a minor extension in the range of radiation dose used as it has already been observed by other authors [26–29]. Therefore, the main

Table 4 Results of melt temperature and crystallinity obtained by DSC

	T_m (°C)	Crystallinity (%)[a]	T_c (°C)
A	166	42	112
HMS-A	165	38	111
B	167	43	110
HMS-B	166	41	116
C	167	44	112
HMS-C	167	41	109
D	168	44	109
HMS-D	167	42	112
E	166	43	115
HMS-E	167	43	113

[a] Error = ±5%

differences in mechanical properties should be attributed to crosslinking, branching and chain scission rather than to crystallinity changes.

Melt strength and drawability

Melt strength increases as the molecular weight distribution (MWD) becomes broader and it is well known that not only the increase in the average molecular weight (M_W) of a polymer results in higher melt strength [1], but also in lower MFI. The increase in M_W is associated with a decrease in MFI (Table 1) and an increase in melt strength (Table 5). All HMS samples exhibited an increase in melt strength and drawability; the observed effect was higher for iPPs with lower molecular weight, which was probably connected with higher concentrations of LCB on iPP chains as discussed bellow. The increase in melt strength of each HMS depends, in part, on the low crosslinking level achieved. On the contrary, the sound increase in melt strength and drawability values confirms the presence of long chain branching resulting from the main radiation modification in presence of acetylene monomer which is in agreement with the literature [2].

Samples D and E showed high values of melt strength, but their drawability was not so expressive. Therefore such samples were more suitable for elongation processing when drawability is the main parameter.

Yoshii [10] has irradiated iPP with accelerated electrons at different doses with polyfunctional monomers (PFM) and observed that high concentrations of PFM led to a network structure of PP by crosslinking. On the other hand, PP modified with lower concentrations of bifunctional monomers displayed higher melt strength without crosslinking at dose of 1 kGy. As the monomers with smaller size such as EGDMA, BBDA and HDDA were able to diffuse faster into PP, one could draw the conclusion that these monomers reacted effectively with the PP chain upon irradiation. In the same manner, the short chain monomer acetylene favored the diffusion into PP bulk and, reacting with PP radicals, produced a branched structure which, in consequence, enhanced the melt strength of different PPs tested.

Table 5 Results of melt strength, drawability and melt flow index

	Melt strength (cN)	Drawability (cm min^{-1})	MFI (g 10^{-1} min^{-1})
A	0.9	8.2	24.0
HMS-A	11.4	16.9	19.9
B	3.3	9.2	10.0
HMS-B	16.7	17.2	15.5
C	8.2	9.4	3.5
HMS-C	44.3	12.6	3.5
D	17.8	9.4	1.5
HMS-D	58.6	10.8	2.5
E	91.2	4.4	0.5
HMS-E	95.7	8.2	0.1

Rheological measurements

In a review concerning the effect of LCB on the linear viscoelasticity of polyolefins recently published by Vega et al. [11] it was shown that the introduction of LCB induces higher elastic modulus than a broad molecular weight distribution in polymers with similar mass weight. The complex viscosity plotted as a function of angular frequency is presented in Fig. 1. At low shear rates the melts of samples A, B, HMS-A and partially HMS-B present a Newtonian behavior (plateau). The viscosity in the Newtonian regime is called the zero shear viscosity, η_o, which gives valuable information of molar mass. The slope of the flow curve of HMS-A became steeper with increase in frequency. The complex viscosity was higher than that of sample A at low frequency, while it was smaller at high frequency. In fact this is a typical behavior of a polymer with long chain branching (LCB). As for the samples C, D, E, HMS-C, HMS-D and HMS-E, they did not display a Newtonian behavior in the angular frequency range studied, probably due to their higher molecular weight.

Rheological properties depend upon the following reactions that occur during irradiation process: degradation by chain scission, branching and crosslinking. Due to those reactions, different behaviors have been observed by other authors. Lee [30] observed a shear thinning for branched PP compared to the linear polypropylene; the modified PP studied by Sugimoto [25] only displayed a decrease in complex viscosity in relation to the unmodified PP; in the samples studied by Tian [26], 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, similar to the result obtained by the samples A and HMS-A in the present paper.

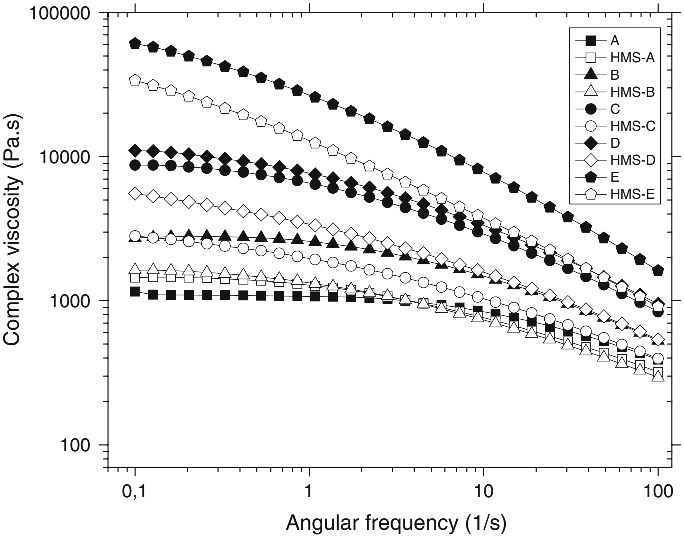

Fig. 1 Complex viscosity as a function of angular frequency for pure polypropylenes and HMS-PPs

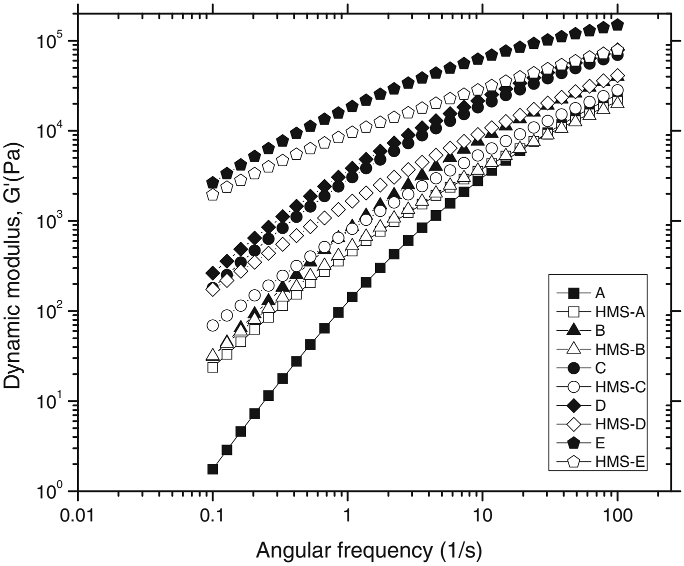

Fig. 2 Dynamic modulus as a function of angular frequency for pure polypropylenes and HMS-PPs

The dynamic modulus (storage) and the loss angle are both sensitive to LCB. In the terminal zone, where only the longest relaxation times contribute to the viscoelastic behavior, G' of linear polymers follow the well-known frequency dependence, i.e., $G' \propto \omega^2$. Besides, the dynamic modulus (G') is not affected at higher frequencies, where it approaches a rubber plateau. Figure 2 shows the G' of all samples plotted as a function of frequency. The dynamic modulus has also indicated a similar behavior of complex viscosity. All modified samples revealed values of this property lower than their respective pure resins, with exception of HMS-A. While the values of dynamic modulus were higher than that of sample A at low frequency, they were smaller than that of sample A at high frequency. Finally, the non-terminal behavior of this sample suggested that there has been a longer relaxation mechanism, which can be ascribed to the presence of long chain branches.

The plot of tan $\delta = G''/G'$ as a function of frequency has been used as a rheological probe for the presence of LCB. All curves were ascending with the frequency decreasing in Fig. 3. Although the modified samples showed a sharp decrease in tan δ at low frequency, they did not show the plateau observed by Tian [26] and Graebling [31], who attributed this behavior to the grafting of long chain branches on the backbone PP with consequent terminal relaxation time increase. Therefore, the G' and G'' indicated presence of LCB in all HMS samples.

LCB formation is favorable to the improvement in both Mw and MWD. In fact the GPC of HMS resins has demonstrated an increase in molecular weight of HMS-A from 223183 to 299265, in minor extension in HMS-B, from 228105 to 295074, and not significantly in the others. Molecular weight distribution values for both cases changed pronouncedly: HMS-A from 4.02 to 7.01 and HMS-B from

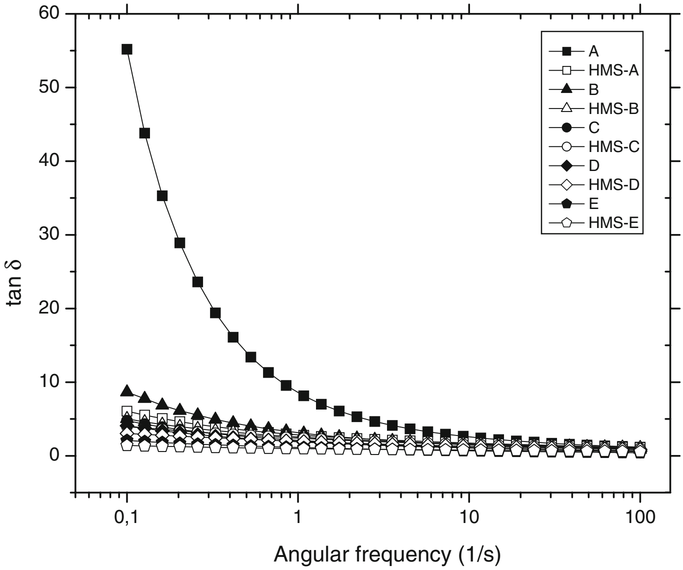

Fig. 3 Tan δ as a function of angular frequency for pure polypropylenes and HMS-PPs

4.94 to 7.40. The fact that gel fraction did not change as much (Table 2), indicated that branching processes predominated over crosslinking. On the other hand, the diminution of melt flow index and tan δ, and the increase in melt strength corresponded to the growth of the molecular weight.

Conclusion

In this work, the results in molecular modifications induced by gamma irradiation of isotactic polypropylenes under acetylene atmosphere were reported. All the performed tests proved the existence of branching, crosslinking and chain scission only in a qualitative manner. The modified samples showed low values of gel fraction, while the results of mechanical and rheological tests confirmed the existence of branching and crosslinking. In terms of crystallinity, only sample HMS-A portrayed a significant 10% decrease.

The molecular structure of irradiated polymers is a result of branching, crosslinking, and degradation by chain scission reactions. For the specific chosen conditions of 12.5 kGy and acetylene, the samples that presented a significant increase in both melt strength and drawability were resins with high melt flow index (A and B). Those properties were promoted in consequence of LCB formation and increase in both molecular weight dispersion and molecular weight after irradiation modification.

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