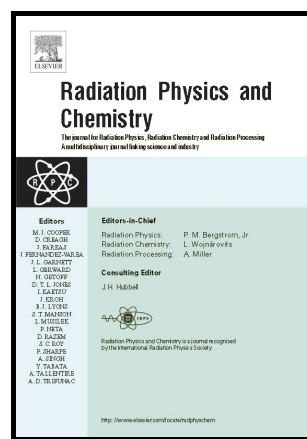# Author's Accepted Manuscript

Rheological Analysis of Irradiated Crosslinkable and Scissionable Polymers Used for Medical Devices under Different Radiation Conditions

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Rheological Analysis of Irradiated Crosslinkable and Scissionable Polymers Used for Medical Devices under Different Radiation Conditions

A.J. Satti [a),b),*], J.A. Ressia [b),c)], M.L. Cerrada [d)], N. A. Andreucetti [a)], and E.M. Vallés [b)]

[a)] INQUISUR (UNS-CONICET) – Alem 1253 - (8000) Bahía Blanca – Argentina
[b)] PLAPIQUI (UNS-CONICET) – Camino La Carrindanga km 7 - (8000) Bahía Blanca – Argentina.
[c)] Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) – (1900) La Plata - Argentina
[d)] Instituto de Ciencia y Tecnología de Polímeros (ICTP–CSIC), Juan de la Cierva 3, Madrid, 28006, España.
*corresponding author

angel.satti@uns.edu.ar ; jressia@plapiqui.edu.ar ; mlcerrada@ictp.csic.es ; andreuce@criba.edu.ar ; valles@plapiqui.edu.ar

ABSTRACT

The effects on different synthetic polymers of distinct types of radiation, gamma rays and electron beam, under different atmospheres are followed by changes in their viscoelastic behavior. Taking into account the two main radioinduced reactions, crosslinking and scissioning of polymeric chains, liquid polydimethylsiloxane has been used as example of crosslinkable polymer and semi crystalline polypropylene as example of scissionable polymer. Propylene - 1-hexene copolymers have been also evaluated, and the effects of both reactions were clearly noticed. Accordingly, samples of those aforementioned polymers have been irradiated with ^{60}Co gamma irradiation in air and under vacuum, and also with electron beam, at similar doses. Sinusoidal dynamic oscillation experiments showed a significant increase in branching and crosslinking reactions when specimens are irradiated under vacuum, while scissioning reactions were observed for the different polymers when irradiation takes place under air with either gamma irradiation or electron beam.

Keywords: rheology, gamma irradiation, electron beam, vacuum, polydimethylsiloxane, metallocenic polypropylenes.

1. INTRODUCTION

Motivated by the useful modifications that ionizing radiation may induce on commercial polymers, the effects of radiation on these materials have been subject of extensive research. The high molar masses exhibited by these materials provokes that comparatively low radiation doses may induce significant changes in their properties. In addition, this approach is, on one hand, economically advantageous and, on the other hand, environmentally friendly when compared with other chemical modification techniques since it avoids the use of elevated temperatures and reagents. The irradiation facilities usually available for these processes: gamma rays of ^{60}Co and electron beams (EB) lead to the formation of very reactive intermediates. The ultimate effects of the involved reactions can be the formation of oxidized products and/or, grafting, scissioning of main chains or crosslinking.

These radioinduced reactions affect the molecular weight, molecular weight distribution and, consequently, the structural and physical properties of the treated material (Andreucetti et. al., 1998, 1999; Charlesby, 1960; Dole, 1972; Li et. al., 2002; Machi, 1995; Perraud et. al., 2003; Portnoy, 1996; Satti et. al., 2008, 2010a, 2010b, 2010c, 2012, 2015, 2016; Vallés et.al., 1990; Maeda et al., 2016). As a result, polymers are generally classified into those that predominantly lead to formation of crosslinking between their chains and those that primarily degrade under the effect of radiation. The degree of these transformations depends on the polymeric structure and the conditions of treatment before, during and after irradiation. The yield of radioinduced reactions may differ depending on dose rate, oxygen availability and treatment duration. Irradiation at low dose rates under vacuum minimizes scissioning and promotes chain enlargement and crosslinking (Sarcinelli et al., 1997; Spadaro and Valenza, 2000). Irradiation at ambient conditions under air is, however, more common, and the use of EB accelerates the time of processing by increasing the dose rate at an order of 10^5 kGy/h (against 10 kGy/h, for ^{60}Co) (Portnoy et al., 2007).

Some polymers such as poly(dimethylsiloxane) (PDMS) and poly(ethylene) are prone to crosslink while others like poly(propylene) (PP) and poly(methylmethacrylate) are more likely to undergo chain scissioning and degradation. Molar masses of the former polymers increase significantly, and can even lead to a crosslinked insoluble material (gel) at certain radiation dose (the gel dose, D_{gel}) (Charlesby, 1960). Therefore, the final properties of these polymers can be significantly modified and/or enhanced by using radiation just as a simple post-reactor process. As a result, for example, the viscoelastic properties of polyethylene are increased by irradiation processes (Satti et. al., 2008, 2010a, 2010b, 2012, 2015, 2016). PDMS can be transformed from a liquid polymer to a solid elastomer, giving rise to a wide range of applications (Charlesby, 1960; Mashak and Taghizadeh, 2006; Satti et. al., 2008, 2010c, 2015; Woo and Sandford, 2002). Morever, the biocompatibility of PDMS makes it one of the more functional polymers for medical applications whose properties can be enhanced by radiation in order to fabricate specific medical devices (Nicolson and Vogt, 2001, Birkefeld et al., 2004, Van den Kerckhove et al. 2001, Aziz et al.,2003; Fuand Kao, 2010; Mashak and Rahimi, 2009). The use of irradiation has the additional advantage to be a very effective sterilization process.

Poly(propylene) is also extensively used for medical supplies and packaging applications that requires to undergo sterilization (Auhl et al., 2004; Fintzou et al., 2006; Abraham A.C. et al, 2010; Makuuchi et al., 2012; Portnoy, 1996, 1999; Portnoy et al., 2007). Because of its high content of tertiary carbons, PP lies in the category of polymers that predominantly undergo scissioning when it is irradiated. Consequently, its molecular weight decreases considerably leading to important losses in the mechanical and viscoelastic properties (Cerrada et al., 2010). A way to revert this drawback is by adding specific multifunctional and nucleating agents that provide crosslinking reactions during the irradiation process resulting in PP with improved mechanical response and viscoelastic properties (DeNicola et al., 1995; Shukushimaa et al., 2001; Gao et al., 2002, Mousavi S.A. et al. 2010).

Previous studies performed in isotactic metallocenic short branched polypropylenes (miPP) showed, however, that a significant degree of branching and crosslinking, with improved viscoelastic properties can be obtained by irradiation without requirement of chemical agents (Satti et al., 2012). Thus, the effect of high energy radiation on miPP and its copolymers is an important topic of research that must be explored in detail because the commercial importance of PP and its derivatives. Propylene–α–olefin copolymers synthesized by metallocenic catalysts systems have many advantages, if compared with copolymers obtained by multi-site Ziegler–Natta catalysts (Suhm et al., 1998; Bubeck, 2002). They show well defined structures, homogeneous comonomer distribution, a narrow polydispersity (PD), and the desired tacticity. In addition, the metallocenic synthesis allows introduction of different lengths of α-olefin comonomers during polymerization, such as 1-butene, 1-hexene, 1-octene or 1-octadecene, among others. As a result, short chain branches with the desired length can be randomly incorporated in the growing chain, leading to copolymers with a wide range of potential applications (Bensason et al., 1996; Wang et al., 2001; Kaminsky and Laban, 2001; Kaminsky, 2004).

For such reasons, it becomes then clear that a better understanding of the changes induced by irradiation on some of these polymeric materials is crucial to be able to control the multiple variables that take part in this process. The aim of this investigation consists of getting a better understanding on the influence of either type of irradiation (gamma vs EB radiation under air) or the environment (vacuum vs air) for gamma radiation, mainly in the viscoelastic properties of both, PDMS and miPP, commercial and synthetic homo and copolymers.

2. EXPERIMENTAL

The propylene homopolymer (iPP) and copolymers with 1-hexene (iPPH4 and iPPH9) described in Table 1 were synthesized in a 1 l Buchi glass reactor under continuous

Table 1: Results obtained for the propylene polymers.

	M_w (kDa)[a]	PD[b]	X_c (%)[c]	T_m (°C)[c]
PDMS1	141.0	1.8	-	Nm
cmiPP	122.3	2.1	57	145
iPP	149.4	2.0	71	151
iPPH4 (3.7[d] mol%)	151.6	1.7	38	115
iPPH9 (9.2[d] mol%)	110.8	2.1	17	76

[a]SEC-MALLS, [b]SEC-RI, [c]DSC, [d] ^{13}C-NMR. Nm: Not measured.

stirring of 1000 rpm at 40 °C. The total propylene pressure was 3 bar. The catalyst/co-catalyst used for this synthesis was $Me_2Si(2$-Me-Ind$)_2ZrCl_2$/MAO, and toluene as solvent. Tacticity and the amount of comonomer incorporated in the copolymers was estimated by ^{13}C NMR at 90 °C using a VARIAN INOVA 300 spectrometer operating at 75 MHz (Quijada et al., 2005). Table 1 shows the obtained results. The nomenclature used to identify the copolymers is of the type iPPH# where H means 1-hexene and # is related to the molar incorporation of comonomer in the copolymer. The synthesized homopolymer is identified as iPP; the commercial one as cmiPP, and the commercial PDMS as PDMS1 (Petrarch Systems inc.).

Molecular weights were determined by size exclusion chromatography (SEC) in a Waters 150C ALC/GPC equipped with three PLgel Mixed-A 300x7.5 mm^2 20 μm columns (Polymer Laboratories). Two detectors were used, a refractive index detector—RI (Waters) and a multi angle laser light scattering—MALLS (Dawn DSP, Wyatt Technology Corporation). The analyses were performed with 1,2,4-trichlorobenzene at 135 °C for propylene polymers, and with toluene at 30 °C for PDMS1. The columns were calibrated with narrow molar mass distribution standards of polystyrene (Pressure Chemical) and polyethylene (NIST). Flow rate was always 1.0 ml/min.

Degree of crystallinity (X_c) and melting temperature (T_m) were determined by differential scanning calorimetry, DSC, using a Perkin-Elmer Pyris 1 calorimeter under argon atmosphere and calibrated with indium and *n*-heptane standards. In order to ensure the same thermal history for all samples, they were first heated from 25 to 200 °C at 10 °C/min, maintained

at 200 ºC for 2 min, and then cooled down from 200 to 10 ºC at 10 ºC/min. After this treatment, the samples were heated again at the same heating rate and the corresponding endotherms were recorded between 10 and 200 ºC. T_m and enthalpy of melting (ΔH_m) were obtained from the thermograms, and the degree of crystallinity of the copolymers was calculated taking a ΔH_m value of 148 J/g for the melting enthalpy of 100% crystalline iPP (Monasse and Haudin, 1995).

The propylene polymers samples were compression-molded to 1 mm thick flat sheets using a hydraulic press at 180° C for 2 min and a maximum pressure of 10 MPa. Then, the sheets were allowed to cool at room temperature outside the press. Liquid PDMS was used as received. All PP and PDMS samples were placed inside Pyrex tubes. Those for irradiation under vacuum were attached to a vacuum glass line, and left under high vacuum up to 24 hours. The samples were then sealed in those same tubes.

Irradiation of the samples was performed at room temperature. Gamma irradiation was performed in the Centro Atómico Ezeiza (CAE) through a ^{60}Co γ-source, with a 10 kGy/h dose rate. Electron beam (EB) irradiation of PP was carried out at IONISOS Ibérica (an industrial installation), with 10^4 kGy/h as dose rate, using a 10 MeV Rhodotron accelerator. EB of PDMS was performed at CRITT AERIAL in Schiltigheim France, using a 2.2 MeV EB accelerator (Model AS2000 from HVEC). This sample was irradiated inside a closed LDPE 1 mm thick bag, also at 10^4 kGy/h. In order to ensure undetectable levels of long-lived radicals, all irradiated samples were annealed after the irradiation for 2 h at 140 ºC or higher (Satti et al., 2008), and under nitrogen flux for the air irradiated samples.

The rheological characterization of the melted polymers was carried out under a nitrogen atmosphere in a Rheometrics RDA-II rheometer with 25 mm parallel plates geometry. The viscoelastic properties of the polymers (the elastic modulus G′, the viscous modulus G″ and the dynamic viscosity η′) were measured in small-amplitude oscillatory shear flow as a function of frequency and temperature. The frequencies covered were in the 0.01 s^{-1} to 500 s^{-1} range. The temperature ranges were varied according to the melting point of the different copolymers (160-220º C for iPP and cmiPP, 140-180° C for iPPH4; 100-160º C for iPPH9; and 30-120 ºC for PDMS1). To ensure the linear relation between stress and deformation, small strains were used in all the dynamic tests, which were selected from previously performed strain sweeps.

A Nicolet 520 FTIR Spectrometer was used in order to find any functional change in the irradiated samples. For this purpose, films were prepared by melt pressing the materials at 150° C using a hydraulic press. The spectra were recorded at a 4 cm^{-1} resolution over the range of 4000-400 cm^{-1} with air as background.

3. RESULTS AND DISCUSSION

The effects of radiation on the polymers were studied by following the changes in their viscoelastic behavior. These changes are due to the scissioning, branching and crosslinking reactions induced by the different irradiation conditions. Scission reactions reduce the molecular weight of the polymer. This modification results in lower values on the region of the Newtonian plateau of the dynamic viscosity (η′). By contrast, crosslinking reactions increase the molecular weight and the degree of branching of the irradiated polymer. Therefore, significant changes on the dynamic viscosity in the low shear rate region are noticeable. η′ increases in this region and it is usually more difficult to reach a plateau due to the significant raise in the relaxation times induced by long branches.

The impact on the rheological properties found in the different propylene derivatives (homo and copolymers) by the various conditions of irradiation explored in this work is shown in figures 1 and 2. Samples irradiated in air, either with a ^{60}Co γ-source or with electron beam showed lower values of η′ in the entire frequency range analyzed. This was also observed in other kinds of propylene polymers irradiated in air (Otaguro et al., 2010). This is due to the prevalence of scission reactions that are favored when irradiation takes place in the presence of oxygen. Since no changes were observed by FTIR on any functional band of the original polymers, a termination reaction as the one proposed by Otaguro et al. (2010) could be happening:

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow \text{Inactive products} + O_2$$
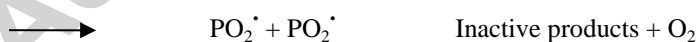
The vacuum gamma irradiated iPP at an identical dose of 20 kGy exhibits lower η′ values than those found in the pristine synthetic polymer but significantly higher than the ones presented in the sample irradiated in air (Figure 1a). This behavior is not observed in the commercial cmiPP homopolymer (Figure 1b). The vacuum irradiated cmiPP sample shows a slight increase of η′ at the low shear rate region that could be attributable to an increase in molecular weight as a consequence of branching formation. The results from the irradiation in air on this cmiPP polymer are coincident with those obtained for the synthesized iPP sample. These air-irradiated specimens display a significant decay of η′ values on the entire frequency range, revealing the predominance of scission reactions. A similar result is obtained when the polymer is irradiated in air by means of an EB source. We should emphasize that a viscosity plateau at low shear rate is not reached for the commercial cmiPP. This may be due to the presence of branches or to a high molecular weight tail existing in the commercial polymer. As shown in Table 1, another difference between iPP and cmiPP is the degree of crystallinity. Incorporation of additives, like for instance antioxidants, should be also taken into account in the commercial polymer. The combined effect of these aspects may be also the reason for the different behavior of the polymers irradiated under vacuum.

Figure 2 plots η′ against frequency for copolymers iPPH4 and iPPH9. In both of copolymers, irradiation in air leads

also to a decrease in the dynamic viscosity values pointing out the prevalence of scissioning. Contrasting with the irradiation in air, the results from irradiation under vacuum reveal a significant increase in the viscosity values, especially at the low frequency region. This outcome is a consequence of crosslinking and branching reactions of the copolymers chains. The raise in η´ is more noticeable on iPPH9, the copolymer whit higher hexene content. The main structural differences between both copolymers are the higher comonomer amount as well as the lower crystallinity and the distinct polymorphs that can be generated in solid state for the iPPH9 copolymer (Cerrada et al., 2009).

Therefore, the more reasonable explanation should be the distinctive micro-structural details that affect among other characteristics, the degree of crystallinity. The presence of comonomeric units disturbs the regularity of the macrochains. The length of the PP sequences is reduced
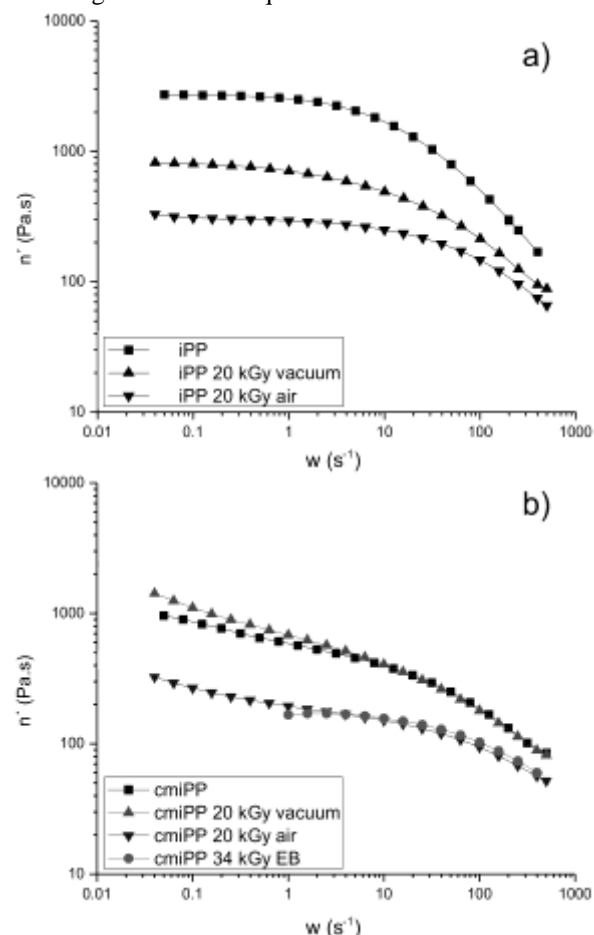

Figure 1: η´ against frequency (180º C) for unirradiated and irradiated homopolymers: a) iPP and b) cmiPP.

and, accordingly, crystallinity degree decreases as well as mobility increases within the chains. This feature might promote the interchain crosslinking reactions leading to the predominance of crosslinking over scissioning (Satti et al., 2012). The higher chain mobility is also reflected by a decrease of the Tg to below -12 ºC for iPPH9, if compared to the homopolymer (López-Majada et al., 2006).

This tendency to obtain a major degree of crosslinking as the amorphous content of the polymers gets higher is also observed in the air irradiated samples. As a result, the decrease between η´ of the original and air irradiated samples, in the entire frequency range, is higher in iPP than in iPPH4, and the effect in the latter higher than for iPPH9.

Reduced van Gurp-Palmen (rvGP) plots of irradiated iPP and iPPH9 are shown as examples in Figure 3. For this purpose, the shift angle δ was plotted versus the reduced complex modulus Gred (Gred=G^*/ G_N^0 with G_N^0= 0.4 MPa for linear iPP, at 190º C (Eckstein, et al. 1998). Evolution of the data for all the original materials can be described in these plots by a single curve free of inflection points, which is the expected behavior for a thermo-rheological simple, truly linear polymer (Trinkle and Fredrich, 2001).

The irradiated iPPH9 copolymer shows a more complex rheological behavior than the original polymer, since the shift angle decreases significantly as the Gred values increase. The difference is even higher for the vacuum gamma irradiated samples. This is attributed to the increase
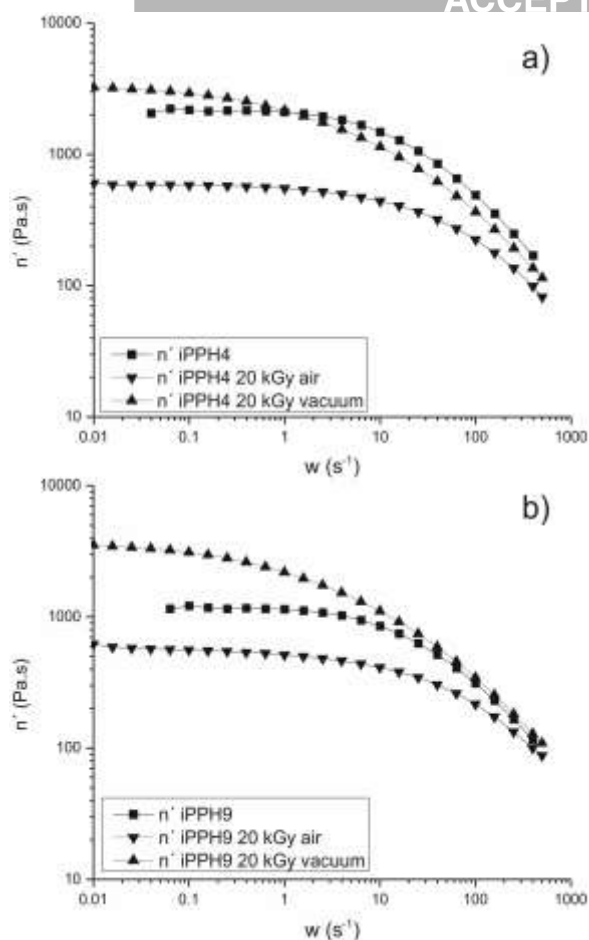
Figure 2: η´ against frequency (140 ℃) for unirradiated and irradiated copolymers: a) iPPH4 and b) iPPH9.

of the elasticity in the melt because of a higher level of long chain branches and crosslinking (Trinkle et al., 2002). This analysis corroborates the results obtained by the dependence of η´ on frequency.

Analogous rheological analyses were performed on PDMS1, at similar doses and experimental conditions. As can be observed in figures 4 and 5, the viscoelastic behavior of the original polymer is always improved on the entire frequency range analyzed irrespectively of the irradiation method employed. As it was mentioned before, crosslinking leads to an increase of the dynamic viscosity in the low shear rate region, making it difficult to reach a plateau due to the significant rise in the relaxation times. Thus, analyzing figure 4, the highly crosslinkable behavior of PDMS is verified since no plateau can be reached at similar doses to those used for the propylene based homo and copolymers, even noticing that iPP has similar molecular weights. Moreover, in a previous publication (Satti et al., 2008), it was shown that, except for gamma irradiation in air at 20 kGy, these doses are near the gel dose for irradiated PDMS1 under different atmospheres (table 2).

Table 2: Crosslinking parameters for irradiated PDMS.

Irradiation Method	EB	γ-air	γ-vacuum
Dgel (kGy)	38.1	35.3	25.0

Comparing amongst the methods, Figure 4 also shows that the crosslinking tendency appears to be higher in vacuum gamma irradiated PDMS, since higher η´ is obtained at the same dose for the sample irradiated in air. Even more, the viscosity behavior is not so different at higher doses with gamma radiation in air or EB. It seems to be no differences between these last two methods in air respect the changes in viscosity, despite the higher dose rate used in EB.

Figure 5 shows that there is a more noticeable difference amongst the G´ moduli between the vacuum and air irradiated samples, than amongst the viscous moduli, G″, which are more related to the viscosity. However, at higher shear rates both moduli became somewhat higher for the vacuum 20 kGy irradiated sample. Anyway, it is clear that the irradiation under vacuum affects the viscoelastic properties of PDMS more than irradiation in air for the two methods employed. Even more, between EB and gamma irradiation in air, the little differences observed could be attributable to the little differences in doses used (35 and 30 kGy, respectively).
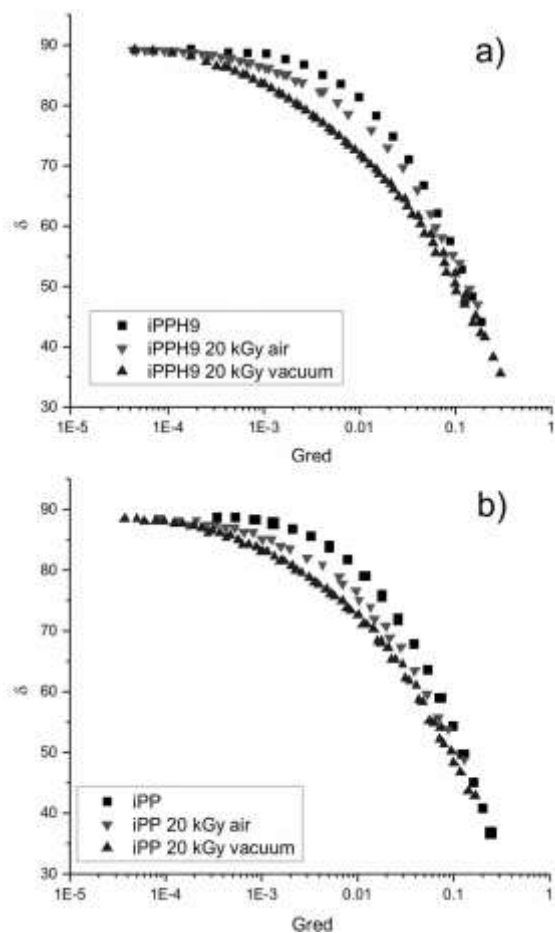
Figure 3: rvGP plots for the originals and irradiated propylene polymers: a) iPPH9 copolymer and b) iPP homopolymer.
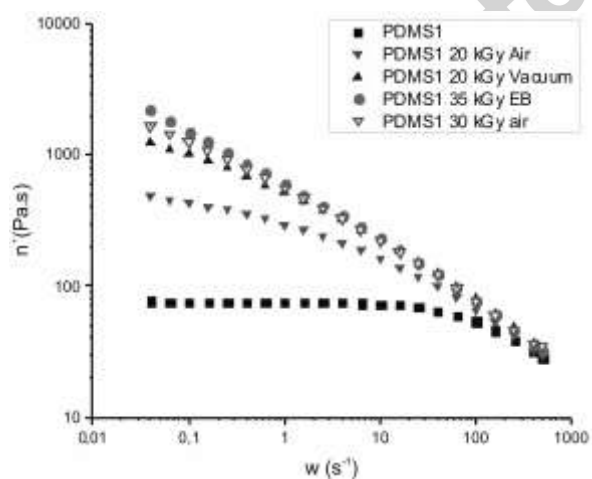

Figure 4: η´ against frequency (30 ºC) for unirradiated and irradiated PDMS1.
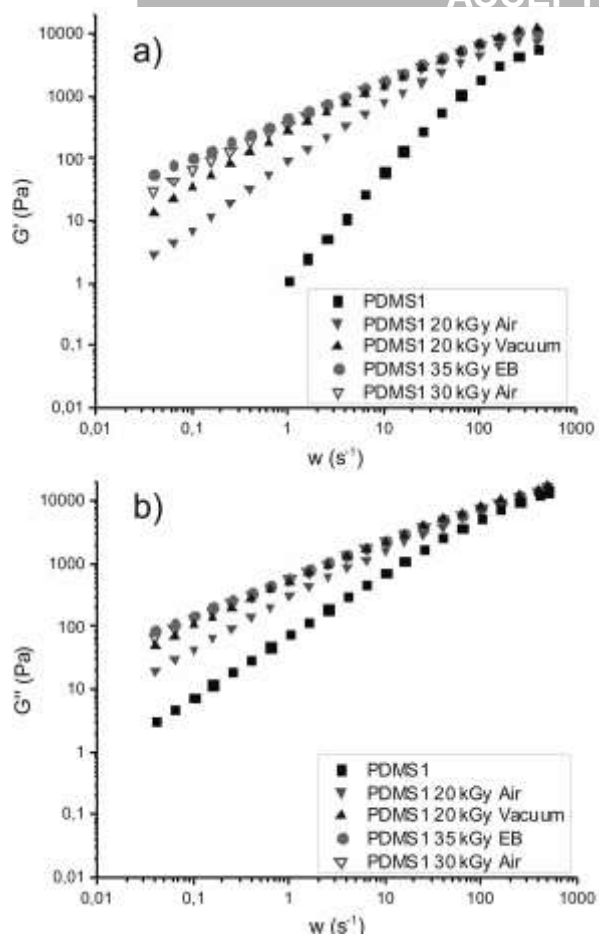
Figure 5: G´ (a) and G″ (b) against frequency (30 ºC) for unirradiated and irradiated PDMS1. (please, notice that in b), PDMS1 30 kGy Air is mostly overlapped by the other curves).
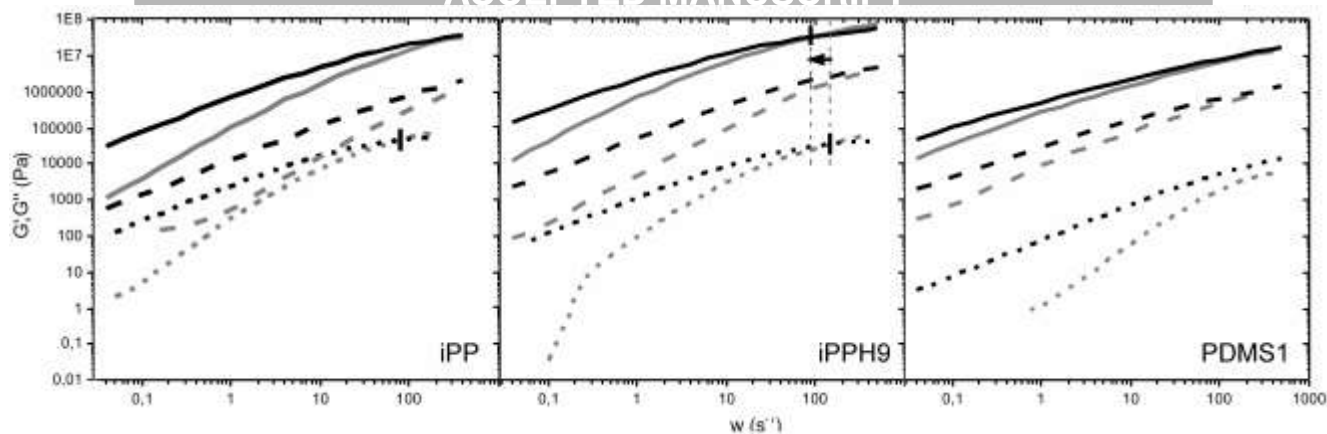
Figure 6: G´(grey) and G″ (black) against frequency for unirradiated (dotted), air (dashed) and vacuum (solid) irradiated polymers. G_{co} is shown as a vertical line. Due to overlapping of the curves, air and vacuum irradiated data was shifted 10 and 100 times, respectively, in moduli.

Figure 6 summarizes the effects of irradiation on the viscoelastic properties of samples irradiated at 20 kGy in air and vacuum. In that figure, we can see both, elastic and viscous moduli for the iPP homopolymer (180 ℃), its most amorphous copolymer iPPH9 (140 ℃), and PDMS1 (30 ℃). A crossover modulus, G_{co}, where G´ equals G″ and defines the beginning of the rubbery plateau, can be observed in the original iPP and shift towards higher frecuencies in the irradiated samples. This indicates less elastic interaction between chains, due to a shortening in molecular weight because of scissioning. For iPPH9 something similar happens for the air irradiated sample, but at vacuum, the effect of irradiation shifts G_{co} towards a lower frecuency, indicating there is a higher elastic behavior in the sample due to chain crosslinking. On the other side, for PDMS1, the slope of the loss modulus tends to that of the elastic modulus. This is a clear evidence that a crosslinking process is going on both irradiation conditions.

4. CONCLUSIONS

Irradiation under different conditions of different synthetic polymers: liquid polydimethylsiloxane and semicrystalline metallocenic isotactic polypropylene and its copolymers with 1-hexene, has been studied by means of rheological analysis.

The results obtained point out the predominance of scission reactions in all propylene based polymeric materials irradiated in air, even with electron beam, leading to a decrease in the overall viscoelastic properties. This indicates that the presence of oxygen contributes significantly in both processes to favor scission reactions. The gamma irradiation under vacuum leads to a higher chance for branching formation and crosslinking reactions, especially in the copolymeric samples. Moreover, crosslinking reactions are more efficient in the iPPH9 copolymer, i.e., with higher amorphous content and more comonomer incorporation.

For PDMS, the results show that branching and crosslink reactions increase the viscoelastic behavior. Once again, although through crosslinking, vacuum gamma irradiation is more efficient and both methods, gamma and EB, in air, trigger similar responses.

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HIGHLIGHTS

- Analysis of gamma and EB irradiated scissionable iPP and crosslinkable PDMS.
- Similar decrease of viscoelasticity of all irradiated samples with air gamma and EB.
- Crosslinking in vacuum irradiation for PDMS, and sort of in iPP copolymers.
- Amorphous iPP tend to branching when irradiated, specially, under vacuum.