Metallocenic polyolefin composites with siloxane polymer additives

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ABSTRACT

Blends and composites were obtained by mixing commercial metallocenic linear low density polyethylene (LLDPE) and isotactic polypropylene, with different molecular weight polydimethylsiloxanes (PDMS), including a vinyl ended PDMS. Gamma ray irradiation at different atmospheres was also applied in order to enhance blending by grafting and crosslinking of the radioinduced radicals. Dynamic rheological behavior results suggested that blending increased the viscoelasticity of the blends. Improvement and changes in the abrasive wear behavior was also followed, along with structural properties.

1. Introduction

Polyolefins are in between the most important thermoplastics because of their low cost, ease in processing and wide range of technical properties. Consequently, the understanding of their synthesis, physicochemical behavior and structure/properties relations has been a topic of interest for more than sixty years, and still constitutes a growing research area (Kaminsky, 2013; Soares and McKenna, 2012; Tolinski, 2012).

During the late 1990s, metallocenic catalysts reached a milestone in the synthesis of polyolefins due to their versatility to obtain homo and copolymers with a good control of their molecular parameters (Brintzinger et al., 1995; López-Majada et al., 2006; Quijada et al., 2005, 1995). Thus, polyolefins with well-defined structures, homogeneous comonomer distribution, narrow polydispersity indexes (PD), and targeted tacticity could be now designed. Moreover, metallocenes allowed the incorporation of 1-olefine comonomers of different sizes during polymerization, such as 1-butene, 1-hexene, 1-octene or 1-octadecene. As a result, short chain branches of a targeted length were incorporated in the growing chain. This well-established procedure allows the synthesis of a great variety of copolymers with a wide range of potential applications (Bensason et al., 1996; Kaminsky, 2004; Kaminsky and Laban, 2001; Wang et al., 2001). In polyethylene (PE), the incorporation of short chain branches allows the synthesis of linear low density PE (LLDPE). LLDPE has gained industrial importance due to

specific properties, such as a greater tensile and tear strength, higher environmental stress crack resistance, and better flexibility when compared to low density polyethylene (LDPE) (Giri et al., 2009).

Isotactic polypropylene (iPP) is another thermoplastic primarily used in industry, with a big growth among commodity polymers because of its good environmental resistance and due to the possibility of being processed by different methods. In addition, iPP can be easily recycled at a moderate cost (López-Majada et al., 2006).

In addition, several modification methods have been developed to further improve polyolefins properties. Among them, post-reactor modification and blending with other materials (to obtain composites for different purposes) may introduce significant changes and enhancements in their final properties (Alonso, 2013; Giri et al., 2012, 2009; Jana and Nando, 2003; Markarian, 2009; Satti et al., 2008, 2010a, 2010b, 2010c, 2012a, 2012b, 2017a, 2017b; Yilgor et al., 2002; Yilgor and Yilgor, 2014; Zhao et al., 2009). In such a sense, siloxane-based polymers have been employed as additives for these purposes. Poly(dimethylsiloxane) (PDMS), for example, is an attractive additive since it has high flexibility; low glass transition temperature (Tg); good thermal and oxidative stability; excellent dielectric, ozone and corona resistance; and physiological inertness or biocompatibility. However, it has limited applications because of its small green strength, lower mechanical properties, handling difficulties, and a higher cost if compared to polyolefins. Therefore, blending of small amounts of silicone with cheaper polyolefins has become a popular practice to achieve a

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compromise between properties and cost (Giri et al., 2012, 2009; Rymuza, 2007; Satti et al., 2017a; Yilgor et al., 2002; Yilgor and Yilgor, 2014; Zhao et al., 2009). Compatibilization of blends by using chemical agents in order to enhance their final properties was also studied (Jana and Nando, 2003; Zhu et al., 2007).

On the other side, irradiation of polymers has become an important post reactor process for the development of new materials with improved technical properties (Shkolnik, 1993). The process is neat and leads to the formation of macroradicals which react with each other to form inter and intramolecular crosslinks. This process leads to the formation of grafted, enlarged, branched, and three dimensional network structures. Irradiation can also generate the scission of polymer chains. This process is very low when irradiation is applied to ethylene and siloxane polymers, but is the main reaction on propylene polymers due to the presence of tertiary carbons in the main chain (Charlesby, 1960; Ferreto et al., 2012; Satti et al., 2008, 2010a, 2010b, 2010c, 2012a, 2012b, 2017b). The effects of radiation on LLDPE-PDMS blends is scarcely reported in the literature, but indicates a further compatibilization and enhancement of the final properties from blends when high PDMS amounts and electron beam at doses higher than 100 kGY are used (Giri et al., 2009, 2012). An important advantage of the irradiation process is its efficiency without the need of additional chemical agents and at room temperature.

Taking into account the above-mentioned facts, the present work focuses on investigating the effect of blending small quantities of different PDMS, including a vinyl ended PDMS, with commercial metallocenic LLDPE and iPP. Moreover, the effect of gamma radiation on the rheological, tribological and structural properties of the composites is analyzed.

2. Experimental

Commercial metallocenics LLDPE ("11", Mw = 46,100 Da, DOW Engage 8411) and isotactic polypropylene ("ciPP", Mw = 133,150 Da, Purell HM671T, Lyondell Basell) were selected as base polymers for this study. Two commercial PDMS (P1, Mw = 141,000 Da and P2, Mw = 70,100, Petrarch Systems Inc.), and two anionic synthesized PDMS, hydroxyl terminated (Pa, Mw = 3240 Da), and vinyl terminated (PVi, Mw = 92,730 Da) (Satti et al., 2012a, 2012b, 2015, 2017a, 2017b), were used as additives.

A typical mixing procedure was developed in order to obtain the final polymer composites (Satti et al., 2017a). Firstly, about 2 g of polyolefin was dissolved in 50 mL of hot xylene, under constant stirring. A similar procedure was employed for the required amount of polymeric additive (each required amount as weight % – wt% – of additive incorporated in the blend). Then, the additive solution was gently added to the polyolefin solution, and the resulting mixture was kept half an hour under continuous stirring. The final solution was placed under hood until the complete evaporation of the solvent was achieved. A cast film was obtained, which was subsequently molded in a hydraulic press. Regarding the analysis required, molds of different sizes were employed. Samples were named as POPX(#), where PO is the polyolefin matrix that can be 11 or ciPP, PX is the chosen additive, and # the approximate wt% amount of additive (# = 1 for 0,84%, and 8 for 8,40%).

Gamma irradiation of the mixtures was performed in the Centro Atómico Ezeiza (CAE) through a ^{60}Co γ-source, with a 10 kGy/h dose rate. Previously, 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. Those for irradiation under vacuum were placed inside Pyrex® glass tubes, attached to a vacuum glass line, and left under high vacuum up to 24 h. Samples were then heat-sealed in tubes by using a flame torch. Irradiated samples were labelled as "a" or "v" depending on irradiation atmosphere (air or vacuum, respectively), and # dose value (kGy).

The rheological characterization of the samples was carried out under nitrogen atmosphere, in a Rheometrics RDA-II rheometer with 25 mm parallel plates geometry. The viscoelastic properties of the polymers were measured in small-amplitude oscillatory shear flow tests, as a function of frequency and temperature. The frequencies covered were in the 0.04–500 rad/s range. To ensure a linear relation between stress and deformation, small strains were used in all the dynamic tests, which were selected from previously performed strain sweeps. The temperatures covered in the rheological measurements was selected according to the melting point of the different polyolefins studied.

Fourier Transform Infra-Red (FTIR) spectra were determined by using a Nicolet 520 FTIR Spectrometer. The spectra were recorded at a 4 cm^{-1} resolution using air as background.

The molar mass of the materials was determined by size exclusion chromatography (SEC) in a Viscotek 350A HT – GPC System (Malvern Instruments) equipped with two PLgel 20 µm Mixed-A 300 × 7.5 mm columns (Polymer Laboratories). 1,2,4-trichlorobenzene was used as solvent. The analyses were performed at 135 °C and 0.8 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene ranging from 2450 to 44.8 × 10^6 Da (Pressure Chemical). The Mark-Houwink calibration constants used with TCB at 135 °C were Kps = 0.0121 g/mL, αps = 0.707 for the polystyrene standards, Kpe = 0.0406 g/mL, αpe = 0.725 for the polyethylene samples and Kpp = 0.0150 g/mL, αpp = 0.760 for the polypropylene samples.

Abrasive wear behavior of the materials was determined carrying out "pin-on-disc" tests, according to the ASTM G99-05 norm. Samples obtained from hydraulic press (10 mm wide × 10 mm length × 6 mm thick) were put into direct and constant contact with the surface of a rotatory disc, which had been covered with 600 and 60 grit silicon carbide sand paper (Buelher) for ciPP and 11 respectively. A central track diameter of 29 mm was followed for every revolution, in a rotation speed of 345 rpm, with a normal force applied of 7.5 N for ciPP, and 20 rpm and 3 N for 11. In order to keep tests with controlled temperature (25 ± 1 °C), a chamber was built as described elsewhere (Satti et al., 2017a). No external lubrication was used. Wear was measured as the loss of weight of the sample divided by the sliding distance covered in the range of time used (sliding distance = rpm × central track diameter × test time).

The worn surfaces of the polymers were observed by SEM. The surface of the materials was coated with gold (vacuum evaporation technique), and observed by using a SEM JEOL EVO 40XVP operating at 15 kV.

3. Results and discussion

Stability from blends and irradiated samples was confirmed after immersing samples in toluene either for half an hour at room temperature (RT), or at boiling temperature for three hours. The presence of PDMS in blends was confirmed by FTIR analysis of characteristic absorption bands as it was reported in a previous work (Satti et al., 2017a). As example, Fig. 1 shows results obtained for 11PVi and iPP P2. Characteristic absorption bands from PDMS are shaded in the spectra, and they remain almost unchanged even after solvent immersions.

Fig. 2 shows the evolution of the dynamic viscosity (η´) as a function of frequency for the blends 11P1(1) and 11P1(8). Dynamic viscosity slightly increases in the blend with lower PDMS content. The change is mostly observed in the Newtonian plateau region, at lower frequency values.

When irradiated in air at 21 kGy, all samples undergo crosslinking, branching and grafting processes that are characteristic for LLDPE and PDMS (Charlesby, 1960; Giri et al., 2012, 2009; Satti et al., 2008, 2010a, 2010b, 2010c, 2012a, 2012b). As a consequence of this, the Newtonian plateau is highly affected. Once again, the effect is mostly noticed in 11P1(1). For 11P1(8) the dynamic viscosity is slightly below
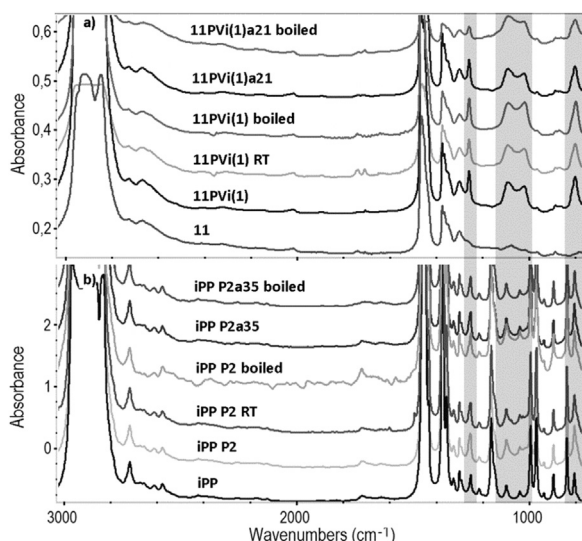
Fig. 1. FTIR spectra for **a)** LLDPE and **b)** iPP, composites. Characteristic absorption bands of PDMS from neat, blended, irradiated, and final samples are shaded in spectra.
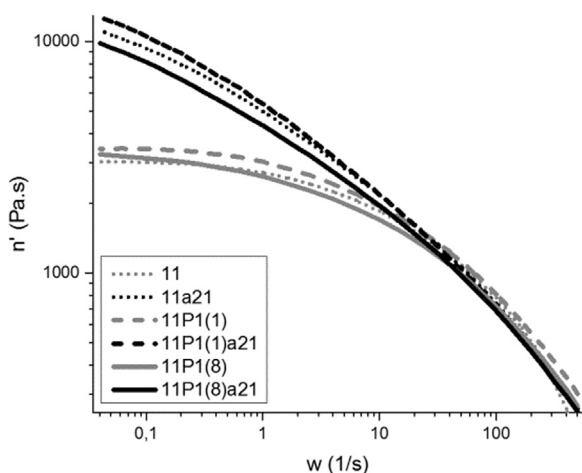

Fig. 2. η' for 11P1 composites and its irradiated samples in air at 21 kGy, at 120 °C.

Fig. 3. η' for 11PX(1) composites and their irradiated samples in air at 21 kGy, at 120 °C.

Fig. 4. η' for 11 and 11P1(1) irradiated in air and vaccum at 45 kGy, at 120 °C.

Fig. 5. G′ (black) and G″ (grey) for 11P1(1) (dashed lines) and 11PVi(1) (solid lines) irradiated under vaccum at 45 kGy, at 120 °C.

than that of the irradiated LLDPE in the entire range of frequencies. This fact could be explained by radioinduced grafting reactions between LLDPE and PDMS.

Fig. 3 compares LLDPE composites with different types of PDMS, at the same content. P1 is the additive that slightly increases the viscoelastic properties of the original LLDPE. Blending with the other PDMS polymers don´t seem to introduce significant changes in the rheological behavior. The reason for the differences between the blend with P1 and the other blends might be due to its higher Mw value. Moreover, this is also reflected in the effects of radiation on the blends. 11Pa(1)a21 is the composite with the lower PDMS Mw. The dynamic viscosity at low frequencies exhibited by this irradiated blend is below those attained for the irradiated blends with P1 and PVi. This behavior might be that this Pa has a molecular weight that is more than an order of magnitude lower than those two PDMS polymers.

The effects of crosslinking reactions are more noticeable when irradiated under vacuum, as it can be seen in Fig. 4. The lack of oxygen prevent scissioning reactions, which significantly compete with crosslinking (Satti et al., 2008, 2012a, 2012b). As a result, higher dynamic viscosity values are obtained over the whole range of frequencies. When irradiation is performed in air, the oxygen diffusion into the polymer may react with radioinduced radicals, by yielding inactive species. This
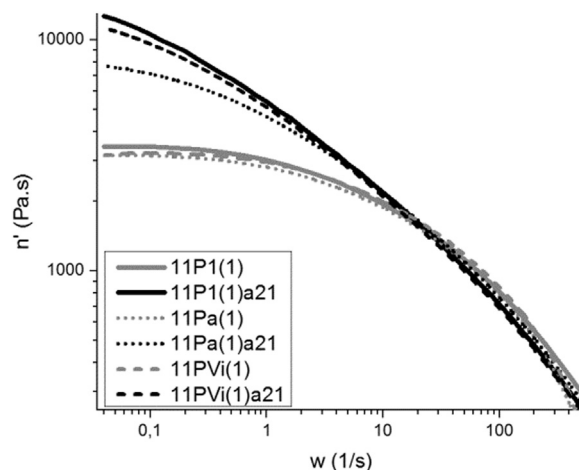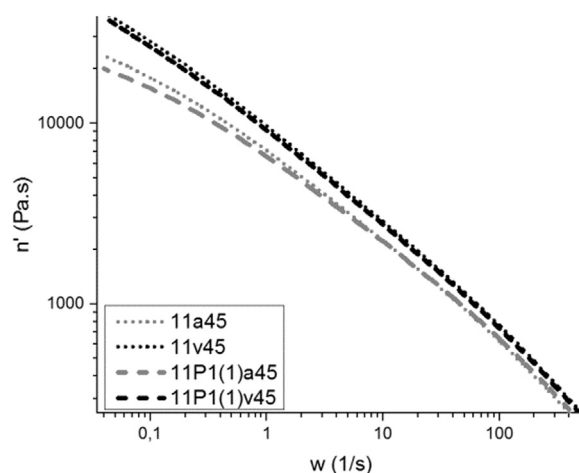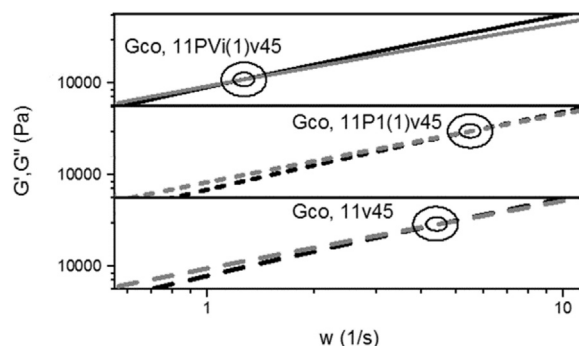
has a two-fold effect: the number of scission reactions increases, while fewer free radicals remain available for crosslinking.

Fig. 5 shows the effects of radiation under vacuum over the elastic and loss moduli evolution of LLDPE blends with 1 wt% of commercial and vinyl terminated PDMS. In this case, as the composite with P1 increases almost the same as LLDPE alone, the composite with PVi reaches higher elastic and loss moduli. Moreover, the value of the crossover modulus, Gco, where G′ equals G″ and defines the beginning of the rubbery plateau, shifts towards lower frequencies in the irradiated 11PVi(1). This fact indicates that there is a higher elastic

Table 1
Wear values of original and irradiated LLDPE blends.

Blend	Wear ($\times 10^{-5}$ g/m)
11	7.36
11a21	4.57
11PVi(1)	6.40
11PVi(1)a21	4.34
11P1(1)	6.65
11P1(1)a21	4.57
11P1(8)	0.42
11P1(8)a21	0.42
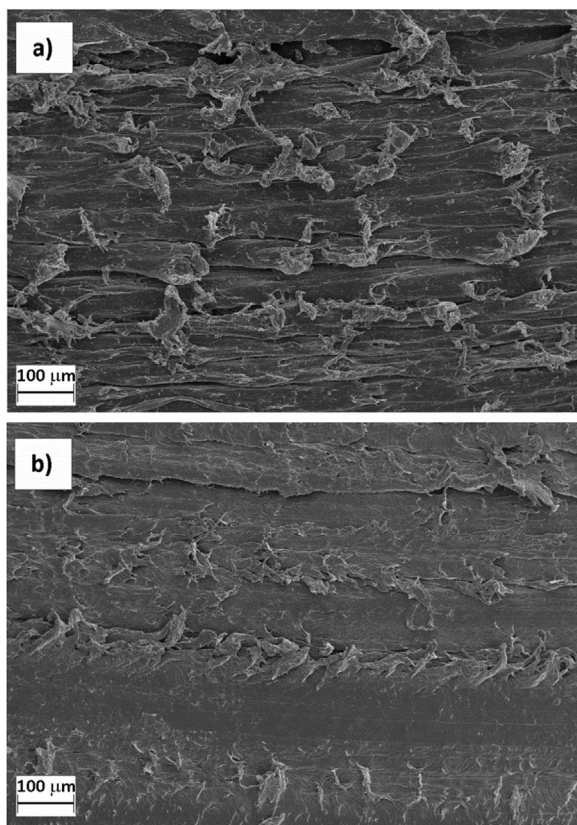
Fig. 6. SEM microphotographs of selected worn surfaces. a) 11P1(1), b) 11P1(8).

Fig. 7. Dynamic viscosity for ciPP and ciPP P1(1) (black solid lines), air irradiated samples at 21 kGy (grey dot lines), and vacuum irradiated samples at 45 kGy (black dashed lines), at 200 °C.

Fig. 8. Dynamic viscosity for ciPP PVi(1) (black solid line), and vacuum irradiated samples (dashed lines: grey for 21 kGy and black for 45 kGy), at 200 °C.

behavior in the sample due to chain crosslinking. That is probably due to the higher reactivity of the terminal vinyl groups in PVi with the macroradicals formed under radiation, leading to enlargement of the branching reactions, as it was already discussed in previous papers (Satti et al., 2010a, 2010b, 2010c, 2012a, 2012b, 2015).

Table 1 shows wear results for the blends and their irradiated samples. It can be seen that adding 0.84% of P1 or PVi additive only reduce wear slightly. However, tribological studies indicate that the incorporation of 8.4% P1 reduce wear in an order of magnitude. Fig. 6 shows the SEM pictures at 300× zoom of the worn surfaces of 11P1(1) and 11P1(8). Although both seem to follow an abrasive wear behavior, 11P1(1) seem to be more affected, meaning that the sample with more PDMS is indeed more protected against wear. On the other side, the crosslinking effects of radiation seem to reduce wear in the polymer and its blends with 0.84% of additive up to a 40%. The improvement in wear resistance of LLDPE with irradiation is scarcely reported in the literature, and scientific reports regarding this fact are even less at dose values close to that employed for sterilization purposes. However, it has been reported that radio-induced crosslinks in the network structure diminishes the formation of wear debris, leading to an improved wear
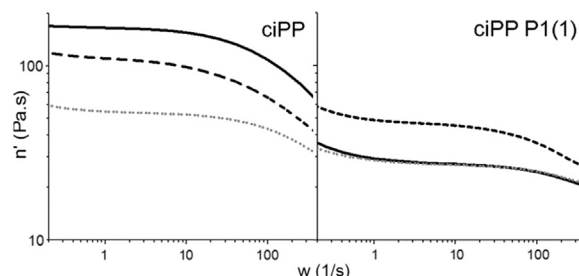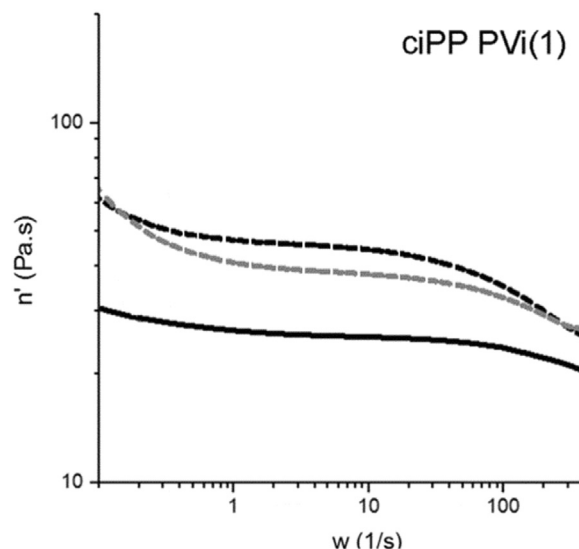
behavior (Asano et al., 2007; Gul and Khan, 2014).

The viscoelastic behavior was also followed for the ciPP-PDMS blends. Figs. 7 and 8 show the dynamic viscosity for ciPP and its composites with 0.84% of P1 and PVi, and its irradiated samples in air and vacuum. Firstly, it can be seen that when any additive is added, viscosity values fall considerably in the whole frequency range.

Also, when irradiated, ciPP predominantly undergo scissioning of the main chain due to its high content of tertiary carbons. Consequently, molar mass decreases considerably leading to important losses in the viscoelastic properties (Cerrada et al., 2010), as it is shown in Fig. 7.

When the composite ciPP P1 is irradiated with 21 kGy in air, viscosity changes are not significant. This fact might be due to the combined effect of chain scission and crosslinking reactions. On the other hand, when samples were irradiated under vacuum, a significant increase of η´ values over the whole spectra of frequencies is observed. This effect could be due to PDMS crosslinking and grafting onto iPP radio-induced macroradicals. Moreover, when ciPP is mixed with PVi the effect of irradiation under vacuum is similar to that observed with P1, which have a higher Mw value. Vinyl groups could be involved in crosslinking reactions as stated above for LLDPE. This result is important since iPP commonly degrades at these dose values, even in vacuum (Satti et al., 2012a, 2012b, 2017b). Therefore, by adding a vinyl terminated PDMS as additive it is feasible to improve crosslinking reactions and probably to increase grafting of PDMS onto iPP matrix.

SEC results from ciPP samples irradiated with 45 kGy under vacuum are shown in Fig. 9a. There, a peak shifted towards higher elution volume corresponds to a lower molar mass chain, which remains longer in
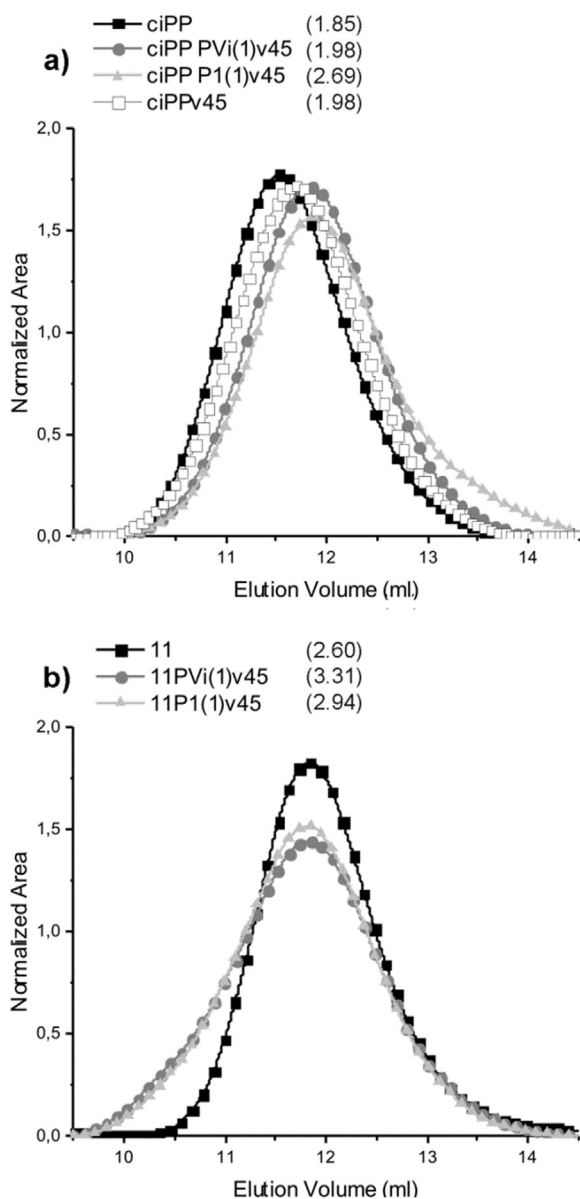
Fig. 9. SEC chromatograms for irradiated samples. PD is shown between brackets.
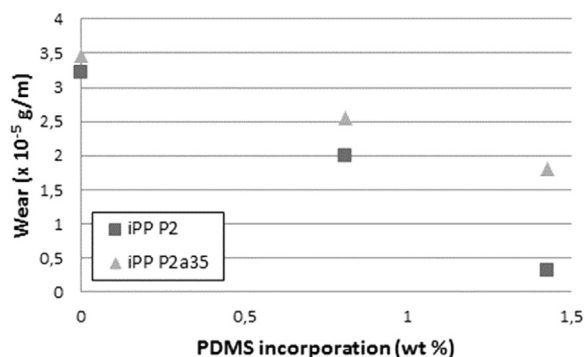

Fig. 10. Abrasive wear against P2 incorporation for original and irradiated samples of the composites, in air at 35 kGy.

the pores of the silica seeds. In contrast, Fig. 9b shows vacuum irradiated LLDPE with the characteristic increase in the higher molar mass side of the peak, low retention volume, due to crosslinking. These

results confirm what was observed in rheology. Also, for both LLDPE and PP it can be seen that samples prepared with PVi are slightly shifted towards higher molar masses. Because of these crosslinking and scissioning, molecular weight distribution of the samples increase, as it is shown between brackets, for each sample.

Tribological studies of iPP-PDMS blends were also followed, by continuing the work started in a previous work (Satti et al., 2017a). There, a synthesized metallocenic iPP, with similar molecular weights to the ciPP used along this work, was mixed with different amounts of a commercial PDMS (P2). The results obtained indicate that an increasing amount of PDMS led to a significant decrease in the abrasive wear rate, as it can be seen in Fig. 10. Their irradiated samples were also analyzed in this work, and are shown in the same figure in terms of comparison. It can be concluded that wear increased after irradiation of these samples. Opposite to what happened with LLDPE, this could be due to the radioinduced scissioning of the polypropylene matrix. Still, an irradiated blend of iPP with a small quantity of PDMS as additive, wears almost the half of a non-irradiated sample of iPP.

4. Conclusions

The viscoelastic properties of polyolefin-PDMS composites and their irradiated samples were analyzed along with tribological and structural properties.

Different amounts of PDMS were studied as additives. The composite with the lower content gave an increase in the viscoelastic properties. Then, a comparison of similar composites with different PDMS was approached. Blending with a lower molecular weight PDMS gave lower viscoelastic results. On the other side, abrasive wear decrease of the LLDPE blend was significant for the sample with higher PDMS content (8,4%).

As expected, the moduli of all irradiated samples under vacuum were higher than those irradiated in air, due to crosslinking without oxidative degradation. The irradiated sample with the vinyl functionalized PDMS additive gave the higher moduli. This could be due to enlargement reactions through vinyl scavenging of macroradicals.

Viscoelastic properties of polypropylene composites were also followed. Dynamic viscosity decreased when adding the additives. However, it increased in vacuum irradiated composite samples, while on pure iPP decreased because of expected scissioning of polymer chains. Abrasive wear decreased in the composites, although not that much in their irradiated samples, probably due to the scissioning of the polypropylene matrix.

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