



Metalloccenic polyolefin composites with siloxane polymer additives

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ARTICLE INFO

Keywords:

Metalloccenic
LLDPE
Isotactic polypropylene
PDMS
Composites
Rheology
Tribology
Wear
Gamma radiation

ABSTRACT

Blends and composites were obtained by mixing commercial metalloccenic 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, metalloccenic 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, metalloccenes 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 (T_g); 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 \times 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 $\times 10^6$ Da (Pressure Chemical). The Mark-Houwink calibration constants used with TCB at 135 °C were $K_{ps} = 0.0121 \text{ g/mL}$, $\alpha_{ps} = 0.707$ for the polystyrene standards, $K_{pe} = 0.0406 \text{ g/mL}$, $\alpha_{pe} = 0.725$ for the polyethylene samples and $K_{pp} = 0.0150 \text{ g/mL}$, $\alpha_{pp} = 0.760$ 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 \times 10 mm length \times 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 \times central track diameter \times 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

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