Improvement in abrasive wear resistance of metallocenic polypropylenes by adding siloxane based polymers

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HIGHLIGHTS

- Wear rate of metallocenic polypropylenes decreases with lateral chain length.
- Addition of siloxane-caprolactone copolymer decreases wear rate up to ten times.
- Addition of PDMS as additive decreases wear rate depending on its molecular weight.

GRAPHICAL ABSTRACT
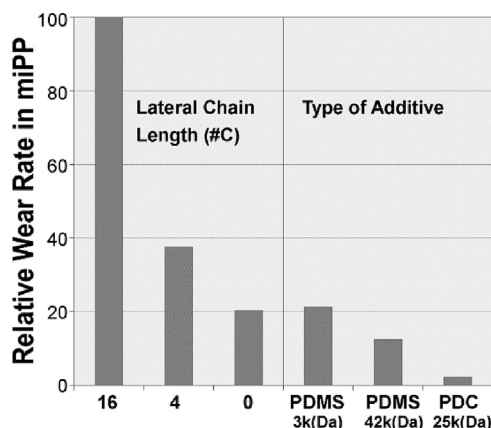
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ABSTRACT

In this paper, the abrasive wear behavior of different metallocenic isotactic propylene homo and co-polymers was studied along with their mixtures with siloxane based polymers. These mixtures were prepared with poly(dimethylsiloxane) homopolymers of different molar masses, and a block copolymer with ε-caprolactone. The crystallinity degree of the samples, as well as their thermal, mechanical and rheological properties was also studied in order to infer the effect of the presence of the PDMS based additives in the mixtures. Wear rate was decreased in most of the cases, and a dependence with the molecular architecture of the additives was observed.

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1. Introduction

The development of Ziegler-Natta polyolefins is present in the everyday use due to their wide range of applications. Their good thermal and mechanical properties, low cost of production, excellent chemical resistance and easy processability make them ideal starting materials for a wide range of applications such as packaging, food and automotive industries, as well as surgery or medical devices just to mention a few of them [1,2].

The synthesis and the physicochemical properties of polyolefins, as well as their structure/properties relations have been studied for more than sixty years, and still constitute a growing research area [1–3]. During the late 90s, metallocenic catalysts introduced an important innovation in the synthesis of polyolefins due to their versatility to obtain homo and copolymers with a good control of their molecular parameters [4–8]. In addition, several modification methods have been developed to further improve polyolefins properties. The introduction of lateral chains by copolymerization with different comonomers; post-reactor modification; and blending with other materials (to obtain composites for different purposes) may introduce significant changes and enhancements in their final properties [8–12].

Siloxane-based polymers are frequently employed as additives for these purposes. Poly(dimethylsiloxane) (PDMS), for example, is an attractive additive since it has high flexibility, very low glass transition temperature (T_g), good thermal and oxidative stability, and physiological inertness or biocompatibility. For example, by using PDMS and PDMS-based copolymers (like PCL-*b*-PDMS-*b*-PCL, in which PCL corresponds to a ε-caprolactone block) it was possible to improve and alter the superficial, crystalline, tribological and extrusion properties of commercial polyolefins [9–13]. Moreover, the scratching resistance of polypropylene (PP) can be enhanced with polyester modified siloxane copolymers. This enhancement is becoming increasingly important in several specific applications, such as the automotive industry [9,11]. In fact, the frictional and wear behavior of such viscoelastic materials as polyolefins can be somehow controlled by producing composite materials [14].

The study of the mechanical properties of commercial polyolefins regarding their wear behavior has become an area of great interest for many technological applications, ranging from automotive to packaging industries. In the last decades, different studies in this field have shown that the blending of commercial polyolefins with suitable materials may enhance their final properties, such as barrier or wear properties. In this work, wear rates of different PP metallocenic homopolymers and copolymers are studied and compared with the properties of the samples of these polyolefins mixed with PDMS based polymers. In order to determine how the presence of the polymeric additives modifies the properties of the matrix structure, a study regarding on their abrasive wear behavior (together with their mechanical, thermal, microscopic and spectroscopic features) was performed. As far as we are concerned, this is the first time in which a research of these characteristics is made from metallocenic polypropylenes blended with PDMS derivatives.

2. Experimental

2.1. Isotactic poly(propylene)s synthesis

The PP homo and copolymers employed in this work were synthesized at 40 °C, by using toluene as solvent in a 1 L Büchi glass reactor, under continuous stirring (1000 rpm). The total propylene monomer pressure was 3 bar, and the catalyst/co-catalyst used for this synthesis was Me₂Si(2-Me-Ind)₂ZrCl₂/MAO [4]. Some physicochemical properties of the metallocenic isotactic propylene (iPP)

homo and copolymers used in this work are shown on Table 1. The tacticity and the amount of comonomer incorporated in the copolymers were measured by ^{13}C NMR at 90 °C using a VARIAN INOVA 300 spectrometer operating at 75 MHz. Size Exclusion Chromatography attached to Multi Angle Laser Light Scattering (SEC-MALLS) analysis was used to elucidate the molar mass distribution of the samples. Differential Scanning Calorimetry (DSC) was used to determine the crystallinity percentage (X_c) and melting temperature (T_m) of the synthesized materials [4,7]. A commercial metallocenic isotactic polypropylene (ciPP) was also used (Purell HM671T, Lyondell Basell). The nomenclature employed to identify the copolymers is of the type iPPX# where X and # refer to the comonomer used (H for 1-hexene, OD for 1-octadecene) and the molar amount of comonomer incorporated to the polymer (mol%), respectively.

2.2. PDMS and PDMS derivatives

A dimethylsiloxane-block-ε-caprolactone copolymer (PDC) was synthesized through anionic ring opening polymerization (AROP) of 1,3,5-hexamethyl(cyclotrisiloxane) (D₃, Sigma-Aldrich) followed by conventional ring opening polymerization (ROP) of ε-caprolactone (ε-CL, Aldrich). For such a purpose, in a first stage a hydroxyl terminated PDMS (PDMS-OH) was previously synthesized through anionic polymerization, under high vacuum techniques, in glass Pyrex® reactors equipped with break-seals for the addition of the reagents [15–18]. Experimental details regarding the controlled synthesis of PDMS-OH were already published in a previous paper [15].

The PDC copolymer was obtained by following a conventional ring opening polymerization reaction (ROP) of ε-CL monomer in a Schlenk glass reactor, under nitrogen atmosphere. About 0.5 g of the PDMS-OH, 2 g of ε-CL monomer, and 6 mL of toluene were put inside the glass reactor. Stannous octanoate (Sn(Oct)₂, Sigma-Aldrich) was used as catalyst, in a molar ratio of [Sn(Oct)₂]:[PDMS-OH] equal to 0.5. The reaction was left to proceed at 120 °C during 24 h. The overall process for the synthesis of PDC is briefly summarized in Fig. 1. The resulting copolymer was precipitated in cold methanol (Ciccarelli), re-dissolved in pure THF (Ciccarelli), precipitated again in cold methanol, filtered, and finally vacuum dried. The final product presented a 15.5 wt % of PDMS and weight average molar mass $M_n = 24,900$ g/mol, according to SEC and ^{1}H NMR [19].

An anionic PDMS (PDMS$_a$, $M_n = 2550$ g/mol), was also synthesized by following the standard procedures already reported [15]. Finally, a commercial PDMS (PDMS$_c$, Petrarch Systems Inc.), with a higher molar mass ($M_n = 41,800$ g/mol) was also employed.

2.3. Anionic poly(caprolactone) (PCL) synthesis

An anionically synthesized PCL homopolymer (PCL$_a$, $M_n = 11,000$ g/mol) was obtained by employing the standard procedures also reported in Satti et al., 2016 [19]. Briefly, *sec*-butyl(silanolate) lithium obtained after reaction between D₃ (Aldrich) and *sec*-butyl lithium in a molar ratio 4:1 respectively,

Table 1
Propylene-based polymers employed in this work.

Polymer	Comonomer (% M)	Mw (kDa)	PD	Xc (%)	Tm (°C)
iPP	–	149.4	2.02	70.9	151.2
ciPP	–	122.3	2.10	57.0	145.0
iPPH4	3.7	151.6	1.72	37.8	114.6
iPPH9	9.2	110.8	2.10	15.6	78.6
iPPOD3	3.0	181.9	2.09	36.1	111.1