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Unprecedented dependence of stiffness parameters and crystallinity on comonomer content in rapidly cooled propylene-*co*-1-pentene copolymers

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ABSTRACT

A thorough evaluation of the mechanical behavior exhibited by fast crystallized propylene-1-pentene copolymers, synthesized in a broad range of 1-pentene compositions, is here described. Different mechanical magnitudes derived from loading, creep and unloading processes in depth sensing indentation measurements are correlated to structural features. Several ordered forms are able to be developed applying a fast cooling processing at the composition interval analyzed in these propylene-1-pentene copolymers. Moreover, either a single polymorph or distinct ratios of two crystalline lattices can be obtained, depending on comonomer content. Crystallinity as well as the type of existing crystallites play a critical role in the value of those mechanical magnitudes. An uncommon dependence of either crystallinity or stiffness on 1-pentene content is observed in these copolymers, associated with their capability of crystallizing in the trigonal form.

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1. Introduction

More than a decade has elapsed already from the first description in literature of a new crystallographic form in the metallocene iPP copolymers with 1-hexene as comonomer [1], appearing at contents higher than around 10 mol %. That polymorph was characterized by a trigonal unit cell [2–4] and was deduced that the driving force inducing its crystallization was an increase of density due to inclusion of 1-hexene units in the crystal [2]. Its structure was similar to those exhibited by the form I of isotactic polybutene and the semicrystalline polystyrene. This lattice did not crystallize in polypropylene homopolymer because it would have too low density [2]. An identical crystal polymorph was observed by substitution of 1-hexene by 1-pentene [5,6] in propylene based copolymers. Its inclusion in the crystal cell involved an enough increase of density that allowed crystallization of the trigonal δ polymorph. Formation of this lattice was also described more recently in propylene terpolymers incorporating both 1-pentene and 1-hexene as comonomeric units [7–9].

This δ polymorph was not, however, developed in the 1-heptene copolymers at any comonomer content [10] or crystallized under different conditions [11]. This was ascribed to the fact that the packing of macromolecules was also regulated by energy (principle of close packing) in addition to the entropy-density factor [2]. Though incorporation of 1-heptene in the crystals would lead to an increase in density, these larger units could not be easily accommodated at low energy cost in the trigonal structure. On the contrary, this trigonal form was allowed by the partial substitution of 1-pentene by 1-heptene in propylene-1-pentene copolymers, *i.e.*,

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in propylene-*co*-1-pentene-*co*-1-heptene terpolymers [12]. This feature indicated that 1-heptene was capable of being incorporated as a defect into the trigonal lattice, especially when 1-pentene was the mayor component.

Attention has been mainly focused up to now on the evaluation of crystalline and structural aspects in these copolymers/terpolymers capable of generating this trigonal form. Nevertheless, there are very few articles that deal with an additional thorough estimation of properties. This knowledge is mandatory, mainly taking into account the great importance at industrial level of polypropylene derivatives. Tensile stress-strain experiments were carried out for propylene-1-hexene copolymers [1,13,14], propylene-1-pentene-1-hexene terpolymers [7] and propylene-1-pentene-1-heptene terpolymers [12]. Yield stress values were in the propylene-1-hexene copolymers superior to those attained in the corresponding propylene-1-octene copolymers at comonomer contents higher than 10 mol% because of presence of the trigonal lattice [1] in the former ones. In these propylene-1-hexene copolymers a gradual reduction was also observed in Young's modulus [13,14] and stress at yielding [1,14] with increasing hexene content. These results, together with the corresponding variation of crystallinity, have been represented in Fig. S1 of Supporting Information.

Propylene-1-pentene-1-hexene terpolymers at high content in comonomers exhibited a very small strength due to their low crystallinity [7], although mechanical magnitudes, like Young's modulus or yield stress, were not estimated. García-Peñas et al. [12] showed in rapidly crystallized propylene-1-pentene-1-heptene terpolymers that dependences of modulus and yield stress upon overall content exhibited two trends. At low total composition, both parameters decreased rather independently of comonomers ratio. At content of 10 mol % and higher ones, those mechanical magnitudes were, however, strongly dependent on 1-pentene/1-heptene proportion. Those two tendencies were ascribed to the crystalline lattices that were developed at the different ratios and global compositions.

The aim of this research consists of getting knowledge on the mechanical behavior of propylene-*co*-1-pentene copolymers synthesized in a broad composition interval since there are no articles in literature related to mechanical properties in these interesting copolymers. A fast cooling from the melt is chosen for their processing since this treatment is rather similar to the crystallization rate applied to commercial films. Correlation of the resultant mechanical magnitudes with crystalline features will be established. Depth sensing indentation (DSI) measurements have been selected, for evaluation of mechanical response, because information on elastic, plastic and creep parameters can be obtained from these tests for all the copolymers if an experimental protocol that involves loading, creep and unloading processes is triggered. Accordingly, a quite complete picture can be achieved.

2. Experimental section

2.1. Synthesis of poly(propylene-co-1-pentene) copolymers

Preparation of the different copolymers, using 1-pentene as comonomer, were carried out for 30 min in a stainless steel autoclave (250 mL) in toluene as solvent in presence of *rac*-dimethylsilyl*bis*(1-indenyl)zirconium dichloride/MAO as the catalyst/cocatalyst system ([Al]/[Zr] = 3648) at −5 °C. The initial propylene pressure was 1.35 bar, the catalyst amount was 1.48×10^{-6} mol and the comonomer/propylene molar ratio in the feed ranged from 0 to 0.75 Isotactic polypropylene (iPP) was synthesized at the same conditions. The reactions were stopped after 30 min by adding 5 mL of ethanol and enabling the unreacted propylene goes out from the reactor. The polymer was obtained as a powder by pouring the reaction batch on a mixture of ethanol/HCl (30:1). The precipitated solid was stirred thoroughly overnight, filtrated, washed again with ethanol and, afterward, dried under vacuum at room temperature.

The main microstructural results for the different copolymers attained are summarized in Table 1. Copolymers are referred as cPPe followed by the closest integer value related to their 1-pentene mol % content.

2.2. Size exclusion chromatography

The molecular weights were evaluated by size exclusion chromatography (SEC) in a Waters GPC/V 2000 equipment with both refractive index and viscosimeter detectors. A set of three columns of the PL Gel type was used with 1,2,4-trichlorobenzene as solvent. The analyses were calibrated with polystyrene standards of narrow molecular mass distributions. The molecular weights and polydispersity index, PI, are listed in Table 1.

Moreover, the intrinsic viscosity values were determined at 135 °C in decaline stabilized with Irganox 1010 (1 g/L).

2.3. Nuclear magnetic resonance characterization

The comonomer composition and tacticity were determined at 80 °C by carbon nuclear magnetic resonance, ^{13}C NMR, using 1,1,2,2-tetrachloroethane-*d*4 (70 mg 1 mL^{-1}) as solvent, using an Innova 400 spectrometer (100 MHz). A minimum of 8000 scans were recorded with broad band proton decoupling and using an acquisition time of 1 s, a relaxation delay of 4 s and a pulse angle of 45°. The homopolymer was characterized in a Bruker Avance DPX-300 (75 MHz) spectrometer, from solutions in 1,2,4-trichlorebenzene at 100 °C, using deuterated *o*-dichlorobenzene as an internal reference. Fig. S2 of Supporting Information shows the ^{13}C NMR spectra for some of the copolymers under analysis. A detailed NMR study has been recently reported [15] on the effect of comonomer in these copolymers.

2.4. Preparation of film samples

The different samples were prepared as films by compression molding from the reactor powders in a Collin press between hot plates at a pressure of 1 MPa for 4 min. The temperature used at a given specimen was 20 °C above its melting temperature estimated by DSC. Afterward, a rapid cooling between plates refrigerated with

Table 1
Composition and molecular characteristics for the different copolymers and isotactic polypropylene homopolymer.

Sample	[1-pentene]	$[\eta]^{decaline}$	M_w	M_n	PI	[*mmmm*]
	mol %	(mL/g)	(g/mol)	(g/mol)		
iPP	0	152.0	326,120	146,140	2.25	90.3
cPPe2	1.9	125.0	248,590	109,580	2.25	92.5
cPPe3	2.6	120.4	218,210	109,860	2.00	90.5
cPPe4	4.1	87.1	150,940	75,620	2.00	86.1
cPPe5	4.6	84.0	156,650	77,270	2.05	95.5
cPPe6	5.8	86.0	143,970	71,150	2.00	97.3
cPPe8	7.9	81.0	126,050	63,690	2.00	97.3
cPPe9	8.6	78.9	–	–	–	96.9
cPPe10	10.1	63.0	–	–	–	98.2
cPPe11	10.9	56.0	70,830	33,760	2.10	96.4
cPPe12	11.9	65.0	–	–	–	97.2
cPPe14	14.4	–	63,320	29,350	2.15	97.4
cPPe17	16.8	54.0	59,610	27,740	2.15	97.5
cPPe20	20.2	46.0	54,200	25,430	2.15	100
cPPe30	30.2	39.4	42,570	20,360	2.10	100

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