



Material Properties

Influence of structure on the properties of polypropylene copolymers and terpolymers



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ABSTRACT

Several Ziegler-Natta copolymers of iPP with ethylene or 1-butene, and terpolymers with both counits have been characterized, devoting special attention to the effect of composition and processing conditions on the crystal structure and final properties. DSC and X-ray diffraction were used to study the polymorphism of copolymers and terpolymers. Comonomer insertion interrupts the isotactic sequences, acting as a structural defect, and the formation of γ form is enhanced. Moreover, crystallinity decreases and crystal structure is modified. Comonomer type and concentration determine the extent of these modifications, resulting in important changes in macroscopic properties. In particular, the excellent optical properties of the analyzed terpolymers make them very attractive for applications such as transparent film or packaging.

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1. Introduction

Isotactic polypropylene, iPP, is a widely used thermoplastic in a variety of applications, combining exceptional mechanical properties and low cost. Polypropylene versatility is mainly due to the possibility of being appropriately modified in order to obtain enhanced properties.

Moreover, iPP exhibits a remarkable polymorphism, depending on microstructural features, crystallization conditions and other factors such as the use of specific nucleants. Three different polymorphic modifications, α , β , and γ have been reported [1–4], which can be induced conveniently. In addition, a new trigonal form has been described in the case of copolymers of iPP with high contents of 1-hexene or 1-pentene as comonomers [5–10].

Furthermore, a kind of mesomorphic form has been found to appear, not only in the homopolymer, but also in different random copolymers with comonomers such as ethylene, 1-butene, 1-pentene and other α -olefin copolymers [11–14].

Among the different paths for modifying the ability to crystallize iPP and the type of polymorph desired, this paper focuses on the

introduction of comonomer units. Comonomer type and concentration determine the extent of these modifications, resulting in important changes in the macroscopic properties. Comonomer acts as a structural defect, interrupting the isotactic sequence, therefore reducing the global crystallinity and modifying the crystal structure. Additionally, comonomer insertion, together with specific crystallization conditions, enhances the formation of γ form [15–19].

The tolerance of counits by the crystalline entities is also an important factor. Thus, the inclusion of 1-butene units into the iPP crystal lattice is high, due to its similarity with propylene monomer, although crystals formed are not as perfect as those created with polypropylene homopolymer. This crystal structure results in a great balance between mechanical and optical properties. Ethylene is also incorporated into the iPP crystal lattice, but to a lower extent than 1-butene [20,21].

On the other hand, longer chain α -olefin copolymers, such as 1-hexene and 1-octene, present different morphology and crystallization kinetics than ethylene and 1-butene copolymers. They are excluded from the crystal, due to their strong steric hindrance caused by molecular size, and incorporated in greater amount in the amorphous fraction [22].

Ethylene and 1-butene copolymers have been widely studied in the literature. This is not the case of the terpolymers, a family of

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polymers that has received increasing interest in recent years [23–26].

Therefore, the aim of this paper is to study the structural differences and related macroscopic properties of a selected group of terpolymers, with different comonomer content, comparing the results with those of copolymers with ethylene or 1-butene, with an equivalent total comonomer content. All polymers were synthesized on a laboratory scale and were analyzed using different characterization and property analysis methods. The investigation endeavors to reveal the influence of the comonomer on the crystal structure as well as the effect of thermal treatment. Also, the structural differences are correlated with macroscopic properties of terpolymers and copolymers, which determine their eventual commercial applications.

2. Experimental part

All the polymer samples were supplied by Repsol and were produced at laboratory scale. The characteristics of the samples are listed in Table 1, including the comonomer content obtained by ¹³C NMR and their molecular weights measured by gel permeation chromatography.

Films of the original samples were obtained by compression molding in a Collin press between hot plates (200 °C) at a pressure of 10 MPa for 4 min. Two different thermal treatments from the melt were applied: slow cooling (ca. 1.5 °C/min) and fast cooling (ca. 200 °C/min), labeled S and Q, respectively. The specimens for the different samples are designated as follows: PR standing for “Polypropylene Random copolymer”, followed by the letter E or B to indicate the type of comonomer, ethylene or 1-butene, respectively, followed by the mol percentage of comonomer. The terminology used for the terpolymers is either PRT or indicating the molar content in the two copolymers. The corresponding code for the cooling conditions, Q or S, is indicated when pertinent. The sample code for the homopolymer is simply HOMO.

The thermal properties were analyzed in a TA Q100 calorimeter connected to a cooling system and calibrated with different standards. The sample weights ranged from 5 to 7 mg, and the scanning rate was 20 °C/min. For crystallinity determinations, f_c^{DSC} , a value of 168 J/g has been taken as the enthalpy of fusion of the α/γ modification of iPP with 100% crystallinity [18,27,28].

Wide-angle X-ray diffraction (WAXD) patterns were recorded at room temperature in the reflection mode by using a Bruker D8 Advance diffractometer provided with a PSD Vantec detector (from Bruker, Madison, Wisconsin). Cu K α radiation ($\lambda = 0.15418$ nm) was used, operating at 40 kV and 40 mA.

The X-ray determinations of the degree of crystallinity were performed by subtraction of the corresponding amorphous component by comparison with the totally amorphous profile of an

elastomeric PP sample [29,30].

The relative content of γ -phase, K_γ , can be evaluated by the following equation [31]:

$$K_\gamma = \frac{H_{\gamma(117)}}{H_{\gamma(117)} + H_{\alpha(130)}} \quad (1)$$

where $H_{\gamma(117)}$ represents the area of the γ (117) reflection and $H_{\alpha(130)}$ the area of the α (130) diffraction.

Dynamic mechanical relaxations were measured with a Polymer Laboratories MK II Dynamics Mechanical Thermal Analyzer, working in tensile mode. The storage modulus, E' , loss modulus, E'' , and the loss tangent, $\tan\delta$, of each sample were obtained as function of temperature over the range from –140 to 150 °C, at fixed frequencies of 1, 3, 10, 30 Hz, and at a heating rate of 1.5 °C/min. For these analyses, strips of 2.2 mm wide and 15 mm length were cut from the molded sheets.

A Vickers indenter attached to a Leitz microhardness (MH) tester was used to perform microindentation measurements. The experiments were carried out at 25 °C with contact load of 0.98 N for 25 s. MH values (MPa) were calculated according to the following relationship [32]:

$$MH = 2 \sin 68^\circ \left(P/d^2 \right) \quad (2)$$

where P (N) is the contact load and d (mm) is the diagonal length of the projected indentation area.

Stress–strain measurements were performed using an Instron dynamometer equipped with a load cell and an integrated digital display. Dumbbell samples with an effective length, L_0 , of 15 mm and a width of 1.9 mm were cut from the compression-molded sheets. At least three specimens of each sample were stretched at a strain rate of 10 mm/min at 23 °C, and average Young's modulus (E) and elongation at break (ϵ_B) were calculated according to UNE-EN ISO 527. The elongation was measured as percentage deformation: $100 (\Delta L/L_0)$.

Optical properties were measured with a BYK Gardner model Haze-Gard Plus. To quantify transparency, three parameters are used: transmission of visible light (TGLV), haze and clarity as ISO 14782. Haze is defined as the percentage of light that deviates from the direction of the incident beam an angle greater than 2.5°, and clarity is defined, analogously, as the percentage of light transmitted that deviates from the direction of the incident beam an angle lower than 2.5°.

3. Results and discussion

3.1. X-ray diffraction: influence of comonomer nature on crystal structure

The X-ray diffractograms of the different samples rapidly cooled from the melt are shown in the upper part of Fig. 1. As expected, the diffractions characteristic of the α modification are observed, with main diffraction peaks, in the homopolymer, at 2θ values of 14.1, 16.9, 18.4, 21.1 and 25.8°, corresponding to the (110), (040), (130), (111), and (040, 131) reflections of the α modification of iPP [33,34]. The α -modification is not the most kinetically favored, nor the most thermodynamically stable but, nonetheless, is the one that reaches the best compromise between those criteria, therefore being the most common form in polypropylene [35].

It is also observed in Fig. 1a that the diffractions for the 1-butene copolymer and the terpolymer show a displacement to lower angles (higher spacings), as a consequence of the distortion of the crystal cell produced by the introduction of comonomer. This effect

Table 1
Characteristics of the Ziegler-Natta iPP samples studied.

Sample	comonomer content (mol %)		M_w (g/mol)	M_n (g/mol)
	Ethylene	1-Butene		
HOMO	0	0	544000	82000
PRE2.5	2.5	0	323000	90000
PRE4.8	4.8	0	385000	88000
PRE8.9	8.9	0	617000	125000
PRB1.6	0	1.6	717000	140000
PRB5.0	0	5.0	523000	122000
PRB8.8	0	8.8	630000	147000
PRE1.0B1.0	1.0	1.0	262000	89000
PRE1.5B3.0	1.5	3.0	250000	59000
PRE4.2B5.6	4.2	5.6	638000	173000

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