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Analysis method

Microstructural characterization of semicrystalline copolymers by Raman spectroscopy

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ABSTRACT

We employ Raman spectroscopy to characterize several microstructural aspects of a family of ethylene-propylene copolymers (EPC). Focus is made on the simultaneous analysis of crystallinity and chemical composition. A curve fitting procedure is used to isolate Raman bands ascribed to polypropylene chains in the crystal lattice from contributions of the amorphous phase. Crystal contents of EPC calculated on this basis are in the range 10–34 wt%, in good agreement with independent wide angle x-ray diffraction and differential scanning calorimetry measurements. Besides, Raman spectroscopy captures in some of the samples a mixed crystalline structure with both, polyethylene and polypropylene crystals, indicating a distinctive molecular architecture. The chemical composition of EPC is obtained from Raman spectra in the melt state to decouple peaks characteristics of the crystal lattice from fundamental vibrational modes of the polymer chain. EPC present ethylene contents in the range 5–26 mol%, in good agreement with parallel results from ^{13}C nuclear magnetic resonance analysis. Remarkably, a rather complete characterization of EPC can be achieved on the base of a single experimental technique.

1. Introduction

Propylene- and ethylene-based polymers are the two most important thermoplastics commercialized worldwide, not only as homopolymers but also as many of their copolymers. For instance, copolymerization with ethylene has been an effective and economically viable way to improve impact properties and span of application temperatures of polypropylene (PP). Copolymerization modifies the PP microstructure at several levels. The insertion of ethylene units along the PP backbone disrupts chain regularity reducing the average length of isotactic segments or crystallizable sequences, thus lamellar thickness and, ultimately, melting temperature ranges. On the other hand, the presence of ethylene units in the amorphous phase modifies its chemical nature thus lowering glass transition temperature.

Modern metallocene-based catalytic systems allow ethylene-propylene copolymers (EPC) producers a precise control of the distribution of ethylene monomer units along the main propylene-based backbone, either in nearly random fashion (i.e. Vistamaxx from Exxon) or with more blocky structures (i.e. Versify from Dow). It is also possible a high degree of control over the incorporation of regio- and stereo-defects, structural imperfections that disrupt the main chain regularity in a way similar to that of the insertion of comonomer units, which adds another degree of freedom in product design [1–3]. New combinations between ethylene content, crystallinity and glass transition temperature have generated a vast family of EPC that combine in different proportions thermoplastic and elastomeric behaviors.

From the point of view of fabrication and end-use properties, chemical composition and crystal content and type are two essential characterization data of the material, along with others as molecular weight. In the polymer field, this information is traditionally obtained from wide angle x-ray diffraction (WAXD) or differential scanning calorimetry (DSC) for crystallinity determinations and from ^{13}C nuclear magnetic resonance (^{13}C NMR) for the case of chemical composition. Vibrational spectroscopies have the potential to provide this level of information with some extra advantages: simple and less expensive instrumentation,

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suitability for on-line monitoring and, particularly for Raman, the virtual no need for sample preparation plus the ability to perform spatially resolved measurements, important in situations that require local analysis. Specifically, several applications of Raman and IR to the characterization of chemical composition of amorphous copolymers have been reported, many of them implemented at industry level [4–7]. On the other hand, crystal content of homopolymers as polyethylene (PE) or PP has been a subject of interest for Raman spectroscopy, generating a rather well established body of knowledge. Distinctive vibrational signatures associated with polymer chains in ordered crystal units have been identified in both polymers [8–10]. Some attempts have been made in using Raman spectroscopy to differentiate the most common and stable α crystalline form (monoclinic) of PP from the β (trigonal) or γ (orthorhombic) polymorphs, but more studies are still needed to be conclusive [11,12].

In semicrystalline EPC, however, simultaneous quantification of chemical composition and crystallinity from room-temperature Raman or IR may be hampered by the fact that fundamental frequencies of each of the repeating units appear superposed with those associated to regular helical conformations of crystals. Recent work on characterization by Raman of semicrystalline EPC copolymers produced at industrial level illustrates very well this issue [13,14]. The problem has started to be approached through empirical correlations between band shifts and EPC chemical composition, with the limitation that the method is by no means universal but only applicable to EPC produced under a given catalyst system [14]. Powerful methods based on chemometry are a tool to be considered to approach this essentially multivariate problem, particularly if industrial characterization is considered, although they are somewhat complex from the point of view of standard users or when considering research purposes [15–17].

We describe here a first approach for simultaneous quantification of chemical composition and crystallinity of new families of EPC-based materials, entirely based on Raman spectroscopy. Our studies involve a series of commercial Versify EPC grades with a rather wide range of composition and crystallinity. Crystal content and type is analyzed from specific vibrational signatures of polymer chains in the crystal field. Temperature-resolved Raman measurements are used here to decouple crystallinity from chemical composition effects so simple univariate analysis can then be used to correlate spectral features to EPC chemical composition. As a framework for the discussion, the results of EPC characterization carried out by Raman are compared with those obtained from well established techniques such as DSC, WAXD and ^{13}C NMR.

2. Experimental

2.1. Materials

A set of six commercial EPC samples (Versify, Dow Chemicals) were used in this study. Basic characterization data provided by the manufacturers are given in Table 1. Two commercial homopolymers, a low density PE (LDPE 203M, Dow) and a PP (Cuyolen 1100 N, Petroquímica Cuyo, Mendoza, República Argentina) were also used to complement our study. Two random ethylene-propylene-diene (EPDM) copolymers from Dupont, grades 4640 and 4520, PP/PE weight ratios of 0.45/0.5 and 0.4/0.55 respectively, were used as calibration samples for chemical composition determinations. EPC samples, provided in pellets form, were compression molded in a hydraulic press for 10 min at 120–170 °C, depending on the polymer, under a pressure of 5 MPa. Afterwards, the specimens were cooled to room temperature by water recirculation while keeping the sample between the press plates. Final sample thicknesses were in the range 100–120 μm. Specimens for DSC, WAXD and Raman test were directly taken from them.

Table 1
Verify EPC samples grades used in this study.

Grade	Sample ID	Density[a]
2000	V20	0.888
3000	V30	0.888
2200	V22	0.876
3300	V33	0.866
4301	V43	0.866
3400	V34	0.863

[a] Data provided by the manufacturer.

2.2. Raman spectroscopy

Raman spectra were acquired in a Renishaw In Via reflex system equipped with charge-coupled device (CCD) detector of 1040 × 256 pixels. A 785 nm diode laser (300 mW) was used as excitation source in combination with a grating of 1200 grooves/mm. The laser power was kept below 10% to avoid sample damage. A 50X (0.5 NA) long working distance (8 mm) Leica metallurgical objective was used in the excitation and collection paths. Spectra were typically acquired in 10 s with at least 4 accumulations. Raman spectra above room temperature were taken in a Linkam cell, model THM-600, under N_2 atmosphere.

2.3. WAXD, DSC and ^{13}C NMR

X-ray diffraction was measured at room temperature with a PANalytical X'Pert PRO instrument, in $\theta/2\theta$ geometry with a Cu Kα source (λ = 1.54 Å). The equipment was operated at a generator tension of 40 kV and a generator current of 40 mV. The beam was filtered with a graphite monochromator. The scan rate range was fixed between 5 and 40°, with 2θ increments of 0.02°. Analysis of WAXD patterns was carried out assuming the two-phase concept typically accepted for polymeric materials. The intensity of the amorphous scattering was separated from the sharp discrete crystalline reflections by curve fitting analysis following specific rules of background construction [18]. The same apply to the data treatment for quantification of the γ crystalline phase in PP [19]. Crystallinity for each sample was obtained from the ratio between the area under crystalline peaks and total area under the diffraction pattern. DSC was performed in a Perkin Elmer Pyris 1, at rates of 10 °C/min, under nitrogen atmosphere. Melting heats were obtained by integration of the DSC peak endotherm. Ethylene and propylene compositions of EPC were determined from standard analysis of triads by ^{13}C NMR [20,21]. The NMR spectra were recorded at 120 °C with an acquisition time of 1.5 s, pulse width of 74° and pulse delay of 4 s on a Varian Inova 300 spectrometer operating at 75 MHz. Polymer solutions were prepared with *o*-diclorobenzene, benzene-d_6 (20 vol%) in a 5 mm sample tube.

3. Results

3.1. Overall spectral features of EPC

We start revising the spectral features of neat PP and PE as a framework for our analysis, with focus on the rich fingerprint region. Fig. 1 shows the spectra of homopolymers in the melt state (m-PP, m-PE), taken at 175 °C, and those corresponding to the solid semicrystalline state (PP, PE), measured at 25 °C. Overall, the spectra in the melt state allow visualization of fundamental frequencies of the chemical repeating unit of the polymer chain. The