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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.

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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 ($\lambda = 1.54$ 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

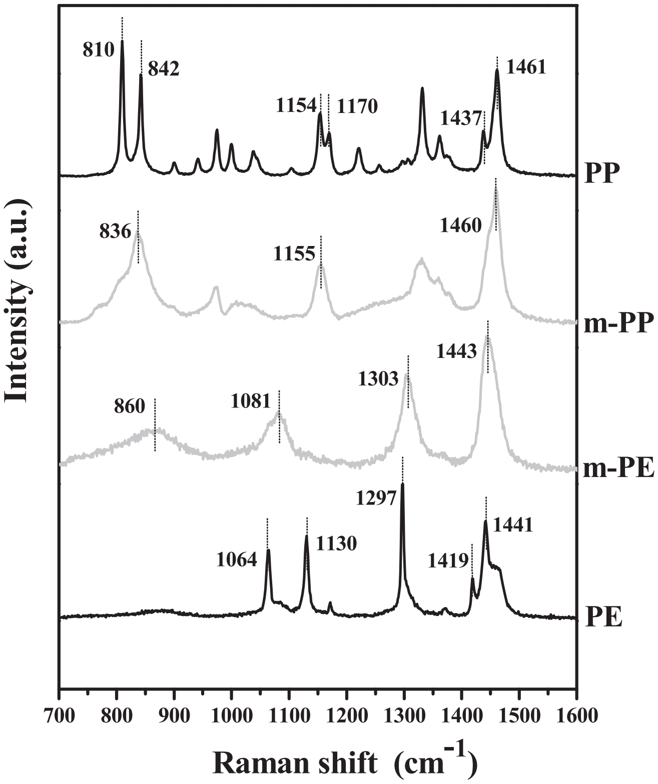

Fig. 1. Raman spectra of PP and LDPE in the fingerprint region, at 25 and 175 °C.

m-PE spectrum shows four major bands in the fingerprint region, whose assignment is fairly well established: twisting and rocking of $-CH_2-$ units along with stretching and bending modes of the C–C backbone (860 cm^{-1}), skeletal C–C stretching vibration (1081 cm^{-1}), $-CH_2-$ twisting (1303 cm^{-1}) and $-CH_2-$ bending (1446 cm^{-1}) [8]. In the same spectral region, the Raman spectrum of m-PP shows several peaks: C–C stretching and $-CH_3$ rocking (836 cm^{-1}), C–C backbone stretching and C–H bending (1151 cm^{-1}) and $-CH_2-$ bending (1436 cm^{-1}) [9].

Many of the fundamental frequencies observed in the melt state give rise to sharp Raman peaks when chains are confined in the crystal lattice, as observed in the spectra of the polymers at room temperature (semicrystalline state). In PE, bands at 1081, 1303 and 1443 cm^{-1} in the melt give rise to 1064 and 1130 cm^{-1}, 1297 cm^{-1} and 1419, and 1441 cm^{-1} sharp peaks in the semicrystalline state. Strobl have analyzed these spectral features in order to characterize crystal content. The intensity of the 1419 cm^{-1} peak has been solely related with polyethylene chains in the orthorhombic PE unit cell, whereas those at 1064, 1130 and 1297 cm^{-1} actually represent a sum of contributions of ethylene units in the crystal plus chains in extended configuration but without lateral order, as found in the transition region between crystal and amorphous phase [8]. The description is completed considering that chains in liquid-like amorphous phase are represented by intensities of bands at 1081 or 1303 cm^{-1}, originally seen as well defined peaks in m-PE but observed as shoulders in semicrystalline PE. Similarly, several sharp peaks are observed in the spectrum of PP at room temperature. Nielsen has shown that most of the analysis of crystallinity can be carried out from information of the 800–900 cm^{-1} spectral window, whereas other group of bands (1154 and 1170 cm^{-1}; 1437 and 1461 cm^{-1}) were found less useful for that purpose. The intensity of the peak at 810 cm^{-1} has been proposed to entirely represent the PP crystal content [9]. Chains in non-helical liquid-like conformation are found to be represented by the intensity of 836 cm^{-1} band, seen as a shoulder of 842 cm^{-1} in semicrystalline PP, whereas 842 cm^{-1} itself has been assigned either to the amorphous phase [10] or to the crystal-amorphous transition region [9].

Fig. 2 shows Raman spectra of some of the EPC grades at room temperature in the fingerprint region. For comparison, spectra of neat semicrystalline PP (top) and PE (bottom) have also been included. Grades V30 and V22, those in the high-end density range, show the same prominent features observed in solid PP. The Raman peaks at 810 cm^{-1}, a signature of PP units in the crystal lattice, appears rather well defined. The intensity ratio between 810 and 843 cm^{-1} decreases in comparison with neat PP and diminishes with the decrease in sample density. In addition, the band at 843 cm^{-1} present minor shoulders, particularly noticeable to the left hand of the peak, revealing an increasing contribution of the band at 830 cm^{-1}, characteristic of the amorphous PP phase. The evidence of ethylene units is much more subtle but discernible in some of the grades. For instance, there is a tiny but noticeable intensity increase of the peak at 1438 cm^{-1} that most likely reflect the contribution of the band at 1460 cm^{-1} observed in the spectrum of melted PE. On the other hand, no obvious signatures of spectral features characteristics of PE crystals are observed, which would indicate that ethylene units are mostly part of the amorphous phase of EPC. We conclude that these sets of samples are essentially PP-based grades, with a relatively low ethylene content and with a crystalline phase primarily composed by PP units.

The Raman spectra of samples in the low-end density range, such as V43 or V34, are somewhat closer to the spectral pattern of m-PP. As a first sight, the intensity of the 810 cm^{-1} band has noticeable decreased with respect to 842 cm^{-1}, whereas prominent shoulders are now observed at both sides of the 842 cm^{-1} peak. Both facts indicate a lower amount of PP crystals compared with

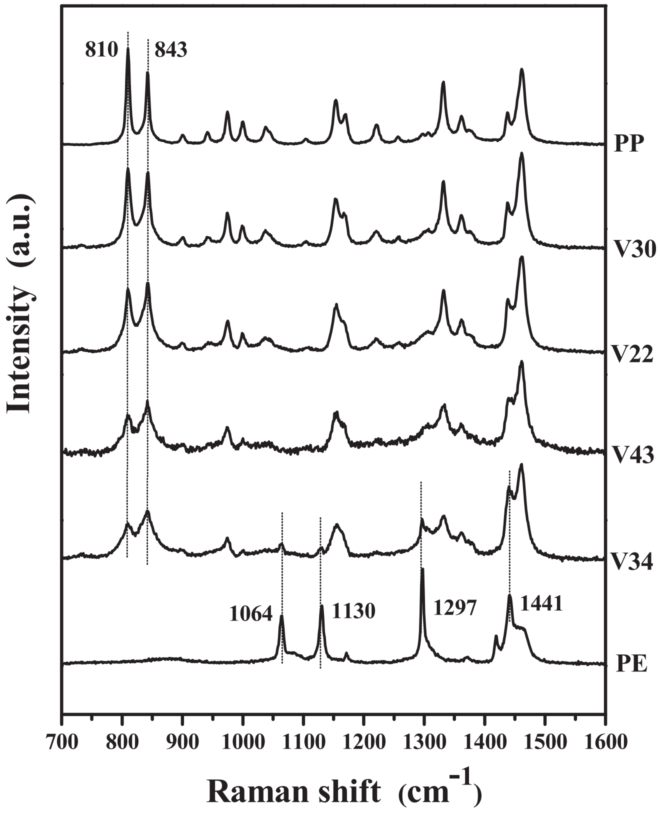

Fig. 2. Raman spectra of EPC grades in the fingerprint region, at 25 °C.

the EPC grades discussed earlier. The spectra also reveal a higher ethylene content, as reflected by the prominent contributions in the 1300 and 1450 cm^{-1} region, as found in amorphous PE. Remarkably, the V34 sample shows three small but discernible peaks at 1064, 1130 and 1296 cm^{-1}, characteristics of ethylene units in the PE lattice. This was the only sample of the series showing that feature. The fact that the Raman spectrum shows signatures of both PE and PP units in the crystalline phase indicates that the V34 sample has a different microstructure that the rest of the samples, an issue that we will further discuss in subsequent sections.

3.2. *Quantitative determination of crystallinity*

EPC crystallinity was evaluated from the analysis of Raman spectra at room temperature. As most of the samples has shown to be primarily composed by PP crystals, except for V34, we focused our analysis on the region 750–900 cm^{-1} proposed by Nielsen to investigate crystal content in the PP homopolymer [9]. This experimental window appears at a first sight as free of contributions due to ethylene units, except for the band at 860 cm^{-1} observed in m-PE, see Fig. 1. In a first approach, we followed Nielsen's analysis using three peaks for the fittings, 810 cm^{-1} (ordered helical chains), 830–835 cm^{-1} (non-helical conformation, amorphous phase) and 843 cm^{-1} (oriented chains between crystal and melt), estimating crystallinity as the intensity of 810 cm^{-1} divided the sum of intensities of 810, 830 and 843 cm^{-1} peaks. We found that the method fails at accurately fitting the overall spectrum envelope and that it systematically overestimates the crystal content, particularly in samples with crystallinity below 40 wt%. A similar observation was reported by Nikolaeva in the analysis of several families of propylene-based copolymers with crystal content in the range 30–60 wt% [14].

While the presence of crystal PP units in the 750–900 cm^{-1} region appears with good evidence represented by the intensity of the 810 cm^{-1} peak, the analysis of the contribution of the non-crystalline phase in EPC certainly requires from a more careful analysis. For instance, ethylene units in the amorphous phase should make some contribution in the spectral window, as seen from the above mentioned 860 cm^{-1} band of the m-PE spectrum. On the other hand, the peak at 836 cm^{-1} in the m-PP spectrum seems to be an envelope of at least three bands located at about 770, 805 and 835 cm^{-1}, see Fig. 1. The rather large amounts of amorphous phase anticipated in virtually all the EPC require accounting for all these contributions if we are looking for a consistent data fitting scheme.

On this basis, we reformulated Nielsen's analysis considering that the presence of disordered ethylene units has a contribution in the 750–900 cm^{-1} region. Therefore, another band freely located in the 850–870 cm^{-1} interval was included to the fitting procedure. To refine the description of PP units in the amorphous phase, we added a fifth band, located at 805 cm^{-1}, as data with lower crystalline content have consistently shown lack of fitting in this region. The minor band at 770 cm^{-1} was excluded from the fitted region as it had a minor influence on the final results. We found that the inclusion of these additional bands yield a much more realistic and precise reconstruction of the overall spectra. A similar strategy was followed by Galiotis to improve the fittings in isotactic homopolymer PP samples with crystal content in the range 35–55 wt%, confirming that the original scheme proposed by Nielsen is somewhat simplistic to account for all the band features in this spectral window. Fig. 3 shows examples of curve fitting for V30 and V33 samples, where it can be seen the overall good fit quality achieved. The intensity of the peak at 810 cm^{-1} representing PP chains in the crystal lattice is well resolved from bands at 805 and 835 cm^{-1} (PP chains in amorphous phase) and that at 855 cm^{-1} (amorphous PE).

Crystallinity, as weight fraction of PP crystals (X_c), was calculated from Raman as the area of the band at 810 cm^{-1} over the sum of the areas of the 805, 810, 835, 843, and 855 cm^{-1}. Results obtained are summarized in Table 2 as percentages. We see that the crystallinity values of EPC samples encompass a rather wide range, from 10 to 50 wt%, much larger than that analyzed by Nielsen, 45 to 55 wt%, exclusively focused on neat PP. Overall, we see a rather good agreement with crystallinity values provided by the manufacturer, see Table 2, although the last values should be taken only as a guide as they may not represent actual crystallinity values of the sample.

A more meaningful comparison can be carried out contrasting Raman data with those obtained by traditional tools such as WAXD or DSC. Fig. 4 shows the representative WAXD patterns of some of the same samples analyzed by Raman spectroscopy. The diffraction pattern of neat PE shows two sharp peaks at 2θ values of 21.4° and 23.7°, characteristic to the 110 and 200 reflections of its orthorhombic cell. PP shows peaks at scattering 2θ angles of 13.7° (110), 16.4° (040), 18.5° (130) and 21.4° (111), indicative of a monoclinic crystal lattice (α form). The diffraction patterns of the EPC grades show patterns that resemble those of PP indicating a similar crystalline structure. In addition, samples V22, V33, V43 and V34 shows a peak at 19.6°, characteristic of PP crystals in an orthorhombic cell (γ form), whose appearance has been reported in EPC copolymers [19,22]. An analysis of the relative contribution of the γ form to the total crystallinity, carried out as detailed elsewhere [19], yielded values of 35, 58, 68 and 70 wt% of γ form with respect to total crystal content for V34, V22, V43 and V33 samples, respectively. The mass fraction of the total PP crystalline phase (α + γ form) obtained by WAXD is shown in Table 2.

A comment needs to be made with respect to V34. A close inspection to the WAXD pattern reveals a tiny but noticeable peak at about 24°, not present in the rest of EPC. This peak is consistent with crystalline diffractions of ethylene crystals. The observation of a mixed crystalline structure containing both ethylene and propylene crystals is in agreement with the evidence found by Raman spectroscopy on this sample. Remarkably, changes in the Raman spectrum are certainly more marked that those observed in WAXD patterns, despite the later technique is a classic tool for the characterization of crystal structure.

DSC traces for this family of materials (not shown) were similar to that reported and discussed in Ref. [23]. We found that the endotherms broaden and that melting temperature of the EPC decreases with respect to neat PP. The total heat of melting (ΔH_m) of EPC obtained by integration of the DSC endotherm, was also found to decrease in comparison with that of neat PP. Crystal content can be estimated from those values as $\Delta H_m / \Delta H_m^\infty$, where ΔH_m^∞ is the heat of melting for a 100% crystalline material. For PP crystals, values of ΔH_m^∞ have been reported in the range from 200 J/g (α-PP) to 145 J/g (γ-PP) [24]. Although previous works estimated crystallinity in this family of materials on the base of the value of α-PP [25], we think that a more reasonable value for ΔH_m^∞ should be lower accounting for the significant amounts of γ phase found in some of the EPC studied. For that reason, we use an average value of 175 J/g to describe grades with important amounts of γ phase, whereas the value of 200 J/g was used for grades that only show the α phase. Table 2 shows the results of estimation of PP crystallinity from DSC for the samples under study.

Fig. 5 compares the result of PP crystal content obtained by Raman spectroscopy with those of DSC and WAXD. Overall, we confirm the very good agreement between the classic methodologies and Raman spectroscopy. Remarkably, the agreement is equally good in pure PP or rich-PP samples as well as in low density grades, which supports the curve fitting procedure based on

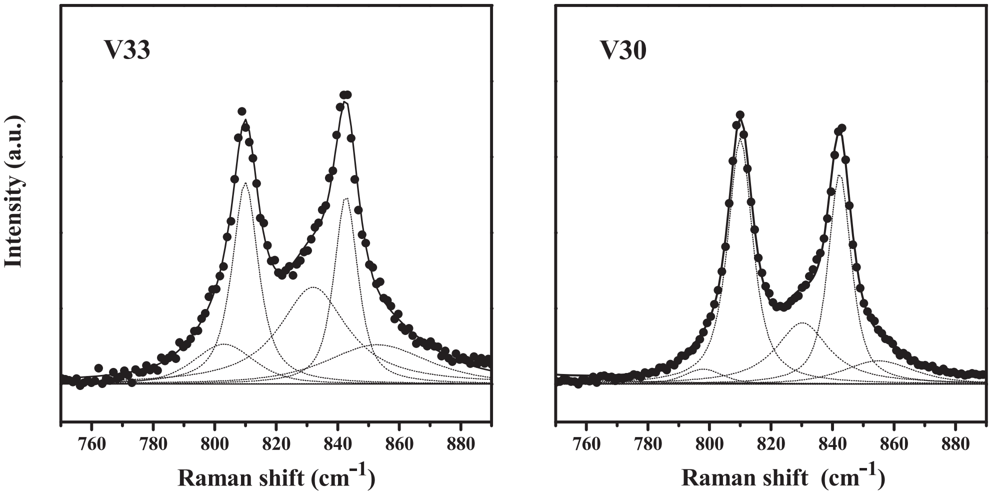

Fig. 3. Curve fitting in the 700 - 900 cm^{-1} region for V33 and V30 samples.

Table 2
Crystallinity (X_c) as wt% and ethylene content (Et) in mol% of the Versify EPC obtained by the different methods.

Sample ID	X_c Raman	X_c Dow[a]	X_c WAXD	X_c DSC	Et Raman	Et^{13}C NMR
PP	49	–	52.3	50.0[b]	–	–
V20	34	35–44	32.4	35.0[b]	5	5
V30	33	44	34.5	32.8[b]	5	4
V22	27	21–28	30.2	32.0[c]	8.5	8
V33	22	11–17	17.0	24.0[c]	8	12
V43	16	18	16.2	17.5[c]	12	14
V34	11.5	14–17	14.6	14.7[c]	26.5	25

[a] Data taken from Versify brochures.
[b] Calculated from $\Delta H_m^{\infty} = 200\,J/g$.
[c] Calculated from $\Delta H_m^{\infty} = 175\,J/g$.

considering the intensity of 810 cm^{-1} band as a marker of crystal content and those at 805, 830, 843, and 855 cm^{-1} as indicative of the amorphous (and eventually transition) phase.

3.3. *Quantitative determination of chemical composition*

Differently from the determination of crystal content where we had a rather clean spectral region for crystallinity evaluation, the quantification of chemical composition from the room temperature Raman spectra turns out more complicated as there is no spectral range only sensitive to the nature of chemical units but not to copolymer crystallinity. Instead of applying rather complex tools of multivariate analysis to address simultaneously crystallinity and chemical composition, we analyze EPC spectra in the melt state, where the interference caused by crystallinity is suppressed and the problem becomes univariate, only dependent on chemical composition.

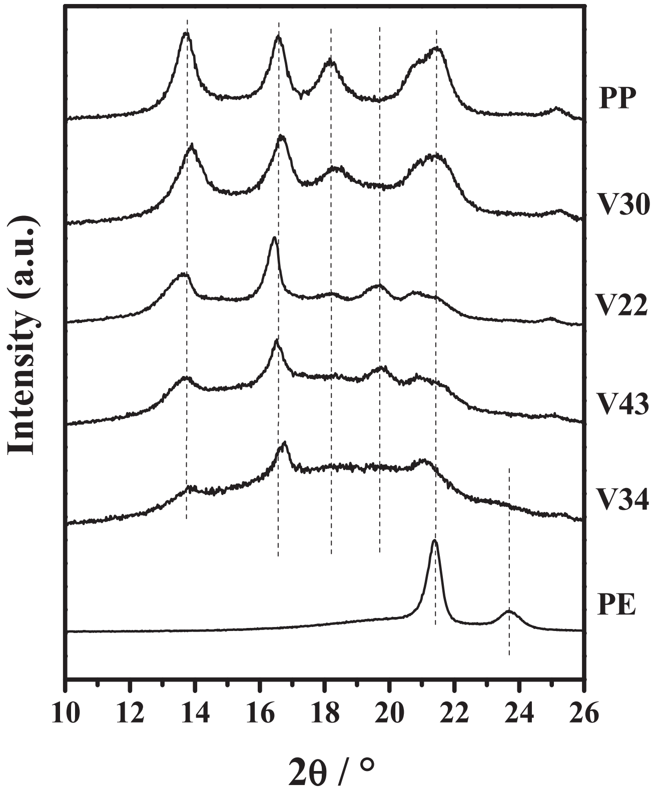

Fig. 4. WAXD patterns of some of samples analyzed.

Fig. 6 shows Raman spectra of some of the EPC at 175 °C, in the fingerprint (600–1600 cm^{-1}) and C–H stretching (2700–3300 cm^{-1}) regions. The Raman profiles show only fundamental frequencies of the monomer units without any sharp peak relative to the crystal lattice. In the fingerprint region, the increasing contribution of ethylene units, observed as peak shoulders at 1303 and 1443 cm^{-1}, can be seen when going from samples with high (V30) to low (V34) density values. The spectral profile of the stretching region reveals even clearer differences in sample chemical composition. For instance, peaks at 2963 and 2877 cm^{-1} assigned to C–H stretching in $-CH_3$ groups progressively decrease from V30 to V34. On the other hand, the band related to C–H stretching in $-CH_2$- units, placed at 2852 cm^{-1} in m-PP, increases and shifts up from V30 to V34, showing its maximum intensity for m-PE.

The analysis of chemical composition was carried out by linear decomposition of EPC spectra in terms of those of neat PE and PP. The relative contributions of each of the neat spectra obtained by direct least squares are related with the amounts of their respective components. A calibration with samples with known ethylene/propylene composition allows obtaining the molar fraction of ethylene units from these relative contributions. Overall, good quality of data reconstruction was achieved for any of the grades in both experimental windows as indicated by the random

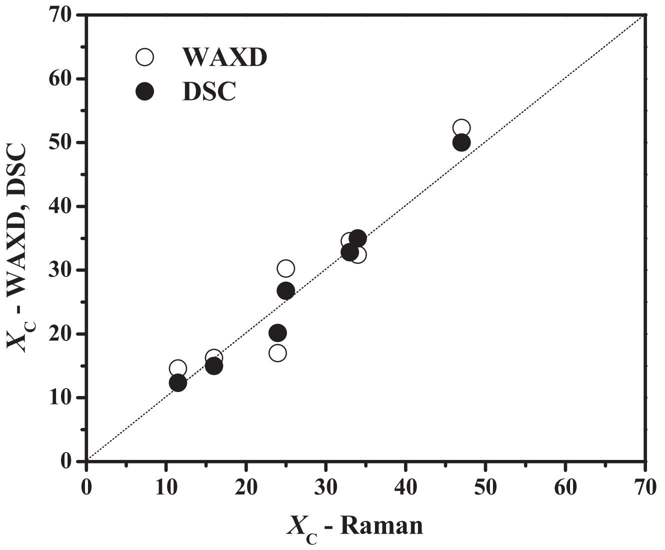

Fig. 5. Comparison of crystal content of EPC as measured by Raman, WAXD and DSC.

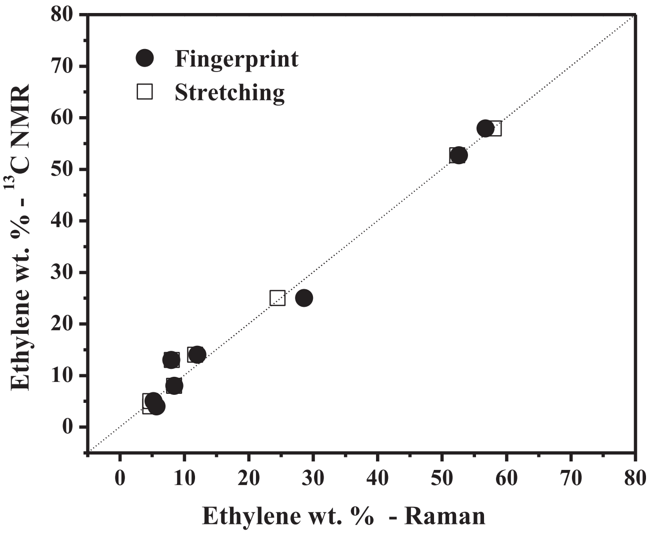

Fig. 7. Comparison of EPC chemical composition obtained by Raman and ^{13}C NMR.

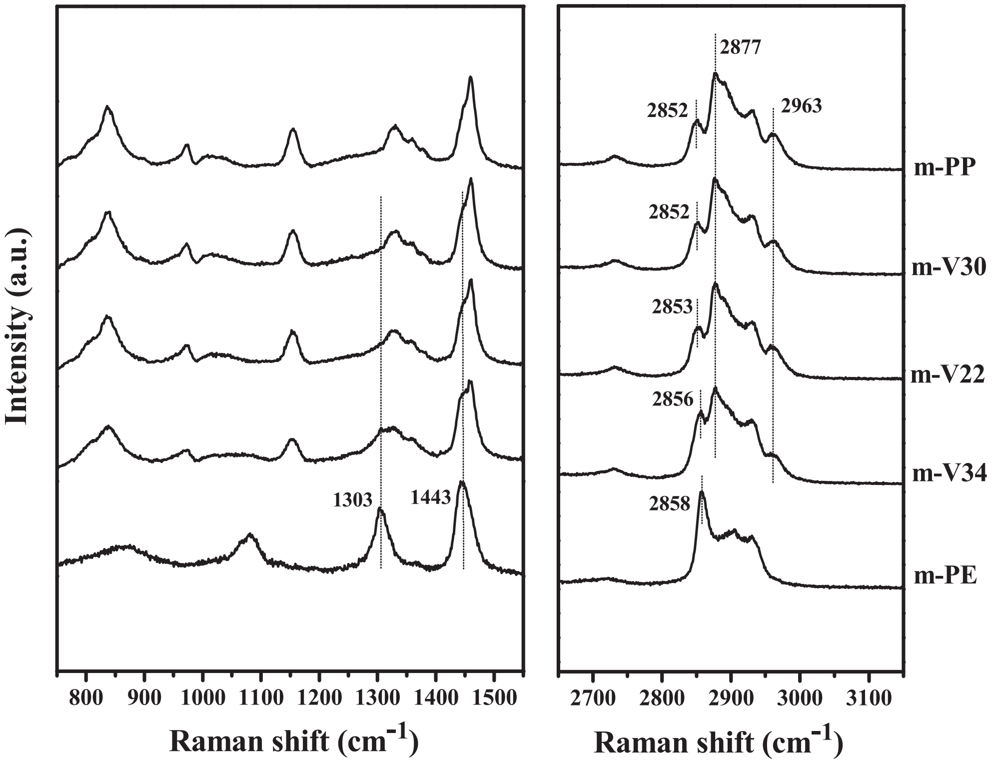

Fig. 6. Raman spectra of PP, LDPE and EPC in the fingerprint and stretching regions, as taken at 175 °C.

distributions of the residual spectrum around zero for the whole spectral range. Results obtained from Raman spectroscopy were compared with those from direct ^{13}C NMR analysis, as shown in Fig. 7. A good agreement between techniques for both, fingerprint or stretching regions of Raman analysis is seen. Results are also shown in Table 2, where Raman data are an average from results of the two spectral regions.

Fig. 8 summarizes the results obtained in the analysis of the Versify series, in the form of a plot of EPC chemical composition (ethylene mol%) versus crystal content as obtained from Raman experiments. Similar data, taken from Ref. [23] have been superimposed to ours. Crystal content in that work is more likely obtained from DSC experiments whereas chemical composition was provided by the manufacturer. Notice that the EPC analyzed in Ref. [23] are not commercial samples, as the ones studied here, but experimental-type grades, supplied by the same provider. Despite that fact, both set of data compares very well for ranges of ethylene content between 0 and 20 mol%.

The common decay of crystallinity with ethylene content indicates that the samples have a similar molecular architecture, where the insertion of ethylene units and, eventually, stereo- and regio-defects, reduces overall crystallinity. At about 15%, one of our

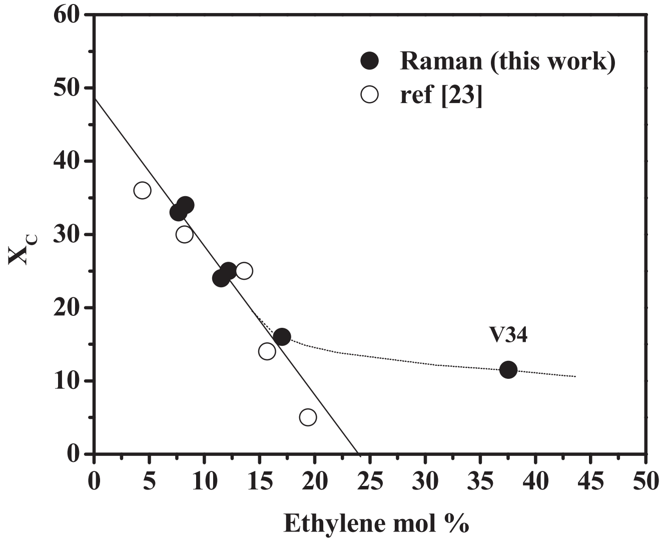

Fig. 8. Crystallinity versus ethylene content for EPC.

data (V34) departs from the common decay line indicating that this sample has a different chain architecture. For instance, V34 shows a rather high crystal content considering that its ethylene content is above 35 mol%. V34 also shows a mixed crystalline structure having both ethylene and propylene types of crystals, as observed by Raman spectroscopy and confirmed by WAXD. To form PE crystals, ethylene units have to be distributed along the chain backbone in rather long consecutive sequences that allow the formation of individual crystals, which lead us to think that the V34 sample has a blocky structure. Analysis by ^{13}C NMR confirmed this blocky character as revealed by the large increase in the proportion of ethylene triads (12.6 wt%) compared with other samples (~0 wt%). In fact, this feature has been reported for the manufacturers as a signature of this new family of EPC, characterized by a *tapered* block-copolymer architecture, i.e., with gradual transitions in properties between blocks [26].

4. Conclusions

Raman spectroscopy has shown to be a powerful tool for the characterization of microstructure in EPC materials. With a single technique, simultaneous characterization of crystal content, crystal type and chemical composition could be achieved. The reformulated analysis of the 700-900 cm^{-1} spectral region allowed a reliable quantification of PP chains in the crystal lattice, yielding results comparable to those of traditional techniques such as DSC or WAXD. On the other hand, the analysis of chemical composition at high temperature gave a clean access to chemical composition of the EPC without interference of the sharp Raman peaks associated to the crystal lattice. The analysis of fingerprint and stretching spectral regions yielded results that compare very well with those obtained by classical ^{13}C NMR analysis.

The samples analyzed are PP-based grades, with a relatively low ethylene content (below 12 mol%) and with a crystalline phase primarily composed by PP chains. Ethylene units are thought to be randomly distributed along the polymer backbone acting as points of disruption that decrease the length of crystallizable PP blocks thus reducing overall EPC crystallinity. The only exception was V34, a sample with a relatively high ethylene content, about 25 mol%, and with a mixed crystalline structure containing both PE and PP crystals. These features indicates a different molecular architecture with more blocky character, an aspect reported by the manufacturers as distinctive for this family of materials.

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