

## Research Article

# Identification of LDPE Grades Focusing on Specific CH<sub>2</sub> Raman Vibration Modes

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The possibilities of applications of vibrational spectroscopy techniques (Raman spectroscopy) in the analysis and characterization of polymers are more and more used and accurate. In this paper, our purpose is to characterize Low Density Poly(Ethylene) (LDPE) grades by Raman spectroscopy and in particular with CH<sub>2</sub> Raman vibration modes. With temperature measurements, we determine different amorphous and crystalline Raman assignments. From these results and on the basis of the evolution of CH<sub>2</sub> bending Raman vibration modes, we develop a phenomenological model in correlation with Differential Scanning Calorimetry and in particular with crystalline lamella thickness determination.

## 1. Introduction

Nowadays, almost 30% of the plastics world production is dedicated to poly(ethylene) (PE) (77 million tons per year) [1]. This polyolefin is considered as a consumer polymer due to its moderate cost of manufacturing and its physical and mechanical properties compatible with various applications in everyday life. Indeed, PE is generally easily processable. It possesses an excellent electric insulation and shock resistance combined with a very good chemical and biological inertia [2].

For each PE grade corresponds of specific applications, presenting different rheological properties. It is then essential to know how to distinguish these products by adapted methods of characterization. Moreover, to be competitive, PE production should be analysed on-line in order to quickly give the main properties of product (Melt Flow Index, additives, flaws, etc.).

Raman spectroscopy is an innovative experimental technique of polymer process analysis, which allows doing this. Its use is nowadays growing fast because of advantages. It is a nondestructive method, capable of also giving useful

information about the morphology of the polymer. This technique can be perfectly used in industry by means of adapted sensors and devices with more and more reduced dimensions [3]. Raman spectroscopy is used to determine the characteristic transition phases of PE and information about the polymer microstructure [4]. By the use of chemometric tools, for instance, it is possible to identify various Low Density PolyEthylene (LDPE) grades.

Polyethylene crystallization can be considered as the transition between fully entangled Gaussian chains and fully extended chain without entanglements ordered in manner to provide crystals. Between two ideal states, “metastable” crystalline and molten states exist [5]. Moreover, it is well known that polyethylene usually crystallizes in an orthorhombic lattice which contains two chains per unit cell with different orientation with respect to each other [6].

Strobl and Hagedorn [7] first proposed using Raman spectroscopy to characterize the three-phase morphological structure of semicrystalline polyethylene. Then, many other authors use Raman spectroscopy to determine the amount of crystallinity of polyethylene [8, 9]. Lagaron [10] presents the analysis of the changes in position of the so-called

Raman crystallinity band of polyethylene, that is,  $1415\text{ cm}^{-1}$  Raman band, as a function of temperature, cold drawing, and material density and its interpretation is also presented. However, few studies are about microstructural attribution of  $\text{CH}_2$  Raman bands. Raman spectroscopy is very sensitive to strain [11], so this work aims to attribute mechanically  $\text{CH}_2$  Raman bands, consolidate the Raman three-phase analysis method, and confirm the correlation of Raman crystallinity ratio with other analytical methods.

## 2. Experimental

To cover a wide range of products, several grades of Low Density PolyEthylene (LDPE) were studied. In the following, they will be designated by letters A to H, from the most viscous (A) to the least viscous (H). Grades A, C, F, and H were particularly investigated to depict the trends. The choice of these products was made on the basis of relative viscosity, from the most viscous to the least viscous; in particular the mechanical properties and applications of these materials depend on their viscosity, as the examples given in Table 1.

The Raman spectra were obtained with a Horiba Jobin-Yvon Aramis spectrometer operating with an excitation wavelength of 532 nm, a grating with 1800 lines/mm, a  $200\text{ }\mu\text{m}$  confocal hole, and a x50 lens. The studied spectral range extended from  $640\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$ . The acquisition time was 2 seconds and in order to obtain a good signal-to-noise ratio, three spectra were averaged.

The calorimetric tests were made by Differential Scanning Calorimetry (DSC) with DSC 200 F3 Maia from Netzsch. It is a heat flux apparatus able to work down to  $-170^\circ\text{C}$  thanks to a supply of liquid nitrogen within the thermostated chamber swept by nitrogen and regulated with an intracooler. The tests were performed in pierced aluminum crucibles with a sample mass of about 20 mg. For the preliminary and detailed study of the grades A and H, the temperature program used is given in Table 2. The rate was  $10^\circ\text{C}/\text{min}$  for each temperature ramp.

The thickness of crystalline lamella can be calculated with the formula of Thomson and Gibbs [12] as follows:

$$L_c = \frac{2\sigma_e}{\Delta H_{f_{th}}\rho_c} \left( \frac{T_0}{T_0 - T} \right) \quad (1)$$

with [13]  $L_c$  being thickness of the crystalline lamellar,  $\sigma_e$  being energy of surface of the principal facets of ends of the crystalline lamella ( $0.070\text{ J}/\text{m}^2$ ),  $\Delta H_{f_{th}}$  being melting enthalpy of the perfect crystal ( $2.905 \cdot 10^5\text{ J}/\text{kg}^{-1}$ ),  $\rho_c$  being density of the perfect crystal ( $1000\text{ kg}/\text{m}^3$ ),  $T_0$  being theoretical melting point of the lamella of infinite size ( $143.5^\circ\text{C}$ ), and  $T$  being melting point of the lamella.

## 3. Results and Discussion

In a first step, the various signatures of PE were determined in order to exactly identify and know the identification of the peaks of amorphous and crystalline phases. Measurements were performed as a function of temperature in order to highlight the specific Raman modes related to the different phases and their transformations [14]. Figure 1(a) shows the

TABLE 1: Designation of the studied samples.

Name	Relative viscosity (from 1 to 100)	Additives	Applications
A	1	No	Film, blowing
B	1	Yes	Film, blowing
C	3	No	Film, molding
D	3	Yes	Film, molding
E	5	No	Film, coating, molding
F	10	No	Film, coating, molding
G	30	No	Injection, molding
H	100	No	Injection, molding

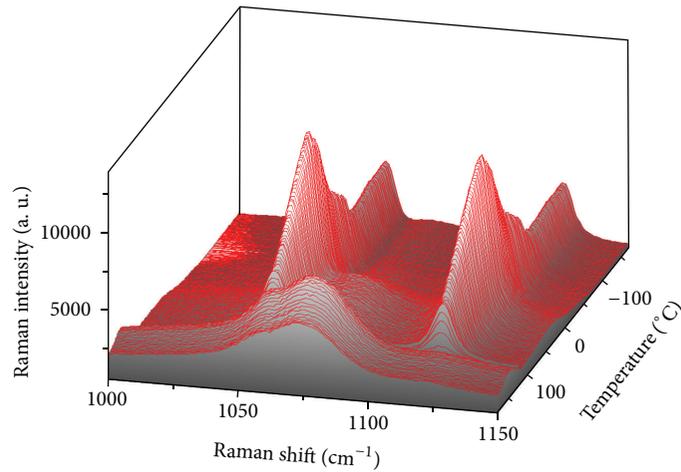
TABLE 2: Temperature program for the grades A and H studied in DSC.

Rise	Start	End	Isothermal (5 min)
1	25	-150	
2			-150
3	-150	150	
4			150
5	150	-150	
6			-150
7	-150	150	
8			150
9	150	25	

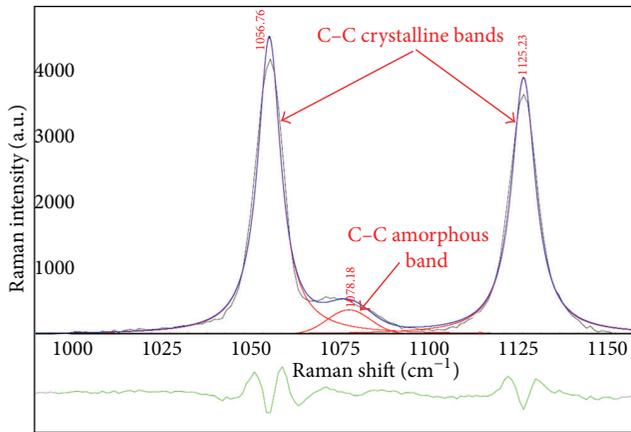
evolution of the part of the Raman spectrum corresponding to C-C bonds vibrations of LDPE. The right side of the figure gives typical examples of spectra recorded at room temperature (Figure 1(b), semicrystalline state) and above  $T_{\text{melting}}$  (Figure 1(c), amorphous state).

Now, we would like to focus on the bands related to the  $\text{CH}_2$  group, (Figure 2(a)). After comparison with the phase at high temperature (purely amorphous), we can fit this part of the spectrum at room temperature with four peaks using three Lorentzian and one Gaussian functions, respectively, assigned to the crystalline phase (c- $\text{CH}_2$ ) and the amorphous phase (a- $\text{CH}_2$ ). The existence of three peaks for the crystalline phase can be interpreted by considering that in a Raman spectrum, and the position of bands depends on the state of strains and the environment of the chemical bonds [15–20]. A shift towards low frequencies corresponds to an elongation of the bond, whereas a shift towards high wave numbers to a compression.

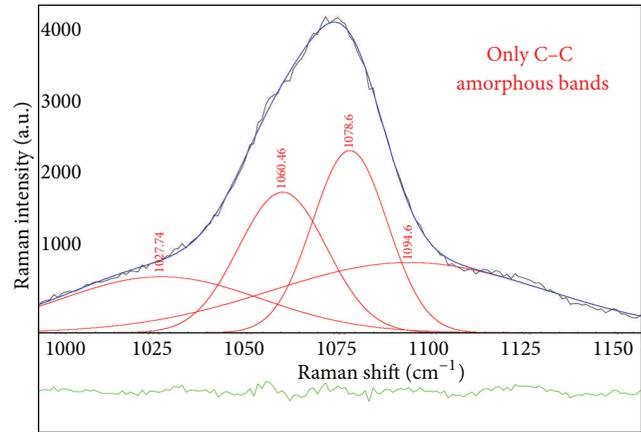
Thus, one can assume that A band, located at  $1432\text{ cm}^{-1}$ , corresponds to a nonstressed situation like that observed for the amorphous phase at the same frequency. The B band observed at  $1411\text{ cm}^{-1}$  would correspond to an elongation of the bond observed with a lower frequency and the C band at  $1460\text{ cm}^{-1}$  to a more compressed state of the CH bonds in  $\text{CH}_2$  groups.



(a)



(b)



(c)

FIGURE 1: (a) Evolution with temperature of the Raman spectrum corresponding to LDPE C–C vibrations. (b) Spectrum recorded at room temperature (semicrystalline material) and (c) spectrum recorded above  $T_{\text{melting}}$  (amorphous material).

Then, these three bands correspond to three  $\text{CH}_2$  different families in the crystalline phase of LDPE.

In a following step, we have attempted to relate these results to the viscosity of LDPE. Figure 3 shows the evolution of the integrated intensity area of the three  $\text{CH}_2$  bands of the crystalline phase according to the different LDPE grades (from viscous to flowing grades). It can be noticed that the relative intensity of the three peaks evolves as a function of the viscosity of the LDPE grades: the integrated intensity of the band corresponding to the compressed  $\text{CH}_2$  increases whereas that corresponding to the neutral  $\text{CH}_2$  decreases.

It is possible to relate these results to the lamellar semicrystalline structure of LDPE (Figure 2(b)). Indeed, in this structure, classically based on crystal lamella formed by the folding of polyethylene macromolecules, three kinds of  $\text{CH}_2$  groups, elongated, compressed, and neutral, can be estimated to exist which is consistent with the preceding attribution of Raman frequencies. As schematized in Figure 4, the elongated bonds are located in the folding zone whereas

the compressed bonds are located in the middle of the lamella. The compression would be due to stronger Van der Waals interactions in this zone. The neutral zone is comprised between these two other domains.

In the classical two-phase model, representative of the semicrystalline structure of LDPE, the periodicity of the structure is described by the long period  $L_p$  with  $L_p = L_a + L_c$  ( $L_a$  is thickness of the amorphous zone and  $L_c$  is thickness of the crystal lamella). In a first approximation, one can consider that the viscosity partly depends on the ratio of the thickness of amorphous and crystalline phases. Then, if the long period  $L_p$  is assumed constant, a decrease of viscosity will be traduced by an increase of the thickness of amorphous zones and a decrease of that of crystalline lamella (Figure 5). This will undergo changes in the amounts of neutral, compressed, and elongated  $\text{CH}$  bonds in  $\text{CH}_2$  groups and therefore changes in the evolution of integrated intensity areas of the corresponding Raman peaks as shown in Figure 3. When the viscosity decreases, the relative proportion of

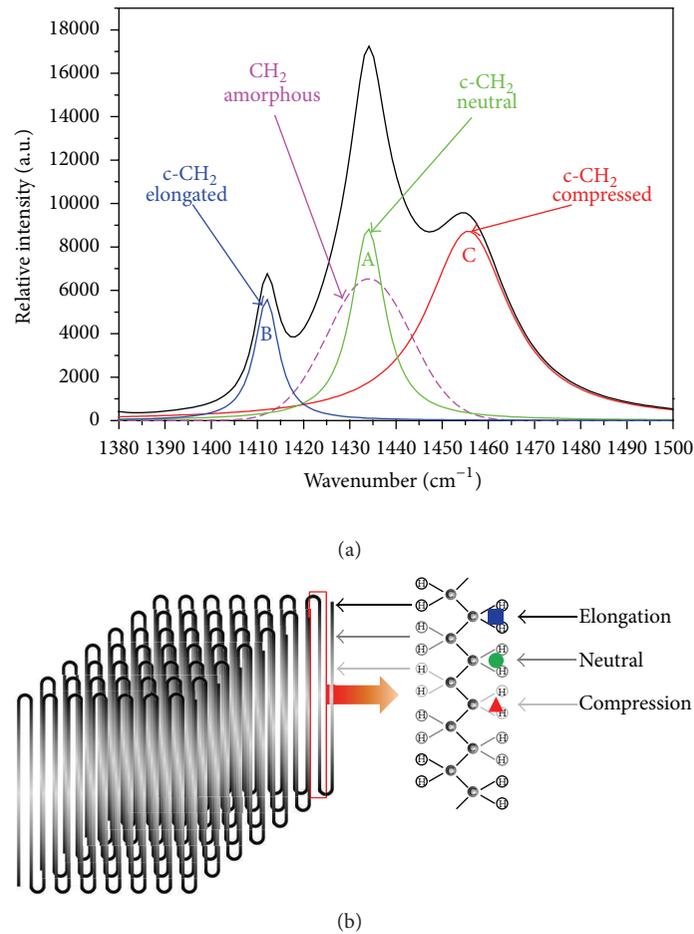


FIGURE 2: (a) Fitting of the LDPE CH<sub>2</sub> spectrum at room temperature with three Lorentzian functions (corresponding to the crystalline phase) and a Gaussian function (corresponding to the amorphous phase); (b) representation of the LDPE lamellar semicrystalline structure.

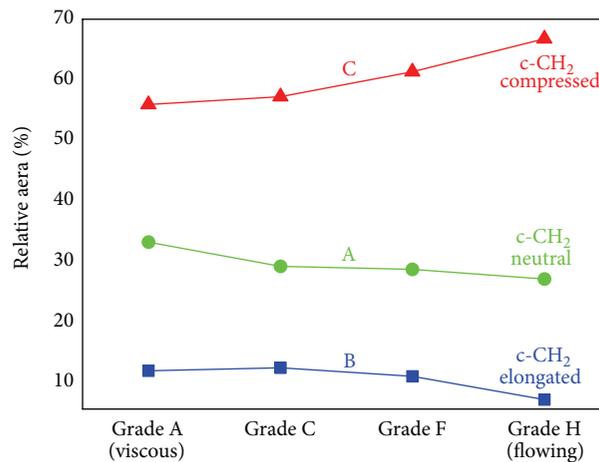


FIGURE 3: Trend of the evolution of the integrated intensity areas of the three CH<sub>2</sub> bands according to the different grades (from viscous to flowing).

neutral and elongated bonds tends to decrease whereas that of compressed bonds increases (the crystalline lamella thickness decreases) undergoing the subsequent decrease or increase observed for the relative integrated intensity areas.

Figure 6 gives crystal lamella thickness determined by DSC for several LDPE grades from viscous to flowing grades. It shows well a reduction of crystal lamella thickness as the grade is more flowing. Thus, this behaviour validates the

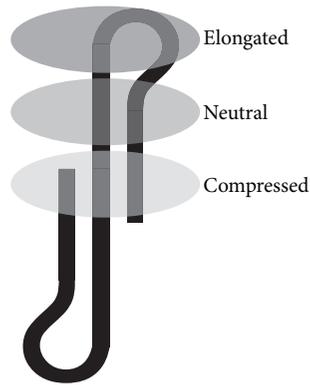


FIGURE 4: Representation of the lamellar crystal structure and position of the three kinds of CH<sub>2</sub> groups (the black lines represent the C–C skeletal structure; CH<sub>2</sub> bonds are perpendicular to these lines).

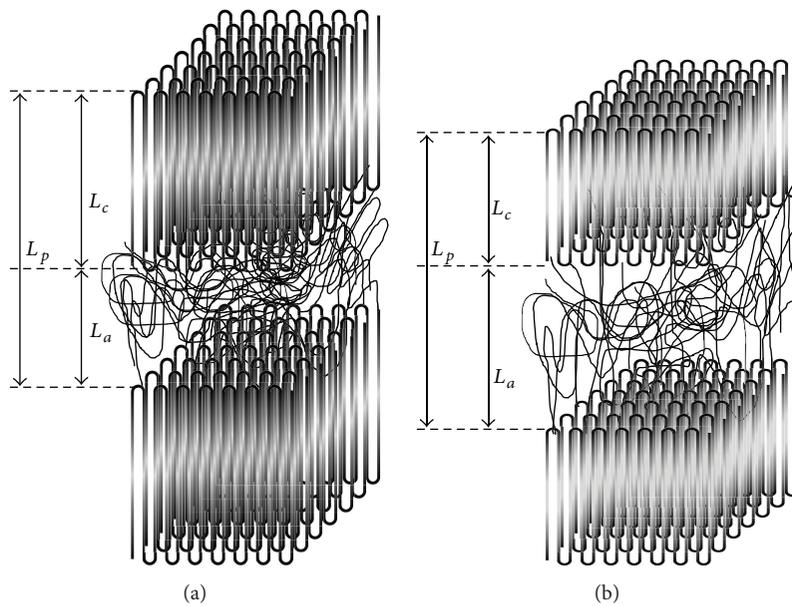


FIGURE 5: Schematic representation of the LDPE structure in case of (a) viscous grade and (b) flowing grade.

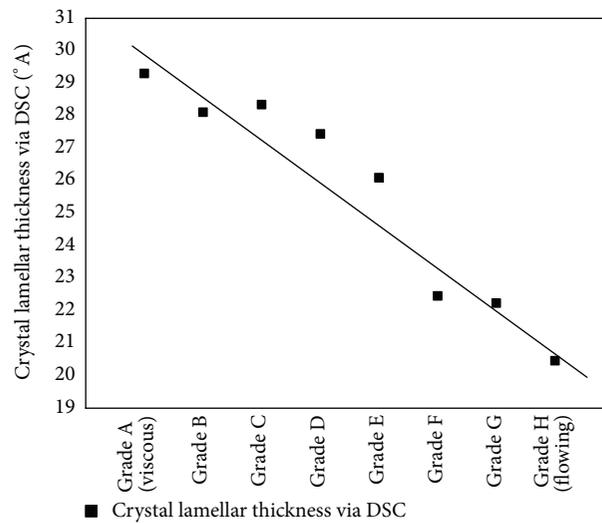


FIGURE 6: Crystal lamellar thickness determined by DSC for several LDPE grades (from viscous to flowing grades).

assumptions made to interpret the evolution of the Raman spectrum and its relations with the structure of the LDPE material investigated.

Consequently, this induces in the interphase, between the amorphous and crystalline phases, more interactions and connections, which can be at the origin of the presence of a mesophase. This involves more bridging and of this fact an increase of the connections known as compressed like observed in Figure 3.

#### 4. Conclusion

In this work, using Raman spectroscopy, a model based on the LDPE semicrystalline structure and involving the presence of three kinds of CH<sub>2</sub> groups in the crystal lamella, has allowed for distinguishing various LDPE grades (from viscous to flowing material). Indeed, Raman spectroscopy proved its efficiency as being very sensitive to weak variations of the environment of the CH chemical bonds. This simple study of CH<sub>2</sub> chemical bands of the LDPE grades can be used to predict the mechanical behaviour or rheological properties (viscosity) of this polymer.

#### Conflict of Interests

The coauthors have not a direct financial relation with the commercial identities mentioned in this paper (Netzsch DSC 200 F3 Maia and Horiba Jobin Yvon Aramis systems).

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