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Mémoire de Thèse

CONTROLE AVANCE DE PRODUCTION DE POLYETHYLENE PAR SPECTROSCOPIE RAMAN

Pour l'obtention du grade de

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Mention : Science des Matériaux

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Contrôle avancé de production de polyéthylène par spectroscopie Raman

Résumé : Depuis sa découverte en 1933, le polyéthylène a connu un essor industriel mondial important. Aujourd'hui, le Polyéthylène Basse Densité (PEBD) souffre d'une grande concurrence avec de nombreux polymères. Ainsi, pour conserver ses marchés et répondre exactement aux besoins des clients, des contrôles de laboratoire de plus en plus précis et de nouvelle génération doivent être envisagés dans les usines de production pour obtenir un produit de la meilleure qualité possible. Ce travail de thèse s'inscrit dans cette optique en faisant le choix de la spectroscopie Raman car, cette technique très performante, d'analyse qualitative et quantitative, est non-destructive et peut s'intégrer parfaitement dans l'industrie. L'usage des statistiques et de la chimiométrie se révèlent indispensable pour mener à bien ce projet.

Dans un premier temps, une étude exploratoire par spectroscopie Raman des différents grades produits par l'usine Total à Carling, avec l'attribution précise des pics du PEBD, la signature des divers réactifs ainsi que le comportement thermique du polymère nous permet une approche microstructurale du problème. Les résultats sont corrélés par Analyse Enthalpique Différentielle (AED) ainsi que par Diffraction des Rayons X (DRX). Ainsi, l'attribution des bandes de vibration en flexion des liaisons CH_2 s'explique d'un point de vue mécanique et diffère d'un grade à l'autre permettant ainsi leur distinction par spectroscopie Raman.

Par ailleurs, au-delà de la mesure de l'indice de Fluidité (IF), du Haze et du dosage des additifs par spectroscopie Raman, les résultats de cette étude montrent qu'il est possible de déterminer et de quantifier la plupart des défauts de production (de type gels, réticulation et oxydation). Des conséquences sur les propriétés applicatives sont mises en évidence et des causes au niveau du procédé de fabrication ont également été recherchées.

L'ensemble des résultats de cette thèse trouve son application dans le développement d'un démonstrateur at-line, lequel permet de valoriser ces travaux en démontrant la faisabilité de la technique Raman pour un contrôle avancé de la production du PEBD.

Mots-clés : Polyéthylène, spectroscopie Raman, AED, DRX, défauts de production, chimiométrie, démonstrateur

On-line control of polyethylene production by Raman spectroscopy

Abstract: Since its discovery in 1933, polyethylene has known an important global industrial development. Today, Low Density Polyethylene (LDPE) suffers from high competition with many polymers. In order to preserve its market shares and meet the exact needs of the customers, more and more precise new generation laboratory controls must be considered in production plants to obtain a product with the best possible quality. This thesis work fits into this context by choosing the Raman spectroscopy, a successful technique of qualitative and quantitative analysis that is non-destructive and can be perfectly integrated into an industrial plant. The use of statistics and chemometrics are necessary in order to successfully implement this project.

First, an exploratory study by Raman spectroscopy of the various grades produced by Total Carling, with the precise identification of LDPE peaks, the signature of the various reactives, as well as the thermal behavior of the polymer allows us a microstructural approach of the problem. The results are correlated by Differential Scanning Calorimetry (DSC) as well as by X-ray Diffraction (XRD). Thus the attribution of CH_2 bending vibration bands is comprehensible from a mechanical point of view and differs from one grade to another, allowing their differentiation by Raman spectroscopy.

Beyond the measurement of Melt Flow Index (MFI), Haze and additives concentration, the results of this study show that it is possible to determine and to quantify most of the production flaws (gels, cross-linking, and oxidation types). Consequences on the applicative properties are estimated and causes from within manufacturing process were also investigated.

All the results of this thesis find their application in the development of an at-line demonstrator, which allows highlighting these works by demonstrating the feasibility of the Raman technique for an advanced control of the LDPE production.

Keywords: Polyethylene, Raman spectroscopy, DSC, XRD, production flaws, chemometrics, demonstrator.

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Research Article

Identification of LDPE Grades Focusing on Specific CH_2 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_2 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_2 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 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 CH_2 Raman bands. Raman spectroscopy is very sensitive to strain [11], so this work aims to attribute mechanically 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 μm confocal hole, and a x50 lens. The studied spectral range extended from 640 cm^{-1} to 1700 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°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°C/min for each temperature ramp.

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

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

with [13] L_c being thickness of the crystalline lamellar, σ_e being energy of surface of the principal facets of ends of the crystalline lamella (0.070 J/m^2), $\Delta H_{f_{\text{th}}}$ being melting enthalpy of the perfect crystal (2.905.10^5 J/kg^{-1}), ρ_c being density of the perfect crystal (1000 kg/m^3), T_0 being theoretical melting point of the lamella of infinite size (143.5°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 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_{melting} (Figure 1(c), amorphous state).

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	

Now, we would like to focus on the bands related to the 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-CH_2) and the amorphous phase (a-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 cm^{-1}, corresponds to a nonstressed situation like that observed for the amorphous phase at the same frequency. The B band observed at 1411 cm^{-1} would correspond to an elongation of the bond observed with a lower frequency and the C band at 1460 cm^{-1} to a more compressed state of the CH bonds in CH_2 groups.

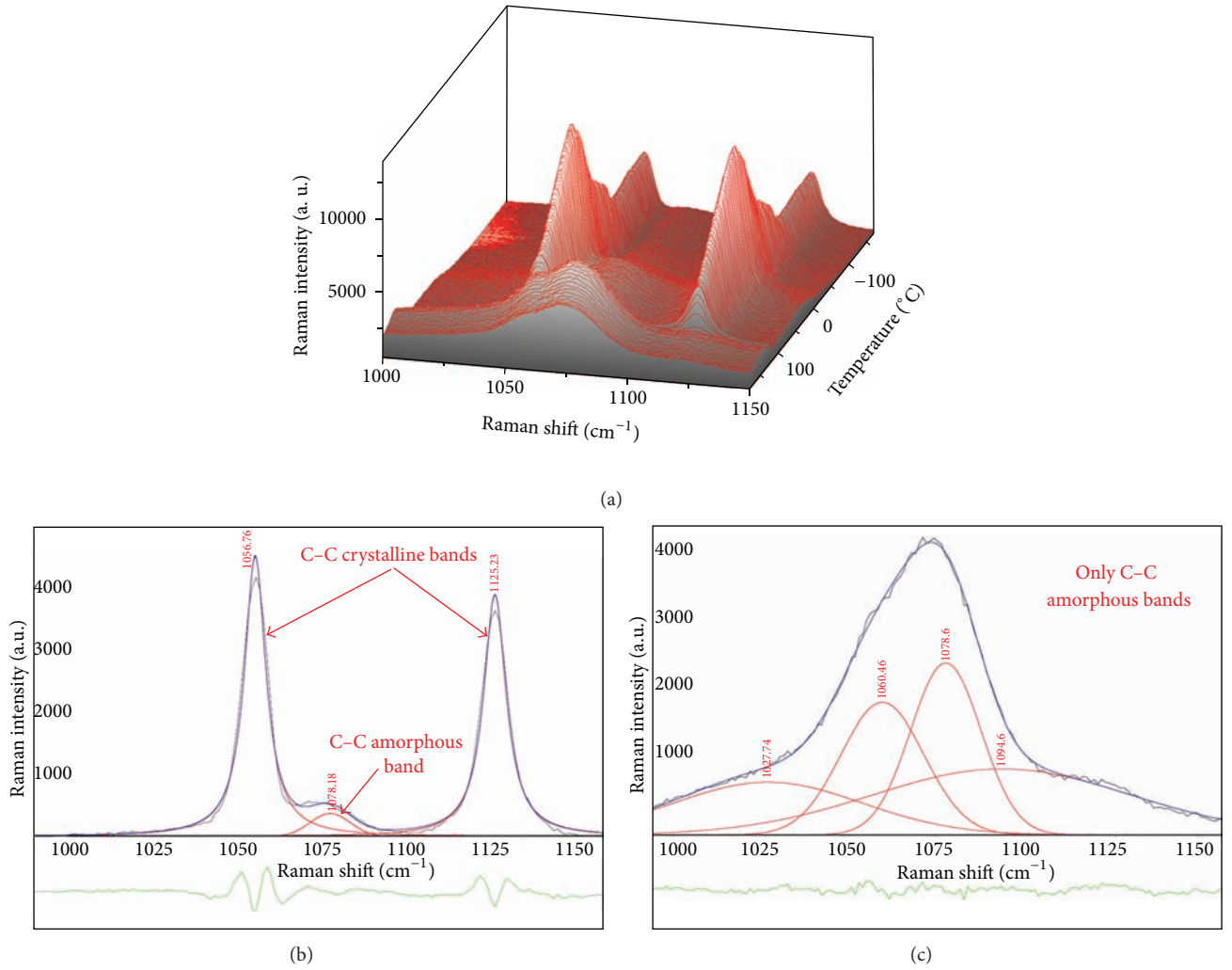

Figure 1: (a) Evolution with temperature of the Raman spectrum corresponding to LDPE C–C vibrations. (b) Spectrum recorded at room temperature (semicrystalline material) and (c) spectrum recorded above $T_{melting}$ (amorphous material).

Then, these three bands correspond to three 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 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 CH_2 increases whereas that corresponding to the neutral 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 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 CH bonds in 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

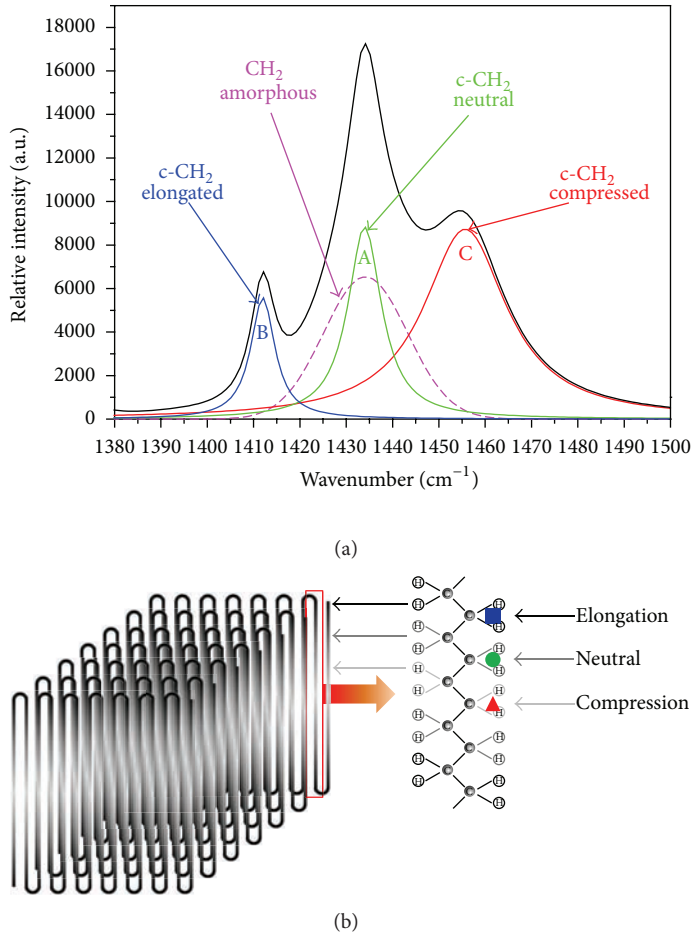

FIGURE 2: (a) Fitting of the LDPE CH_2 spectrum at room temperature with three Lorentzian functions (corresponding to the crystalline phase) and a Gaussian function (corresponding to the amorphous phase); (b) representation of the LDPE lamellar semicrystalline structure.

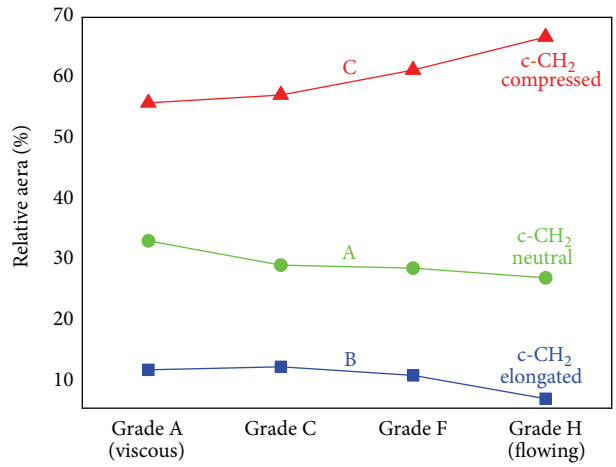

FIGURE 3: Trend of the evolution of the integrated intensity areas of the three CH_2 bands according to the different grades (from viscous to flowing).

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

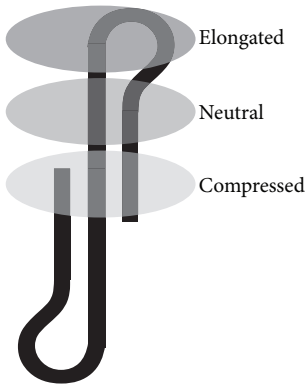

Figure 4: Representation of the lamellar crystal structure and position of the three kinds of CH_2 groups (the black lines represent the C–C skeletal structure; CH_2 bonds are perpendicular to these lines).

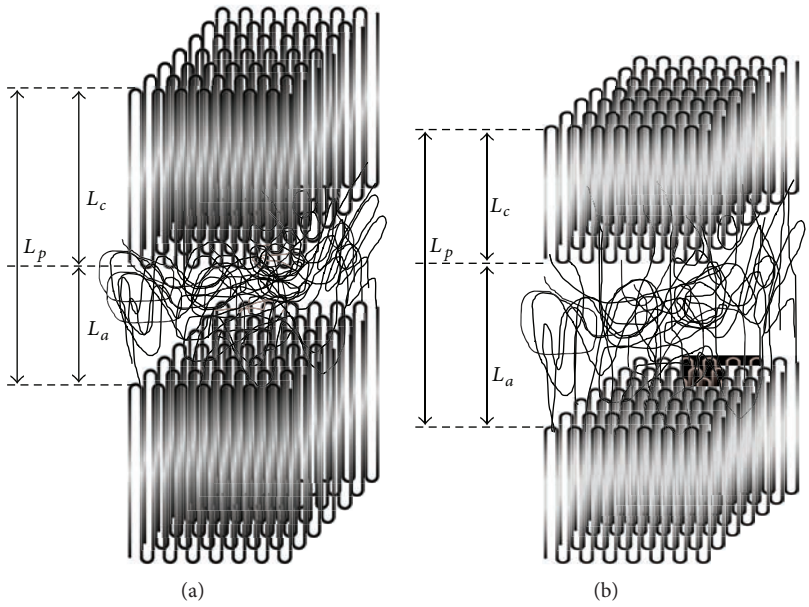

Figure 5: Schematic representation of the LDPE structure in case of (a) viscous grade and (b) flowing grade.

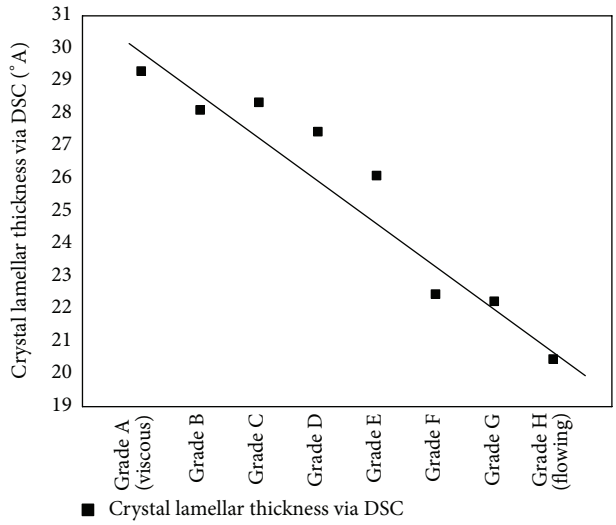

Figure 6: Crystal lamellar thickness determined by DSC for several LDPE grades (from viscous to flowing grades).

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_2 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_2 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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ETUDE COMPARATIVE DE DIFFERENTS GRADES DE POLYETHYLENE PAR ANALYSE ENTHALPIQUE DIFFERENTIELLE CORRELEE PAR SPECTROSCOPIE RAMAN

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1. INTRODUCTION

Le polyéthylène est un polymère de grande consommation en raison de son faible coût de fabrication et de ses propriétés physiques et mécaniques compatibles avec de nombreuses applications de la vie courante [1] auxquelles correspond un grade. Il est alors indispensable de savoir différencier ces produits au moyen de méthodes de caractérisation adaptées comme l'Analyse Enthalpique Différentielle (AED) ou plus originalement par spectroscopie Raman.

L'objet de ce papier est d'établir la relation qu'il existe entre la viscosité et les températures caractéristiques d'un grade à l'aide de l'AED corrélée par la spectroscopie Raman. Il s'agit par ailleurs de suivre l'évolution microstructurale du polymère lors de ses changements d'état afin de déterminer sa structure, ce qui représente un atout majeur dans le monde industriel des polymères.

2. EXPERIMENTATION

L'AED est une des techniques couramment utilisées dans ce but. Les tests ont été effectués avec une DSC 200 F3 Maia® de Netzsch, à flux de chaleur permettant de travailler jusqu'à -170°C grâce à un système de refroidissement par azote liquide. La rampe de température choisie est de 10°C/min. Bien que l'AED permet d'obtenir les températures caractéristiques et de délimiter les phases visqueuse, caoutchoutique et vitreuse [2], elle ne permet pas d'avoir accès à la microstructure et il s'agit d'une méthode lourde lorsqu'il s'agit d'effectuer du contrôle Qualité en ligne, ce qui limite son champ d'action.

La spectroscopie Raman, autre technique d'analyse de polymères et actuellement en grande évolution compte-tenu des avantages qu'elle présente (technique non destructive et quasi-instantanée pouvant parfaitement s'insérer dans le milieu industriel au moyen de capteurs adaptés et de dispositifs de plus en plus réduits [3]) permet non seulement, d'obtenir les températures caractéristiques du polyéthylène mais apporte par ailleurs des informations sur la microstructure du polymère. Le spectroscope utilisé est un iHR320 de Horiba Jobin-Yvon (laser 532 nm, réseau 1800tr/mm, trou confocal 500µm). Une platine cryostatique Linkam® THMS600 alimentée en azote liquide permet d'étendre l'étude de -170 à 190°C. Les acquisitions de spectres Raman durent 2 secondes, tous les 2°C, à une vitesse de chauffage de 5°C/min.

8 grades de PolyEthylene Basse Densité (PEBD) ont été sélectionnés pour cette étude et sont désignés par la suite, de la lettre A à H, du plus visqueux au plus fluide.

3. RESULTATS

Les résultats observés en DSC sont en accord avec la littérature [2] et mettent en évidence les transitions connues du polyéthylène à savoir la fusion (pic endothermique) aux alentours de

120°C, la recristallisation exothermique vers 80°C ainsi qu'une faible transition vitreuse vers -120°C. Selon le grade, ces températures évoluent et permettent ainsi de les différencier. Une représentation originale de tous ces résultats est donnée en figure 1.

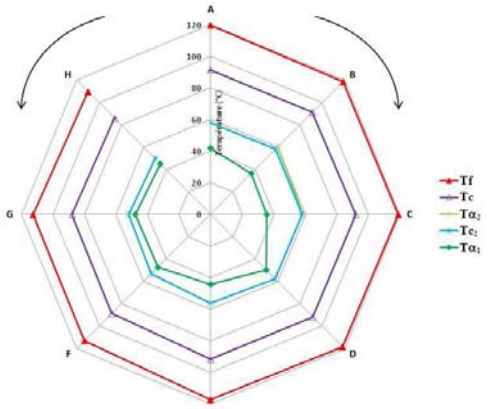

Figure 1 : Radar des résultats DSC pour les 8 grades PE.

De même, par spectroscopie Raman, ces transitions de phases sont visibles et peuvent être interprétées au niveau microstructural grâce à l'attribution précise des bandes Raman et leur évolution selon la température. La figure 2 illustre une partie de ces résultats.

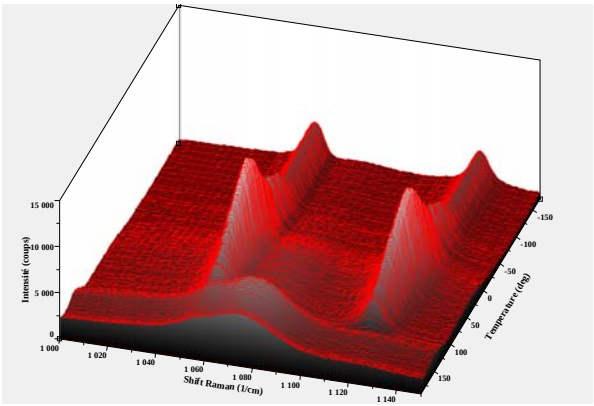

Figure 2 : Cartographie en température du grade A.

La sélection de deux bandes, l'une relative à la phase cristalline et l'autre à la phase amorphe, rapportées au bruit de fond, permet de suivre leur évolution en intensité, ce qui nous renseigne sur les changements structuraux que le PE subit, ce qui est détaillé en figure 3.

Ainsi, on observe d'autres transitions corrélées parfois aux résultats de DSC et connues dans la littérature (transitions α et β) [4] [5] mais aussi des relaxations et des mises en agitation des chaînes s'accompagnant de variations de volume uniquement détectées par spectroscopie Raman. Des analyses complémentaires par Diffraction des Rayons X (DRX) complèteront ces travaux.

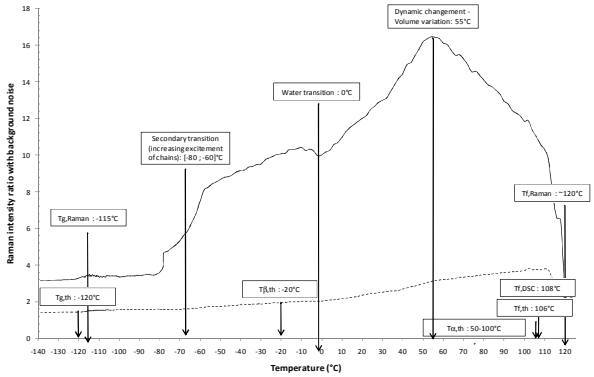

Figure 3 : Evolution de l'intensité normalisée d'une bande cristalline (trait plein) et amorphe (pointillés)

4. CONCLUSION

Le couplage de la spectroscopie Raman et de l'Analyse Enthalpique Différentielle permet de déterminer le comportement thermique et structural du polyéthylène et ainsi de pouvoir différencier des grades. La spectroscopie Raman présentant de nombreux avantages, son intégration en ligne pour du contrôle Qualité est l'objectif final de cette étude.

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Comparative Study Of Various Grades Of Polyethylene By Differential Scanning Calorimetry (DSC) Correlated With Raman Spectroscopy

Richard Jumeau, Patrice Bourson, Michel Ferriol, François Lahure, Franck Ducos et al.

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View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1353&Issue=1

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Comparative Study Of Various Grades Of Polyethylene By Differential Scanning Calorimetry (DSC) Correlated With Raman Spectroscopy

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Abstract. Polyethylene (PE) is a very important material. In 2008, almost 30% of the world plastics production was dedicated to this polymer (70 million tons) [1]. It is a consumer polymer because of 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 application, there is a particular grade, i.e. a polyethylene with well defined rheological properties. Therefore, it is essential to know how to differentiate these different grades by suitable methods of characterization.
Differential Scanning Calorimetry (DSC) is one of the techniques usually used for this purpose. The knowledge of characteristic temperatures such as melting, cold crystallization or glass transition gives information on the viscosity and thus, on the grade of the polymer. DSC also allows the detection of defects, (for example, presence of unmelted pieces). However DSC is a tedious method for on-line quality control, limiting its scope. The determination of the polymer structure represents a major challenge in the industrial world of polymers.
Raman spectroscopy, another technique of polymer analysis, is nowadays growing fast because of the advantages it presents. It is a non-destructive 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]. That technique is used to obtain the characteristic temperatures of PE and information on the polymer structure.
The purpose of this article is to establish the correlation between the viscosity of a polymer and its characteristic temperatures obtained by DSC and subsequent possibilities of quality control in industry. These measurements are correlated with others obtained by Raman spectroscopy, to get additional details concerning the structure and transitions of the material, the final goal being to use these results in on-line analysis.

Keywords: Polyethylene, Differential Scanning Calorimetry, Raman Spectroscopy, quality control, on-line analysis, polymer processing.
PACS: 36.20.Ng / 78.30.Jw / 64.70.dj / 36.20.Fz / 89.20.Bd

INTRODUCTION

Rheology has always been the best way for distinguishing polymers presenting different optical and mechanical properties because it allows reaching the molecular structure while having access to the process ability of the finished product [4]. The present study consists in measuring the viscosity or Melt Flow Index, and then the polymer grade is considered. The measurement consists in determining the amount of material extruded during ten minutes through a calibrated draw, at a given load and temperature [5].

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However, a rheological study does not allow knowing the optical, mechanical and thermal properties of the material. The thermal properties of polymers can be obtained by Differential Scanning Calorimetry (DSC), for instance. DSC is also used to determine the degree of material cristallinity. This property is one of the most important because it has a direct relationship with mechanical properties [6].

But all these conventional tests have the disadvantage to be destructive and to require a long and tedious time for samples preparation and for measurements. The object of this study is to determine the rheological and thermal properties using a non-destructive technique, which will be easy to implement. The study was conducted on low density polyethylene (LDPE) with some selected grades. We have first compared Raman and DSC measurements and then we have investigated correlations existing between them.

POLYETHYLENE SAMPLES

To cover a wide range of polyethylene products, 8 grades of Low Density PolyEthylene (LDPE) were tested, designated by letters A to H, from the most viscous to the least viscous. The grades A and H were the object of a particular attention to find the trends. Table 1 summarizes the choice of the products sorted by relative viscosity, from the most viscous to the least viscous, while specifying the presence of additives and the applications.

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

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

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°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°C/min for each temperature ramp.

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	

The thermogram obtained for the grade A during the temperature cycle is presented in figure 1.

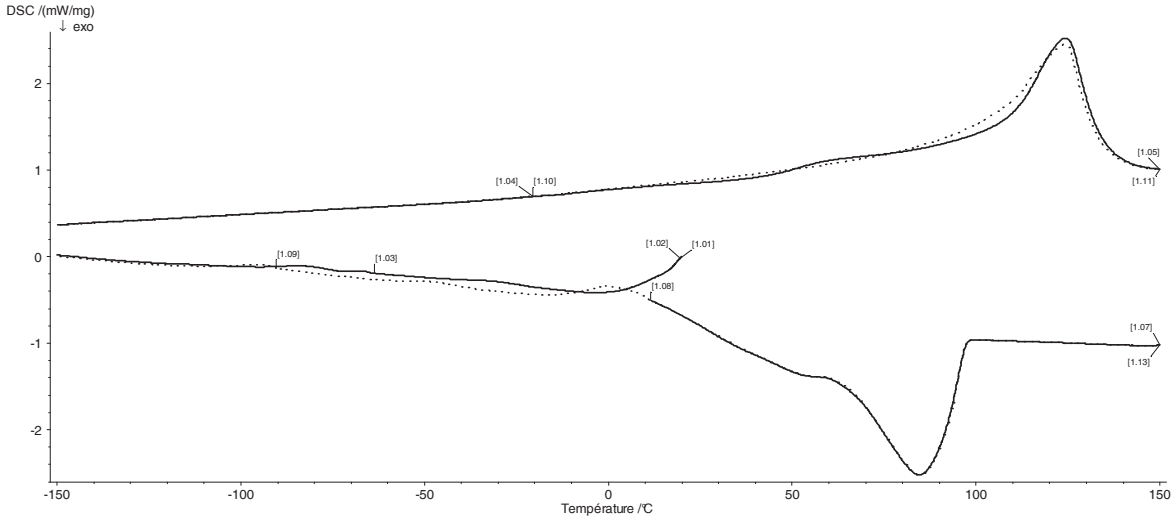

FIGURE 1. Complete thermogram of DSC for the grade A: 1st cycle (downstroke), 2nd cycle (dotted line).

The results obtained correspond to the observations of the literature [2] concerning the most known transitions such as the melting point, the endothermic peak around 120°C, the exothermic peak of cold crystallization towards 80°C and the low glass transition towards -120°C. But the others transitions (transitions α and β) can also be seen in figure 1 with more or less important temperature differences.

To allow the classification of the grades, a simpler temperature program was used from -30°C to 150°C at the rate of 10°C/min in order to easily obtain the wished temperatures without using nitrogen cooling system. The DSC results were analyzed by using the classical determination methods of characteristic temperatures. Thus, melting and crystallization points were determined by taking the temperature at the maximum of the peak and secondary transitions (glass transition, secondary relaxation ...) were obtained with the method of tangents. The results are presented in an original shape on the radar graph of figure 2:

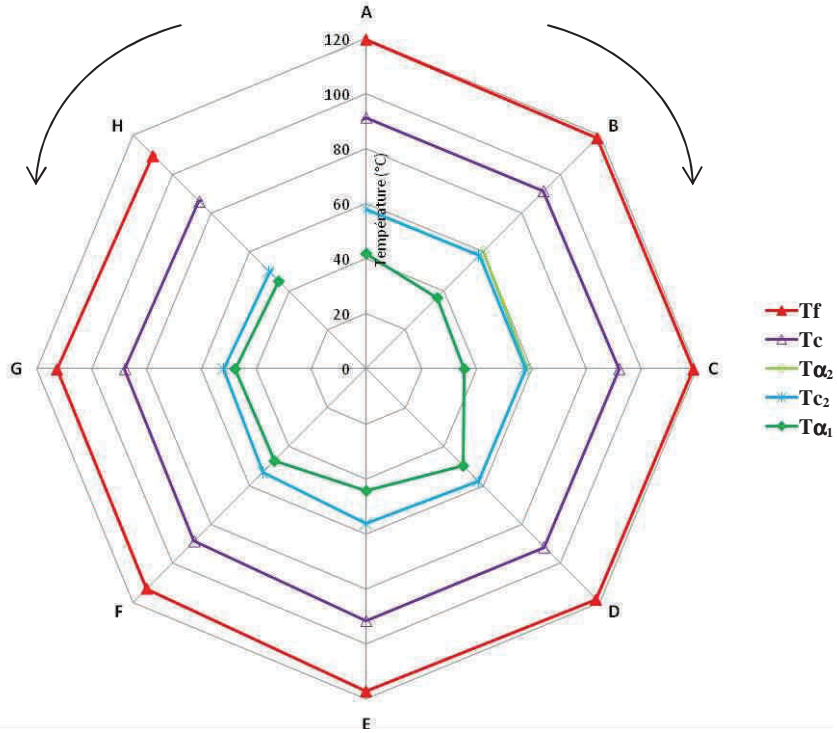

FIGURE 2. DSC results of the 8 PE grades.

We observe for each branch of the radar 4 or 5 characteristic temperatures of each grade which are the melting point Tf, the temperature of cold crystallization Tc as well as the temperature of secondary recrystallizing Tc_2 and finally the temperatures of the secondary transitions α_1 and α_2.

Besides the temperatures of the secondary transitions α_1 and α_2, all the other temperatures appreciably evolve in the same direction when we run through the radar clockwise, from the most viscous to the least viscous i.e. a decrease of these temperatures. Indeed, the more a polymer is viscous and the more the length of its molecules is important and, thus, the more energy will be necessary for moving them and obtaining the molten state.

The secondary transition α_1 corresponding to the homogeneous sliding of chains by shearing has no sensitive evolution but shows that grade D can be distinguished from the other grades. This difference holds in the fact that grades B and D present a slippery agent introduced in small amount for the grade B and in abnormally high amount for this batch of grade D.

On the other hand, the presence of a secondary transition α_2 for the grades B and C corresponds either to an inhomogeneous cristallinity within the polymer material [7] or to an inhomogeneous sliding of the thin lamella (by blocks) [8].

In any case, the addition of the slippery agent in a too big amount for the grade D perturbed the microstructural state of the polymer by flooding polymer chains into this organic matrix. Consequently more energy is required for chains to slide by shearing independently from the others, that is to say, without the protective husk of slippery agent which limits the shearing at lower temperatures. Thus, the slippery agent, which allows the sliding of thin lamellas by block when it is added in small amounts, does not allow this sliding in case of too strong amount addition taking into account the generalized lubrication effect of thin lamellas.

The presence of the secondary transition α_2 in grade C, which does not present a slippery agent in small amounts, can be explained by residual traces during the production of this batch. Additional tests will be undertaken to confirm these results.

The measurement and the combination of the characteristic temperatures of the 8 presented grades show that it is possible to distinguish the grades and that if a grade presents a disorder of production, this one is detectable by DSC. Then, Raman spectroscopy enables these same interpretations, while being non-destructive, less tedious and by giving more microstructural information [3].

Raman spectroscopy

Spectroscopic study was carried out with a Raman spectroscope iHR320 of Horiba Jobin-Yvon fitted with a laser of 532 nm of wavelength, a 1800 lines/mm network, a 500 µm confocal hole and an optical head provided with a long focal X50 objective. The studied spectral range goes from 640 to 1700 cm^{-1}. Acquisitions last for 2 seconds and in order to obtain an interesting signal-to-noise ratio, we average the signal on three acquisitions.

This Raman spectroscope was besides coupled with a Linkam® THMS600 cryostat stage supplied with liquid nitrogen so as to regulate the measure chamber on a temperature range extending from -170°C to 190°C. Some grams of polyethylene (15-20g) are then placed in a quartz crucible of 22mm of diameter. After having cooled the system down to -170°C, we acquire Raman spectrum every 2°C from -170°C to 190°C without imposing an isotherm to the material for the grades A and H, at a constant speed of 5°C/min.

In order to get an overview of the polyethylene Raman spectrum versus temperature, the results visualization in 3 dimensions as presented in the extract (figure 4a) was adopted. Figures 4b and 4c respectively display extracts of deconvolved spectra at low temperature (-170°C) and high temperature (190°C) for the grade A.

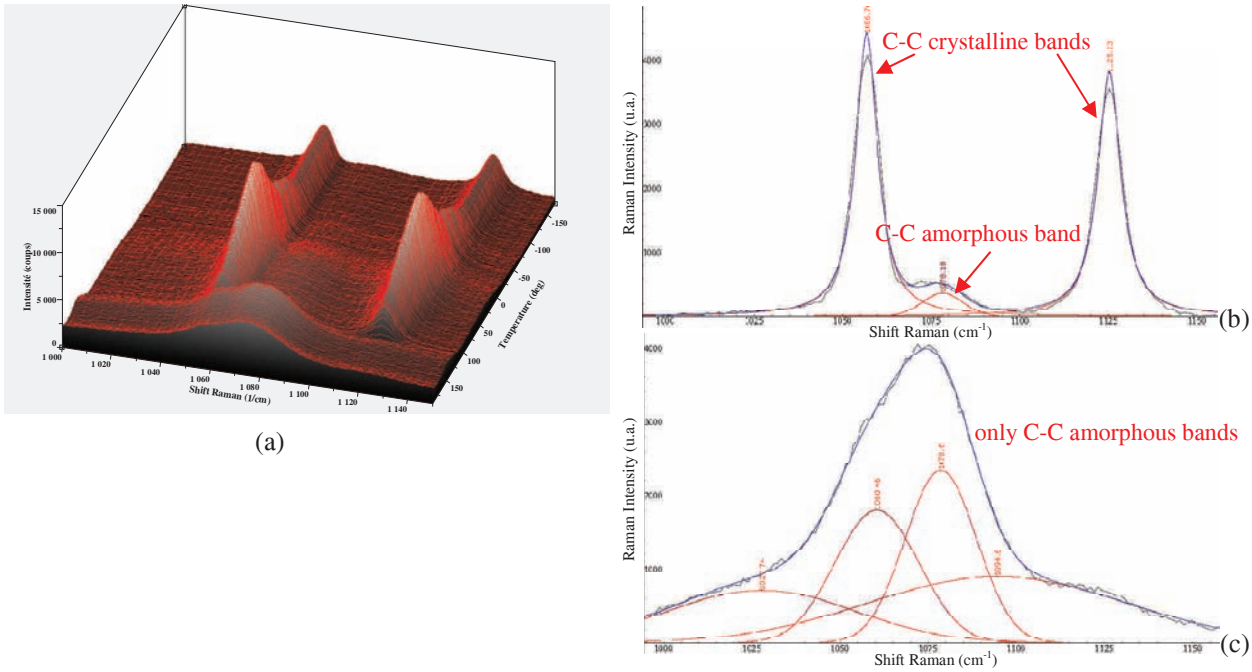

FIGURE 4. (a) Temperature mapping (extract) and fitted spectra at -170°C (b) and 190°C (c) for the grade A.

These results show bands, in a part of the Raman spectrum, relative to the bonds C-C. They highlight the various transitions previously observed in DSC by extrema of intensities. The melting point is the most marked transition because it reveals two domains on the extract of previous mapping and on the spectra also:

- Before Tf=119°C, we note two fine and intense Lorentzian bands and two low and wide Gaussian bands respectively attributed to the crystalline and amorphous phase and visible also in figure 4b.
- After Tf=119°C, we do not note more than some Gaussian bands relative to the amorphous phase, conspicuous results in figure 4c.

The transition from the spectrum 4b to the spectrum 4c means important variations of intensity and width of the Raman peaks. We focus our attention on the evolution of the intensity of these two kinds of bands which permits to have much information. To repeal the background noise and consequently normalize the results in intensity, the variations of ratios of the amorphous and crystalline bands defined in table 3 compared to the intensity of the background noise for the grade H were drawn on figure 5.

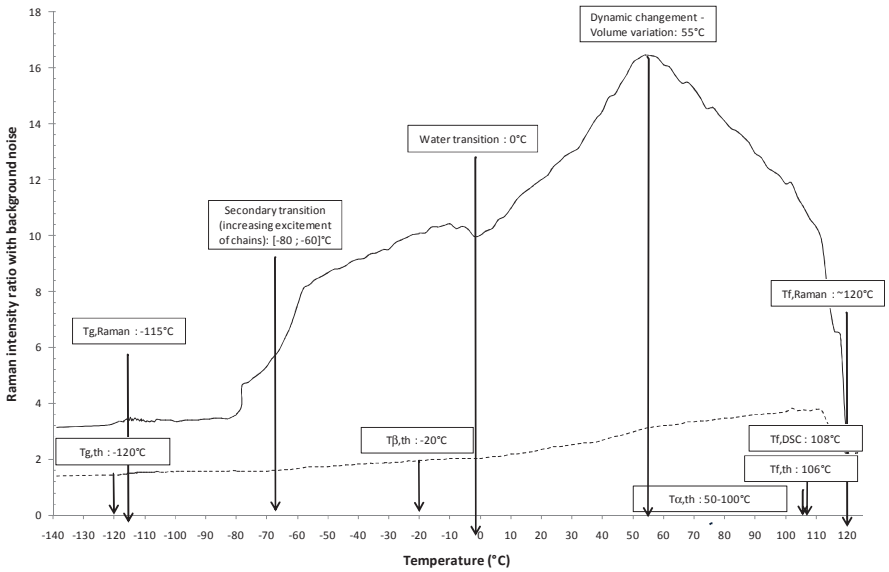

FIGURE 5. Crystalline band (downstroke) and amorphous band (dotted lines) for the grade H.

TABLE 3. Definition of the amorphous, crystalline bands and the background noise in Raman spectroscopy.

Spectral range (cm^{-1})	Associated bond
689 – 953	C-C amorphous
1120 – 1130	C-C crystalline
1549 – 1699	Background noise

At first, these results confirm the results observed by DSC analysis with the presence of the same additional transitions in similar temperatures. Besides, this graph again reveals the melting point of polyethylene whatever the phase observed at the break of the curve towards 120°C. These values correspond to the 3D observation and get closer to theoretical values and those determined by DSC previously.

Other transitions can then be observed by considering slope variations and defining local and global extrema. The most known but the least visible on these curves is the glass transition towards -115°C. By comparing the curves of the figure 5, we can also notice that Raman activity of the crystalline phase is more sensitive than that of the amorphous phase.

Three other transitions are visible. First of all, one observes a transition towards 0°C which corresponds to the solid-liquid transition of the water either present within this polymer or within the measure chamber. The secondary transition found towards -68°C corresponds to a stake in excitement of the chains of the crystalline phase. This phase has a more and more intense Raman activity owing to the internal excitement of the chains which comes to add up to the excitement laser brought by the Raman probe. Finally, the transition occurring towards 55°C is due to a dynamic change, to a variation of the crystalline phase volume. Indeed, from this temperature, the least energy crystallites gradually melt and it has for consequence to decrease the volume of this phase for the benefit of the molten state. The melting (Tf) is then total when the last crystallites melt and the Raman activity of this phase brutally disappears.

These transitions would also have been able to be linked with the well known relaxations α and β of polyethylene occurring towards -20°C and between 50 and 100°C if the noticed temperature difference had not been so important. Additional tests and correlations by X-Ray Diffraction (XRD) will come to complete these works.

CONCLUSION

The association of Raman spectroscopy with Differential Scanning Calorimetry enables to determine the thermal behaviour and the structural information of polyethylene. Thus, these combined data favour the possibility of distinguishing several products having different viscosities and can even establish a new classification of these grades according to other linked more properties, like the presence of a slippery agent whose amount influences the process ability of the product.

The correlation between viscosities and characteristic temperatures having been established, the possibilities of expanding it to the quality control in industry are promising considering the multiple contributions of this new non-destructive, fast technique and the additional information on the material structure it can bring.

ACKNOWLEDGMENTS

The authors wish to thank the teams of Total Petrochemicals France who prepared the sampling of polyethylene and supplied the information useful for this study as well as the staff of the University Institute of Technology of Forbach for their contribution and equipment necessary for the study.

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Contrôle de production de polyéthylène

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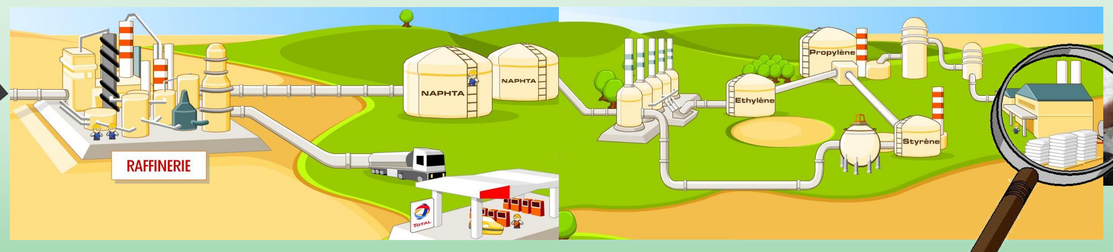
Patrice BOURSON[1], Michel FERRIOL[1], François LAHURE[2]

Contexte & Objectifs

Pétrole

De l'éthylène au polyéthylène…



Polyéthylène

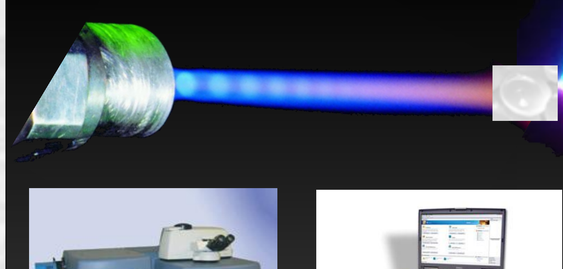
Un polyéthylène de meilleure qualité: + brillant; + résistant

demain

Une nouvelle technique de contrôle on-line: la spectroscopie Raman

Matériel

Spectroscopie Raman



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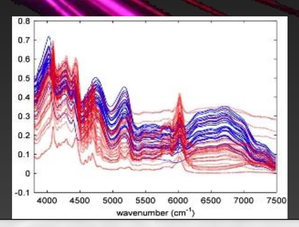


VS

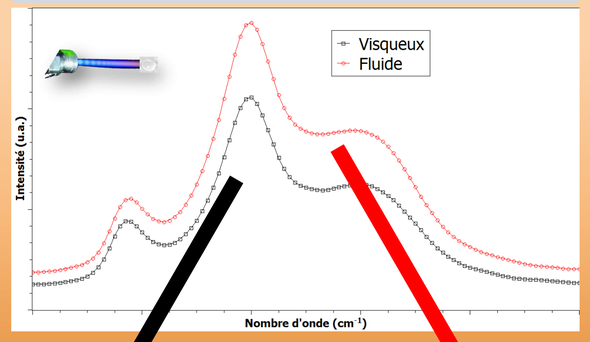
Essais mécaniques (Traction)

Essais thermiques (DSC)

Essais optiques (Hazemètre)

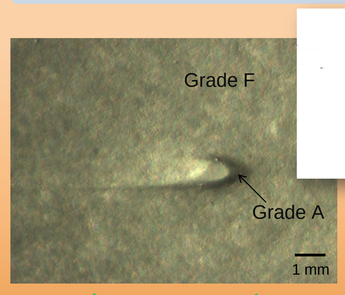
Résultats

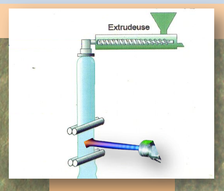
Différentiation des produits sur granulés

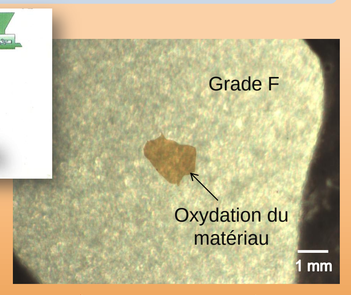


Classification possible du produit

Détection des défauts sur films







Léger ajustement des paramètres de production

Défauts non rédhibitoires chez certains clients après mise en œuvre

Ajustement des paramètres de production ou arrêt pour nettoyage

Défauts rédhibitoires

Déclassement du produit

Conclusions & Perspectives

Intégration d'un nouvel outil d'analyse on-line capable de:

- ✓différentier les produits et
- ✓détecter les défauts et variations du process de fabrication

- ❖Mise au point d'une analyse très fine des spectres (chimiométrie)
- ❖Déterminer les autres propriétés du matériau (mécaniques et optiques)
- ❖Fiabilisation de la technique pour remplacement intégral du contrôle continu actuel
- ❖Etendre ces contrôles à d'autres polymères (EDA,…)

Contrôle avancé de production de polyéthylène par spectroscopie Raman
Thèse CIFRE en collaboration entre
[1] Laboratoire Matériaux Optiques, Photonique et Systèmes E.A. 4423, Université de Paul Verlaine de Metz – Supelec, 2 rue Edouard Belin 57070 METZ, France
[2] Total Petrochemicals France, Usine de Carling – Saint-Avold , RN 33 - BP 61005 57501 SAINT AVOLD, France

Analyse des vibrations CH_2 pour différents grades de polyéthylène par spectroscopie Raman

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François Lahure[2], Abdesselam Dahoun[3]

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En 2008, près de 30% de la production mondiale de plastiques est dédiée au polyéthylène (soit 70 millions de tonnes). En effet, le polyéthylène permet une mise en forme généralement aisée (extrusion, injection), possède d'excellentes propriétés d'isolation électrique et de résistance aux chocs et présente une grande inertie chimique et biologique (contact alimentaire) [1]. A chaque marché, chaque utilisation correspond un grade pour un industriel, c'est-à-dire un polyéthylène dont les propriétés physico-chimiques diffèrent. Il est alors indispensable de savoir différencier ces produits au moyen de méthodes de caractérisation adaptées. Par exemple, la spectroscopie Raman donne des indications sur les vibrations des différentes molécules. Technique non destructive et quasi-instantanée, pouvant parfaitement s'insérer dans le milieu industriel au moyen de capteurs adaptés et de dispositifs de plus en plus réduits [2], la spectroscopie Raman apporte par ailleurs des informations sur la structure du polymère et sa cristallinité.

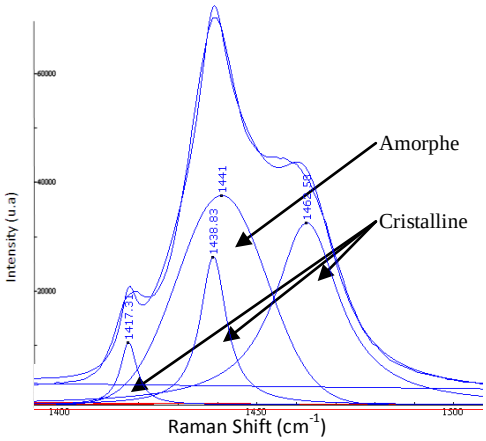

Figure 1 : Déconvolution des bandes CH_2 du polyéthylène

Dans cette étude, nous nous sommes focalisés uniquement sur le suivi et l'étude des bandes CH_2 du polyéthylène en fonction de la viscosité des grades étudiés. La bande caractéristique des vibrations des liaisons CH_2 (bending) se situe vers 1450cm^{-1} (figure 1) et se décompose en 3 lorentziennes caractéristiques de la phase cristalline et une gaussienne à 1441cm^{-1} attribuée à la phase amorphe [3] [4].

Le calcul du ratio de l'aire de ces raies corrélé par des essais de Diffraction des Rayons X (DRX) permet alors de remonter à la valeur du taux de cristallinité du grade étudié [2]. Peu d'études décrivent les vibrations CH_2 de la phase cristalline. Toutefois, en prenant la bande centrale à 1439 cm^{-1} en référence, la bande de plus faible fréquence peut alors être attribuée à une famille de vibrations CH_2 subissant une élongation et inversement à plus haute fréquence, à une famille de vibrations CH_2 compressées [5]. Ce comportement varie d'un grade à un autre (figure 2).

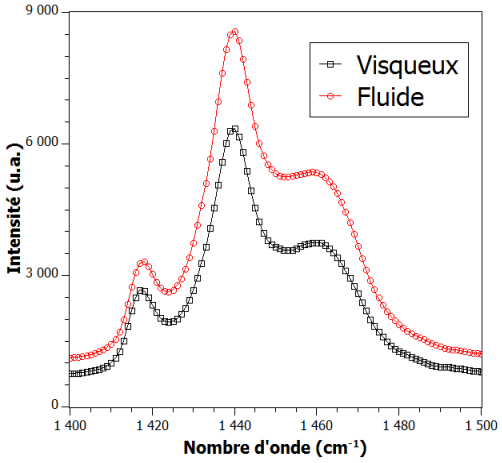

Figure 2: Spectres Raman de deux grades de PEBD

L'objet de cette communication est d'étudier la structure de la phase cristalline par rapport aux liaisons CH_2 et nous proposons un modèle d'interprétation du comportement des vibrations CH_2 en relation avec la structure de la phase cristalline. D'autre part, pour confirmer et corréler ces hypothèses et ce modèle, des mesures de DRX et d'Analyse Enthalpique Différentielle (AED) ont été effectuées. Ce couplage des techniques permet d'obtenir des informations sur la structure du polymère, sa cristallinité voire d'autres caractéristiques. Le but final est d'établir les possibilités de suivi des caractéristiques du produit en laboratoire de contrôle industriel. Cette détermination in-situ et rapide de la structure du polymère représente un atout majeur pour le contrôle de production.

[1] Plastics Europe, *An analysis of European plastics production, demand and recovery for 2008*, http://www.plasticseurope.org/

[2] Martin J., *Etude par spectroscopie Raman du polypropylène isotactique au cours de sa déformation uniaxiale,* Thèse de Doctorat, Laboratoire Matériaux Optiques, Photonique et Systèmes, Science des Matériaux, 2009

[3] M. Pigeon and al., *Characterization of molecular Orientation in Polyethylene by Raman spectroscopy*, Macromolecules, **24**, 5687-5694, 1991

[4] F.J. Boerio, J.L. Koenig, *Raman Scattering in Crystalline Polyethylene*, The journal of chemical physics, **52,7**, 3425-3431, 1970

[5] Herrera Ramirez J.M., Colomban P., Bunsell A., JRS 2004 35 1063

Comparative Study Of Various Grades Of Polyethylene By Raman Spectroscopy: microstructural attribution of bands

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[2] Total Petrochemicals France, Usine de Carling – Saint-Avold , RN 33 - BP 61005 57501 SAINT AVOLD, France
[3] Institut Jean Lamour, Département SI2M, UMR 7198 CNRS, École des Mines de Nancy, Institut National Polytechnique de Lorraine, Parc de Saurupt 54042 NANCY Cedex, France

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Background & Overview

Petroleum

From ethylene to polyethylene…

Polyethylene

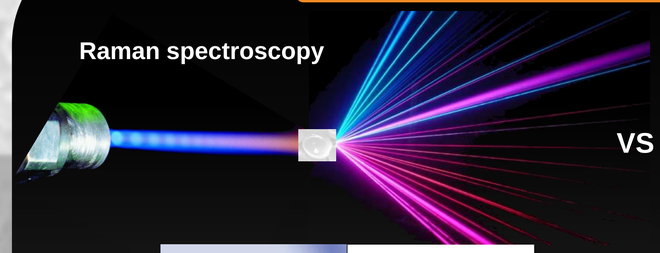
A better quality of polyethylene: glossier, more resistant

tomorrow

A new technique of on-line control: Raman spectroscopy

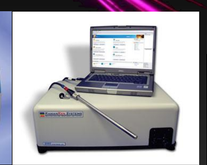
Equipment

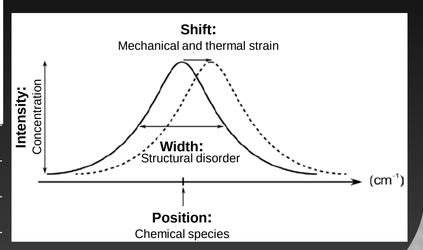
Raman spectroscopy



VS

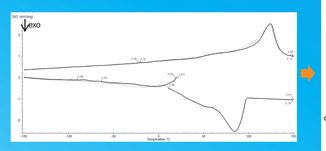
Differential Scanning Calorimetry

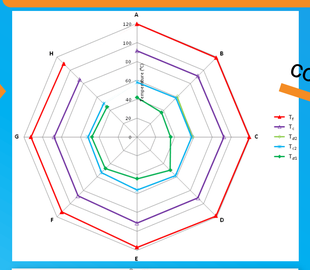
Laser: 785 nm		
Manufacturer	Jobin-Yvon	Kaiser
Modele	LabRAM ARAMIS	RAMANRXN1
Probe	Confocal	PhAT (long distance)
Utilisations	Post-mortem Other studies (temperature, polarization)	On-line processing



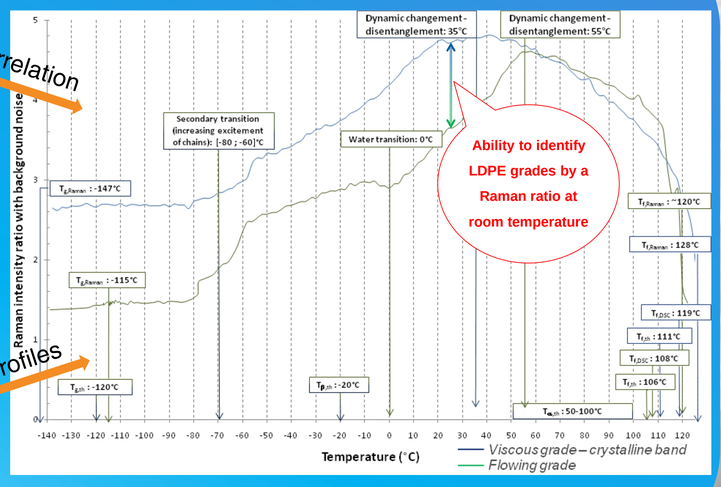
First results

DSC results

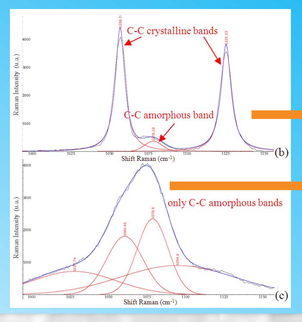


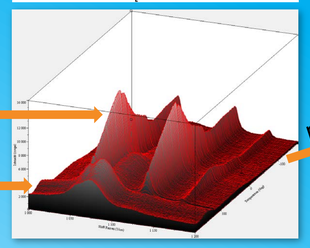


correlation



Raman results
Acquisition time: 2s X3
Spectrum every 2°C





profiles

The CH_2 bands theory

Hypotheses

- ∀ grade: amorphous band is constant
- Mechanical attribution of CH_2 bands [1]:
  - **E** = Elongation → lower frequency
  - **N** = Neutral
  - **C** = Compression → higher frequency
- ∀ grade: L_t is constant [2]

Thomson – Gibbs equation [3]

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

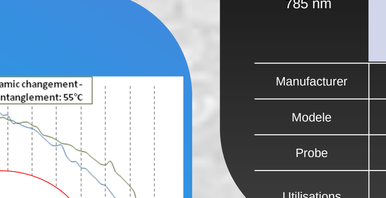
L_c: crystal lamellar thickness
σ_e: surface free energy per unit area of the chain folds (0,070 J/m²)
$\Delta H_{f\,th}$: latent heat of fusion per unit volume of ideal crystal (2,905.10⁸ J/kg⁻¹)
ρ_c: weight density of ideal crystal (1000 kg/m³)
T_0: melting temperature of ideal crystal that has infinite crystal size (143,5 °C)
T: melting temperature of lamellar crystal

[1] Herrera Ramirez J.M., Colomban P., Bunsell A., JRS 2004 35 1063
[2] Etienne S., Summer university Apollor 2010
[3] Wunderlich B., Macromolecular Physics, Volume 2: Crystal nucleation, growth, annealing, Academic Press, New York, (1976)

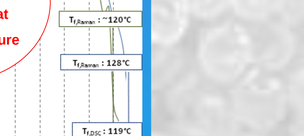
Attributions

* M. Pigeon et al., Macromolecules 24, 5687-5694, 1991
FJ. Boerio and al., Journal of Chemical Physics, 52, 3425-3431, 1970

Results



Interpretations



Conclusions & Prospects

Integration of a new on-line analysis tool permits to:

- ✓ interprete mechanically material structure,
- ✓ differentiate product grades,
- ✓ detect defects of products (gels, contamination) and variations of the industrial process.

- ❖ DMA correlation and additional tests
- ❖ Fine analysis of spectra(chemiometry)
- ❖ Other material properties (mechanical and optical)
- ❖ Reliability of the technique in order to totally replace actual on-line control
- ❖ Expansion to other technical polymers (EDA,…)

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NEW RAMAN OPTICAL SENSORS FOR IN SITU ANALYSES

D. Chapron, S. Margueron, T. Kauffmann, P. Bourson, M.D. Fontana
N. Brun, S. Chaudemanche, A. Filliung, R. Jumeau

There is currently a demand in many industrial fields requiring the use of sensors to achieve rapid, reliable and non-destructive analysis. For instance, in situ monitoring of a process and/or a specific material can provide access to the control of the production efficiency, of the production quality and of the environmental standards compliance. Usual sensors are developed to provide a specific response of material to a physical or a chemical stimuli. In comparison, Raman spectroscopy is a technique that provide a direct access to the intrinsic properties of materials through their non-linear signatures under strong electromagnetic light. One of the advantages of Raman spectroscopy is then to perform a direct on site analysis. The laboratory LMOPS works on the development of Raman spectroscopy to address the questions raised by in situ controlling of a process. We present here examples of using Raman sensors into or through a reactor for chemical reaction monitoring and also how to make a remote measurement of residual salinity of a medium in real time.

Raman spectroscopy and new optical sensors

Advantages of Raman spectroscopy

- *High chemical selectivity*
- *No sample preparation*
- *Water compatible*
- *Non-contact*
- *Non-destructive*
- *Imagery*
- *Coupling with microscope*
- *Coupling with fiber optics*
- *Transportable*

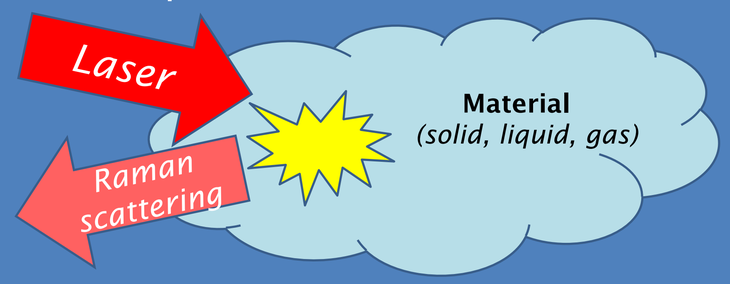
+

Innovation in optical measuring systems

- *Spectrometer miniaturization*
- *Compact lasers*
- *Sensitive IR detectors*
- *Band-stop filter (Notch filter)*

→

New optical sensors for in situ measurements

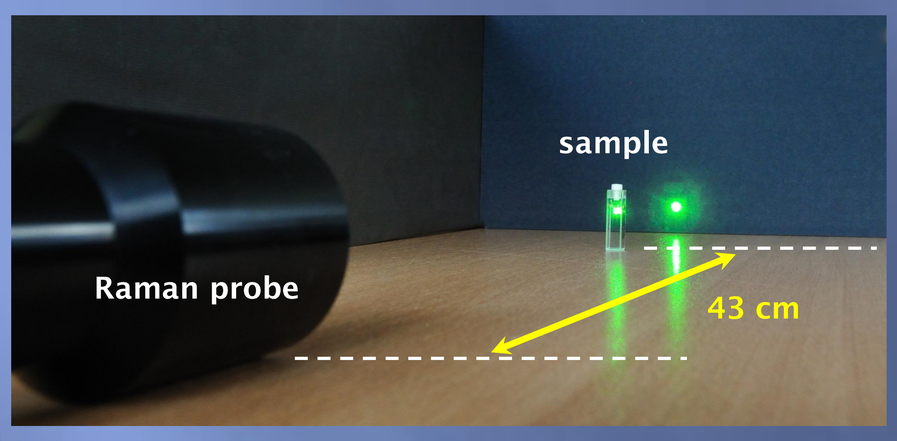


In situ analyze : - identification
- quantification

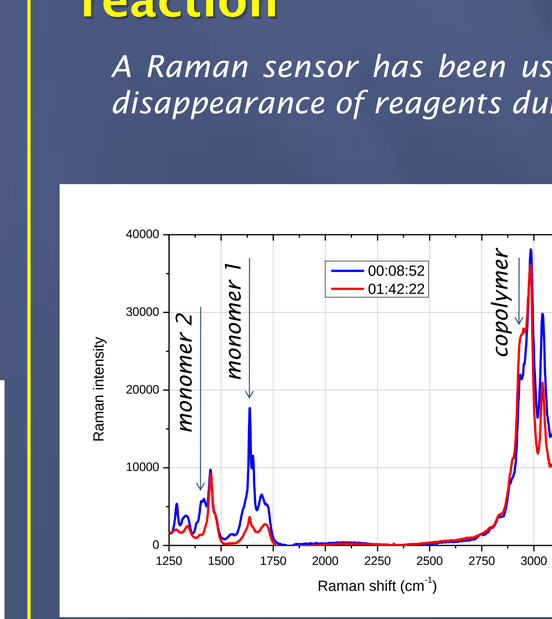
Remote measurement of a medium salinity in real time

Raman sensors allow non-contact measurements of a small volume of the analyzed medium which can be located several millimeters to several centimeters after the probe.

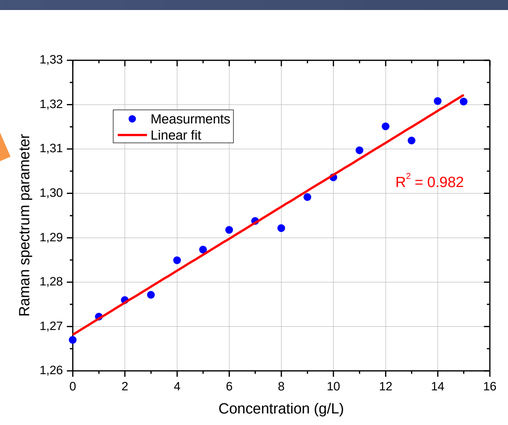
For example, we have developed a Raman sensor which makes a remote measurement of a medium salinity with a one-second measurement.



One-second Raman spectra of water solutions at different NaCl concentrations



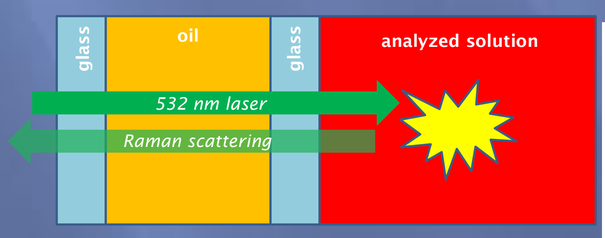
Extraction of a parameter from Raman spectra which is proportional to NaCl concentration

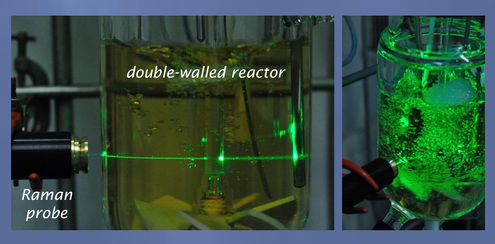


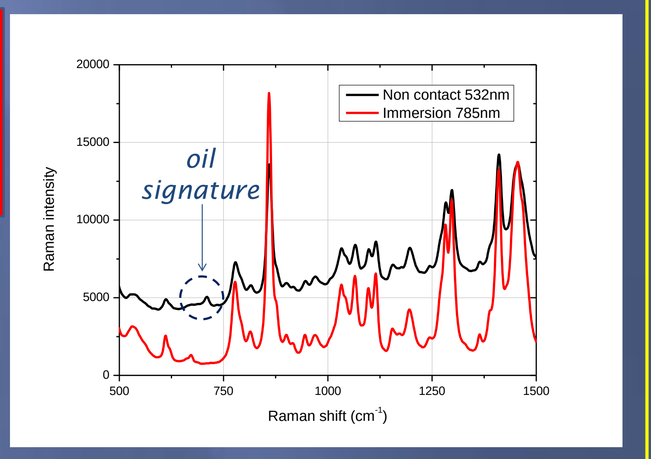
In situ measurement through a double-walled reactor in real time

Different kind of Raman probes are available : non-contact and immersion probes. Usually immersion ones are suitable for chemical reaction following, but in extreme conditions (temperature, pressure,…) non-contact probes could be preferred.

Immersion and non-contact probes have been used simultaneously to follow a chemical reaction in real time through a double walled reactor with oil for thermal regulation : non-contact at 532nm, immersion at 785nm.







The non-contact probe has given the same spectral signatures as the immersion probe even the optical beam round-trip through the glass/oil/glass walls. The oil peak in the spectrum at 532nm can be used as the reference for normalization.

In situ live monitoring of a copolymerization reaction

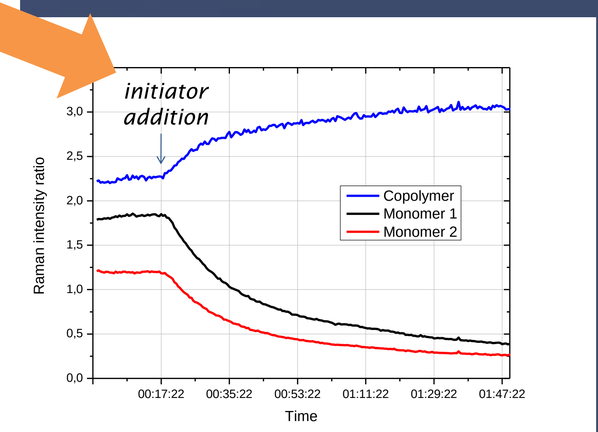
A Raman sensor has been used to follow the appearance of a product and disappearance of reagents during a copolymerization reaction.

Raman spectra at the beginning and at the end of the copolymerization.

Peaks from the two monomers and the copolymer have been identified.

One spectrum every 30s with an integration time of 10s.

By following these peaks, the reaction kinetic could be analyze in real time.



Raman sensors can open a new path in real time and in situ measurements. The ease of implementation and the wealth of information contained in Raman spectra lead industrials to consider this technology as a new opportunity in processes development and optimization. The LMOPS works on the design and the optimization of new Raman sensors to better understand material properties and their behavior in different processes by making lab studies or directly on an industrial site. The laboratory also develops post-processing tools for optimum exploitation of Raman spectra, especially for the study of weak signals or information apparently hidden in spectra.

On-line control of polyethylene production by Raman spectroscopy and chemometrics

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[2] Total Petrochemicals France, Usine de Carling – Saint-Avold , RN 33 - BP90290 57508 SAINT AVOLD, France

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Background & Overview

Petroleum

From ethylene to polyethylene…

Polyethylene

A new technique of on-line control: Raman spectroscopy

tomorrow

A better quality of polyethylene: glossier, more mechanically resistant

Equipments

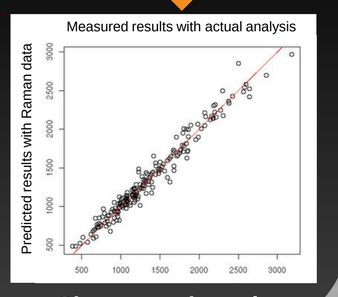
Raman spectroscopy

VS

Actual analysis
- Extruder
- NIR spectroscopy
- camera
- melt indexer
- microscope...

Laser: 785 nm

Manufacturer	Jobin-Yvon	Kaiser
Model	LabRAM ARAMIS	RAMANRXN1
Probe	Confocal	PhAT, MR Probe
Uses	Post-mortem Other studies (temperature, polarization)	On-line processing



Objectives

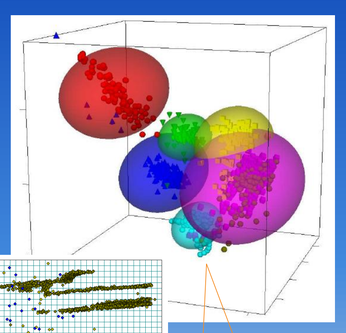
- Grades identification
  - Quantify Melt Flow Index
  - Quantify additives concentrations
- Flaws modelling
  - Quantify level of oxidation
- Flaws analysis
  - Qualify type of flaws (gels, oxidation,…)
  - Quantify flaws size on film

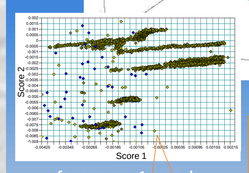
NIR:	Near Infra-Red
ATR:	Attenuated Total Reflectance
MFI:	Melt Flow Index
PCA:	Principal Component Analysis
PLS:	Partial Least Square method

Results

Grades identification: qualify and quantify properties directly on pellets

Raman spectroscopy and PCA



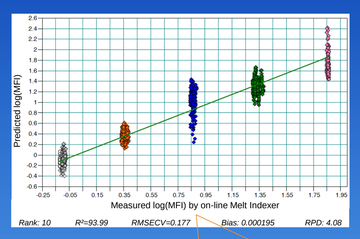


focus on 1 grade

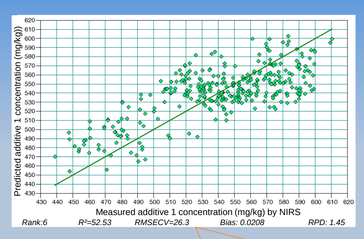
Separation of each grades based on optical properties

Subgroups relative to variation of process parameters (temperatures, pressures, reagent flows,...)

Raman spectroscopy and PLS

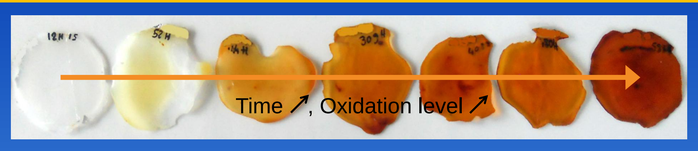


Estimation of Melt Flow Index

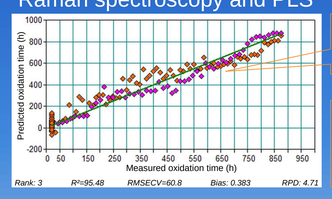


Estimation of additive concentration

Flaws modelling: example of oxidation



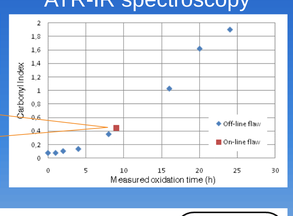
Raman spectroscopy and PLS



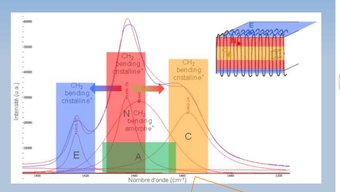
Good estimation of oxidation time

Good correlation with ATR and on-line flaw

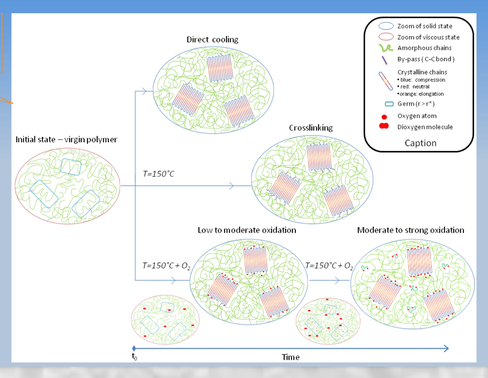
ATR-IR spectroscopy



Oxidation mechanism on microstructure



Microstructural attribution of CH_2 Raman bands

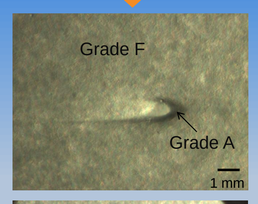


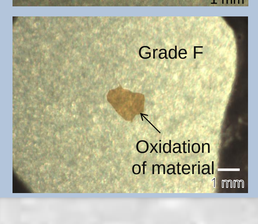
Flaws analysis: from off-line to on-line analysis

Polarized optical microscope

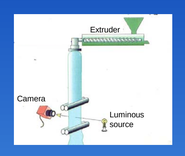
Flaws type and size

off-line



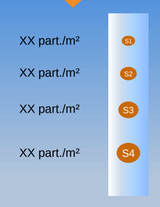


Actual at-line analysis



Flaws size

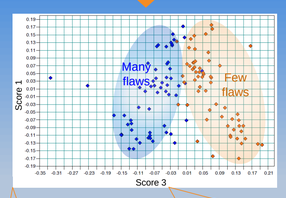
at-line every 2 minutes



Raman spectroscopy

Flaws type

on-line every 30 secon-des



Mainly oxidation flaws (Factor 3: C-O band)

Quantity estimation, not size

Conclusions & Prospects

Integration of a new on-line analysis tool permits to:

- ✓ determine product grades (MFI, additives),
- ✓ detect variations of the industrial process,
- ✓ classify products according to type and quantity of flaws,
- ✓ modelling oxidation flaws to better understand mechanism and microstructure.

Some prospects of this work are to:

- ❖ improve estimation of MFI, additives concentrations and flaws size,
- ❖ apply on-line oxidation flaw modelling,
- ❖ test reliability of Raman spectroscopy in order to replace current on-line control,
- ❖ extend to other technical polymers.

UNIVERSITÉ DE LORRAINE — LMOPS — TOTAL PETROCHEMICALS — TOTAL

O9 (Thématique 2 : Développements expérimentaux)

Contrôle des défauts d'oxydation du polyéthylène grâce à la spectroscopie Raman.

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Le polyéthylène basse densité est le polymère thermoplastique le plus largement utilisé au monde comprenant une vaste gamme d'applications, en particulier dans l'emballage souple. Dans certaines conditions, deux types de défauts issus de la polymérisation peuvent apparaitre: les infondus et les gels (réticulation et oxydation du matériau) et les autres (relargage, poussières…). Pouvoir qualifier et quantifier ces différents défauts est en enjeu majeur dans la caractérisation du polymère. Nous proposons dans ce travail une nouvelle méthode de caractérisation de ces défauts d'oxydation du polyéthylène à l'aide de la spectroscopie Raman.

Afin d'y parvenir, une étude des mécanismes de l'oxydation du polyéthylène à basse densité a été menée, décrivant les phénomènes subit par le polymère. Ces phénomènes ont permis d'établir un système « expert » capable d'identifier et de quantifier l'oxydation, en combinant les spectroscopies Raman et Infra-Rouge à des outils statistiques tels que la chimiométrie. Pour cela, nous avons simulé en laboratoire des défauts à différent temps à partir du polymère vierge fondu à 150°C avec des durées variables. La quantification de l'oxydation a été faite suivant un ratio de pics à partir des spectres Infra-Rouge. Ces données ont ensuite été utilisées pour réaliser un modèle chimiométrique avec les résultats de la spectroscopie Raman, par exemple, pour prédire le temps d'oxydation comme présenté dans la figure suivante.

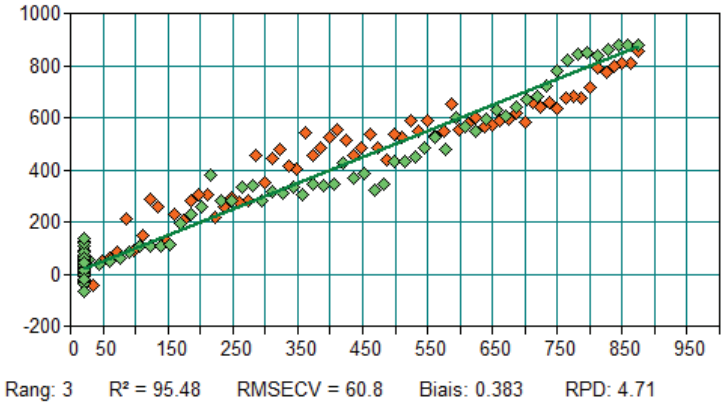

Figure: Durée d'oxydation mesurée par spectroscopie Raman en fonction de la durée réelle d'oxydation.

ON-LINE CHARACTERIZATION OF LDPE GRADES AND FLAWS ANALYSIS BY RAMAN SPECTROSCOPY AND CHEMOMETRIC TOOLS

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Abstract

Polyethylene (PE) is a very important material. Nowadays, almost 30% of the world plastics production was dedicated to this polymer (77 million tons) [1]. It is a consumer polymer because of 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].

However, 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 ...) and so detect or prevent problems in production, which is source of bad pellets. In fact, plastics manufacturers do not want to have unmelted areas or oxidations on their film for example.

Raman spectroscopy, a new technique of polymer process analysis, allows the detection of flaws and some other properties. Its use is nowadays growing fast because of advantages. It is a non-destructive 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 obtain the characteristic temperatures of PE and information on the polymer structure [4], and with chemometric tools, it is possible to characterize grades of LDPE but also determine roots of oxidized pellets.

The purpose of this article is to show how Principal Component Analysis (PCA) allows determining LDPE grades and how Partial Least Square method (PLS) and Raman spectroscopy can allow to quantify flaws of LDPE production and their ascribed causes. These results are correlated with those obtained by other techniques (IR, XRD). Moreover, we aim to understand the role of microstructure (intermediate phase) on these phenomena by Raman spectroscopy [5]. The final goal is to use these results in on-line analysis so that to find possibilities of quality control in industry.

Keywords: Polyethylene, Raman Spectroscopy, chemometrics, quality control, on-line analysis, polymer processing.

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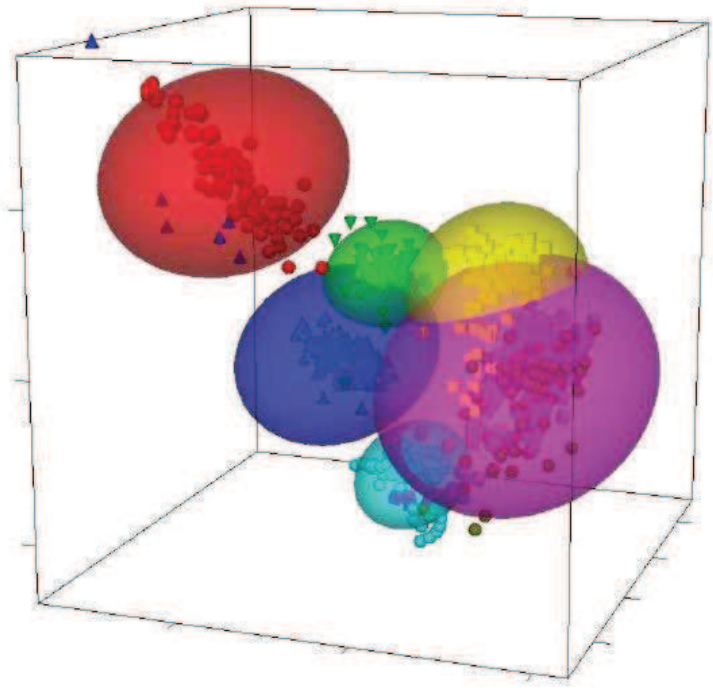

3D diagram of LDPE grades characterization based on PCA and Raman spectroscopy.

Establishment of patterns and **control of high temperature oxidation** flaws of Low-Density Polyethylene (LDPE) with **Raman spectroscopy**

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Abstract

Raman spectroscopy measurement were made on different kinds of oxidation flaws produced in laboratory. A model able to predict oxidation time of this sample was build by using chemometrics tools. Finally, other characterization methods such as Infra-red spectroscopy , Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD) were used in order to determine the high temperature oxidation mechanism in LDPE.

Goal of the study

- Recognize oxidation flaws which occurs during the production of LDPE.
- Understand the impact of high oxidation on the polymer properties.

Oxidized samples

High temperature oxidation : 150°C

• **Disks** - spectra on the surface -

Increasing oxidation

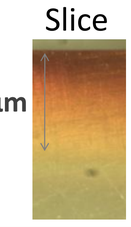
• **"Polymer cake"** - spectra on the deep -

Strong oxidation

cut into slice

Slice

1µm



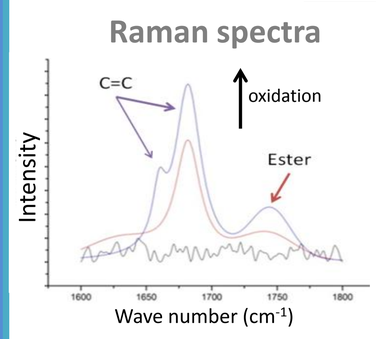
Patterns establishment of LDPE high temperature oxidation

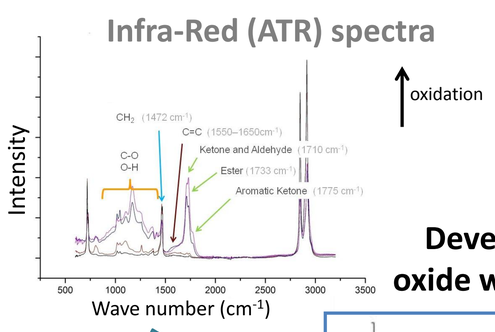
Characterization method

DSC	↘ crystal size
DRX	↘ crystallinity
Hydrostatic balance	↗ density
Tensile test	↘ E & ↘ Re

Oxides formation: ***irregular chain, break the chains***

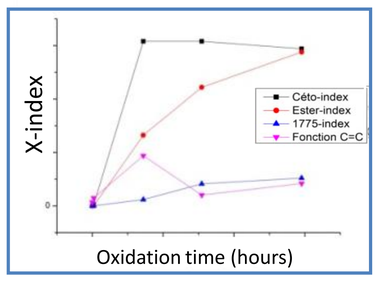
Vibrationnal spectroscopy





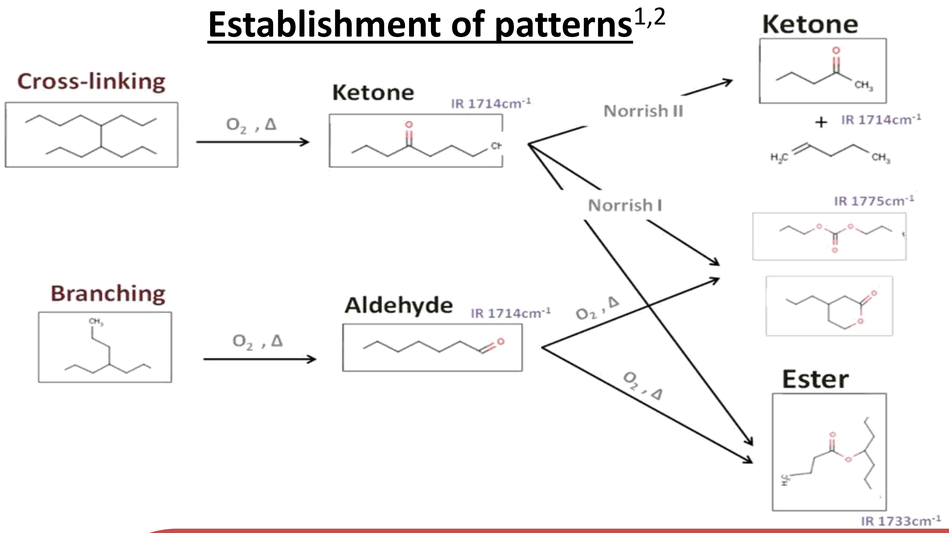
$$\text{X-index} = \frac{Abs\ X}{Abs\ CH_2\ (invariant)}$$

Development of oxide with oxidation



Created oxide: ***Ketone & Aldehyde, Ester, Aromatic ketone…***

Establishment of patterns[1,2]



Prediction of oxidation degree

by the oxidation time — by the ester-index

PLS-regression model

Raman cartography on the slice

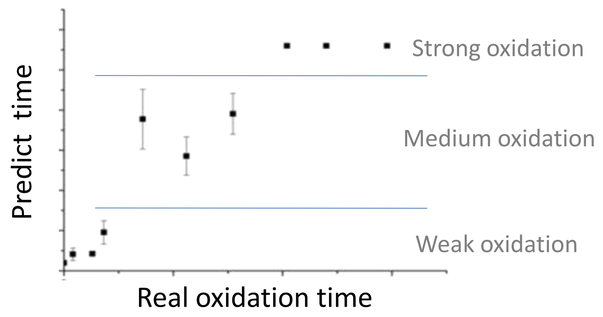
PLS regression: Deep prediction

Prediction of the disk spectra

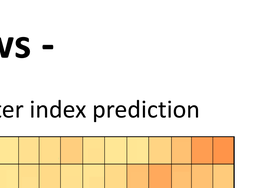
Connection Depth - Time

Time prediction model

Validation : Time prediction of the disk's spectra



Raman spectra on disks

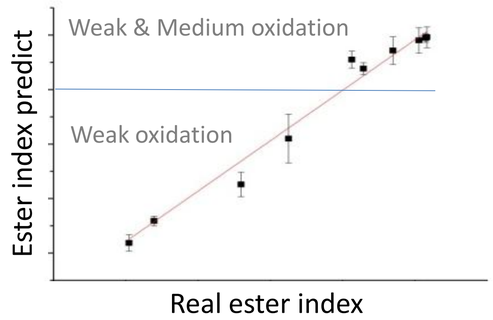


Ester index of disks(IRTF)

$$\frac{Abs\ IR\ 1730\ cm^{-1}}{Abs\ IR\ 1462\ cm^{-1}}$$

Ester index prediction model

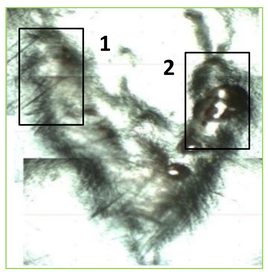
Validation : Ester index prediction of the disk's spectra



3 oxidation degrees : *weak, medium & strong oxidation*

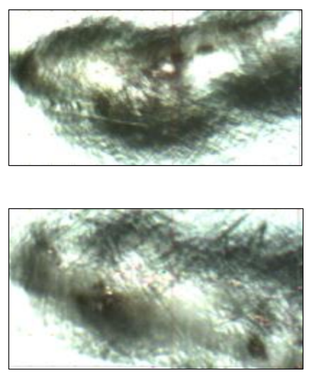
Industrial applications - analysis of production flaws -

PEBD Film (80µm)

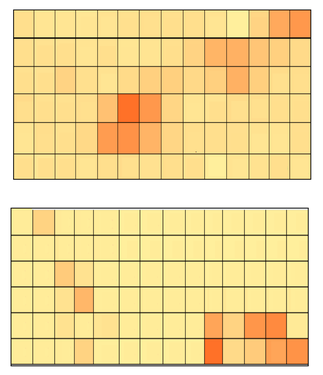


Oxidation flaws

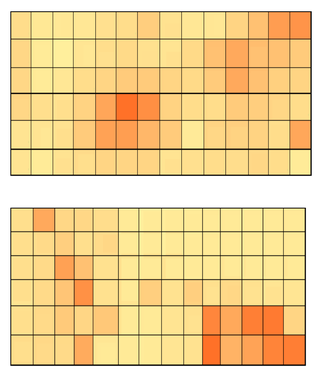
Micrographics of the oxidized flaws



Time prediction



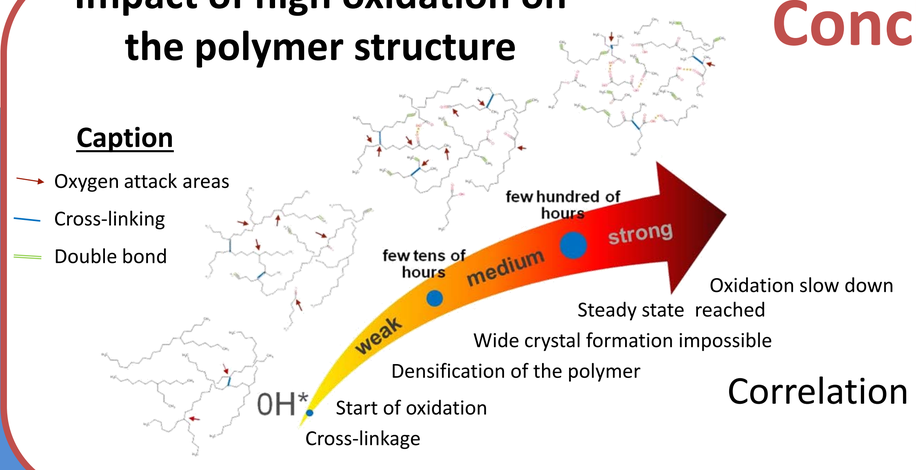
Ester index prediction



Medium oxidation *: Known by time prediction*
Confirmed by ester index prediction

Increasing oxidation

Impact of high oxidation on the polymer structure



Conclusion

Recognition & classification of oxidation flaws

- ✓ Detection of oxidation flaws on the polymer product
- ✓ Classification of oxidation degree
  - in function of the created oxides
  - in function of the impact on the polymer properties

Correlation between production flaws and manufacturing process **in order to reduce the request customer**

4 LDPE

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Control of high temperature oxidation flaws in Low-Density Polyethylene manufacturing with chemometrics.

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Keywords: Chemometrics, Raman spectroscopy, Low-Density Polyethylene (LDPE), High temperature oxidation

1 Introduction

Low density polyethylene (LDPE) is the most popular used thermoplastic in the world, with a wide range of applications, particularly in flexible packaging. According to the Global Business Intelligence Research [1], the global LDPE demand in 2009 was closed to 18.4 million tons. However, high temperature oxidation of polyethylene studies are not much present in literature, and though it can be a real problem especially in polymer production and processing. Indeed, "unmelted flaws" affect the structure of polymer, such as over cross-linking or oxidation. The presence of these flaws in production will lead to a real weakness during polymer processing.

Ability to identify and quantify these specific flaws is thereby a major issue in polymer industry. This study suggests a method to determine degree of flaws that can occur during polymer processing due to oxidation by combining Raman spectroscopy and chemometrics. Thus, in a same way as Skagerberg et al. who demonstrate how the PLS method can be used to perform quality control and Statistical Process Control (SPC) from one section of an LDPE reactor [2], two models able to recognize and quantify oxidation of different samples was created using PLS-regression. Finally, interpretation of Raman spectra linked to scores graph permit to understand phenomenon and its impact on microstructure (interphase).

2 Material and methods

Samples were obtained by melting 30 grams of LDPE pellets to 150°C in an alimentary silicone cupcake mold during 492 hours in a drying oven. Each sample was oxidized by being exposed to 150°C for variable duration, going from 1 to 591 hours and then cooled in a fridge at 2°C during 2 minutes for a homogenous and fast cooling. In order to observe the depth of oxidation in the "polymer-cake", the samples were cut into 2 centimeters slices and then polished with sandpaper of different grading (150, 300, 600 and 1200 gr/inch²).

Raman mapping on the "polymer-cake" slice was performed in order to follow the oxidation depth on the sample. Raman spectra were acquired on the spectral range of 800 – 3000 cm^{-1} with an integration time of 30 seconds and three repetitions per location.

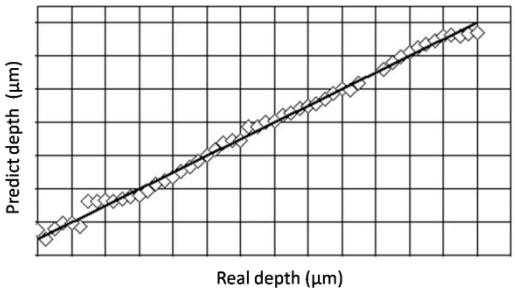
We used QUANT 2 on Opus v7.0 to realize chemometric model.

3 Results and discussion

3.1 Model establishment

Prediction of the oxidation time was based on the assumption that oxidation on the "polymer-cake" thickness can be firstly assimilated to an oxidation time. In this way, we used Partial Least Square (PLS) regression on the dataset collected from the mapping. We obtained the PLS-model presented on the figure 1 and 2, able to predict the oxidation depth on Raman spectra.

With others spectra acquired on sample with different oxidation time, another model (PLS-model 2) can be making out three oxidation degrees: weak, medium and strong oxidation. Characterization tests such as WAXS measurements, tensile tests and DSC analysis were performed on each sample allowed to know modification of polymer properties in function of the degree of oxidation.



Spectral range	Number of factor	R^2	RMSECV
1820 – 1634 cm^{-1} 1500 – 1414 cm^{-1}	4	99,49	27,4

Figure 1 – Validation of the PLS-model 1 'Predicted depth in function of real depth'.

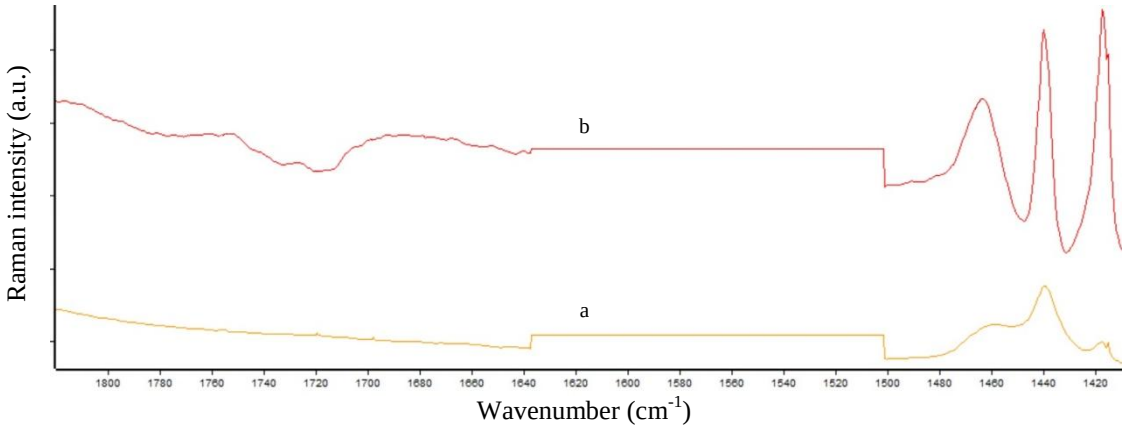


Figure 2 – Factors used to build the PLS-model 1
(a) the first loading recall the intensity of Raman spectra though (b) the second loading seems to be the first derivate of the spectra. The two other factors are not shown.

3.2 Interpretation with scores

The range from 1410 cm^{-1} to 1500 cm^{-1} can be attributed to $–CH_2$ Raman vibration bands [3]. In order to understand the oxidation modification of these species, a model was created using the same loading than the real model but only with the spectral range 1410-1500 cm^{-1}. Evolution of the scores in function of the two first loadings is shown in figure 3. Firstly, the model seems differentiate oxidation depending on the second loading, which, as seen previously, can be attributed to the peaks position. Weak oxidation is therefore characterized by the state of strain of the molecular chains, especially the interphase modification. Interphase is an intermediate phase between crystalline and amorphous phases. In a second time, scores are only classified thanks to the first loading, corresponding to the intensity of the peak. Medium oxidation is thus mainly identified by the concentration of each kind of bond. Finally, recognition of strong oxidation needs the combination between both loadings.

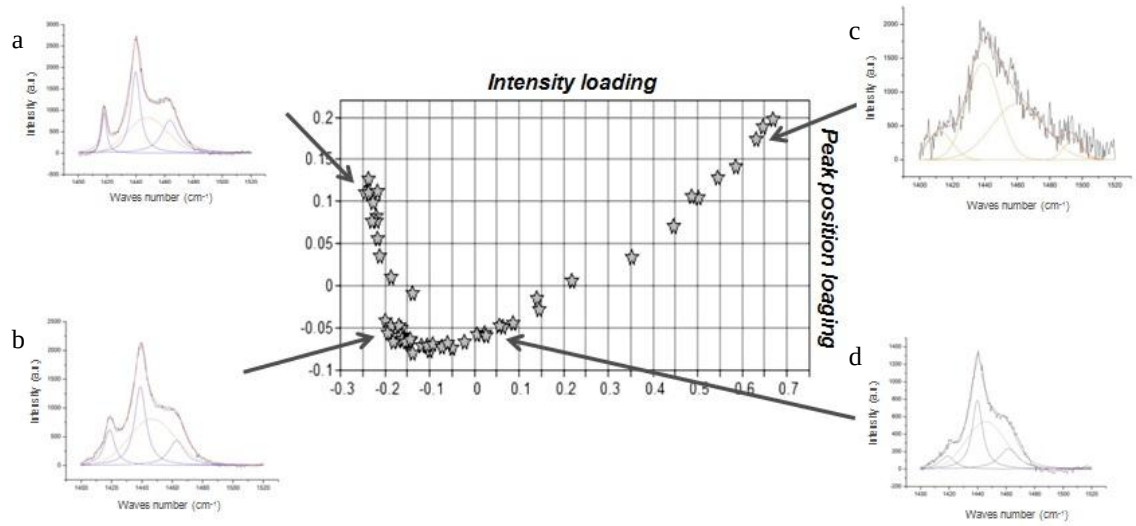


Figure 3 – Evolution of scores in function of the first and the second loadings.
Spectra of four scores are represented in function of the oxidation degree:
(a) non oxidized, (b) weak (c) medium and (d) strong oxidation.

Raman spectra resulting from four of the scores are also represented in order to highlight the described spectral modifications. Spectra were fitted according to Jumeau et al.[4]: Three Lorentzian peaks at 1420, 1440 and 1462 cm^{-1} corresponding to the elongated crystalline phase (or interphase), the crystalline neutral phase and the compressed crystalline phase respectively and a Gaussian peak at 1440 cm^{-1} resulting from the amorphous region. So, when oxidation increase, interphase proportion decrease and mechanical properties too. XRD and DSC experiments confirmed these deductions and showed that crystal size reduces progressively with oxidation, which leads to the reduction of the crystalline fraction.

4 Conclusion

This study develops chemometrics as a useful tool for industrial production control of polymer: a method able to detect and classify oxidation flaws on low-density polyethylene with Raman spectroscopy. Models were built thanks to PLS-regression and successfully tested with laboratory oxidized samples and real production flaws. Oxidation prediction tests made on the laboratory reproduced flaws highlight three oxidation degrees, confirmed with others characterization methods. Finally, interpretation to every characterization tests allowed understanding the impact of high oxidation on the polymer structure and mechanicals properties.

5 References

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Abstract of Contribution 393

ID: 393
Oral presentation
Topics: GFSV
Keywords: Raman spectroscopy, FTIR spectroscopy, High temperature oxidation

Raman and FTIR complementarity for high temperature polymer oxidation detection

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Introduction:

Oxidation flaws, which occur during polymer processing, affect melt polymer and thus bring into play mechanisms other than those involved in solid polyethylene ageing, with different consequences. Following the formation and growth of these flaws is a major issue for polymer industry.

Correlating Raman spectroscopy with Fourier Transformed InfraRed (FTIR) spectroscopy was key to following the different species formed during viscous low-density polyethylene oxidation, and gave primordial clues about the different mechanisms which occur during high temperature oxidation.

Material and Methods:

Two kinds of oxidized polyethylene samples were realized to mimic industrial flaws. A first batch of convenient to characterize samples was obtained by pressing to 4 bars about 20 pellets in a circular mold heated to 150°C. The second batch was made of about 15 thick polymer cakes in order to observe the penetration of oxygen in the melted polymer. In this way 30 grams of LDPE pellets melted in an alimentary silicone cupcake mold in order to observe penetration of oxygen in the melt polymer. Both batches were oxidized in a ventilated oven exposed to 150° C for variable duration, ranging from 1 to 591 hours.

Raman spectroscopy was investigated on both batches. A mapping was performed on a slice from each “polymer-cake” sample in order to follow the oxidation depth, whereas only simple spectra were acquired on the surface of samples from the first batches. All spectra were acquired on the spectral range of 800-3000cm-1 with an integration of 30 seconds and three repetitions per location.

Infra-Red spectroscopy in Attenuated Total Reflectance (ATR) was investigated on thin disk sample. This method was particularly adapted to the study because of the very thin thickness (<5µm) of the analyzed areas. In this way only the oxidized polymer layer is scanned, limiting the pollution of spectra by polymer no affected by oxidation. Five spectra were performed on the surface of each disk, with 32 accumulations.

Results and Discussion:

First, Raman spectroscopy and other characterization method such as X-Ray Diffraction and Differential Scanning Calorimetry were investigated on the sample in order to link the spectral modification to the evolution of the polymer properties. Two Raman spectral ranges are modified with oxidation: from 1400 to 1500cm-1 and from 1600 to 1800cm-1. On one hand, the three Lorentzian peaks at 1420, 1140 and 1462cm-1 of the first ranges to the –CH2 Raman vibration bands are evidence that the oxidation of the polymer leads to a decrease in its crystallinity. This tendency was confirmed with X-ray diffraction investigation. On the other hand, the modification of the second range, shown in figure 1, comes from the apparition of new chemicals bond, principally carbon-carbon double bond, formed by rearrangement of the atoms into the molecule and carbon-oxygen double bond created during the formation of oxide. However, these second new asymmetric bonds are not easily detectable with Raman spectroscopy and cannot be assigned to a specific species.

FTIR spectroscopy was the key to overcome this limitation. Analysis of the spectral range 1500- 1800 cm-1 presented in figure 2 reveals the formation of at least four oxides: ketone and/or aldehyde at 1714cm-1, ester at 1733cm-1 and other complex species such as , β-keto-ester. In the same way as the team of Albertsson1, keto-index, ester-index and “1775-index” were evaluated from the relative areas of each vibration band to that of the methylene band at 1472 cm-1. Evolution of these different oxides in function of the oxidation time plotted on figure 1 leads to think that ketone and aldehyde are created in high concentration at the beginning, and then, once a certain concentration is reached, these oxides are again attacked by oxygen to form a two-oxygen carbonyl function, as ester or , β-keto-ester…

Finally we adapted several work to our result, especially about polyethylene degradation and photo-oxidation which reveals some mechanisms likely to happen in high temperature oxidation in order to establish the patterns of viscous state oxidation of polyethylene.

Thermal energy supplied by the high temperature allows the creation of free radicals at the levels of the branching and the cross-linking, which are the frailest bonds. Oxygen present in the air can then be absorbed by the macro-radicals and form peroxide, which leads to the formation of aldehyde and ester. Prolonged exposure leads to the creation of new carbon and carboxyl radicals through Norrish I and Norrish II reactions. Rearrangement between all present radicals in the molecules leads to the formation of all different species observed by spectroscopy, such as carbon-carbon double don and as ester, β-keto-ester, α,β- unsaturated five-membered ring acid anhydride…

1. Albertsson, A.C.; Andersson, S.O.; Karlsson, S. Polymer Degradation Stability,18 (1987) 73-87.

Conclusion:

Thanks to the ability to detect symmetrical bonds with Raman spectroscopy combined with the high sensibility with which

asymmetric bonds can be detected, we were able to recognize oxidized polymer through both its oxide composition and its structural state. Thus, we could quantify the degree of oxidation, depending of the temperature and time of oxidation, by following the resulting oxide with FTIR spectroscopy or by Chemometric with Raman spectroscopy. Moreover, we were able to make the first hypothesis about the mechanisms of viscous oxidation of the polyethylene, which were unknowns until then.

Novelty Statement:

Originality of the study is to shows how we manage to follow the impact of high temperature oxidation, not much knows until now, by combining both vibrational spectroscopy techniques, Raman and FTIR.

Summary:

High temperature oxidation flaws can appear during polymer processing and affect all the production. To be able to recognize this flaws are a major issues. We manage this challenge by correlating Raman spectroscopy with Fourier Transformed Infrared (FTIR) spectroscopy, using the advantageous of both techniques.