

Classification of polyethylene by Raman spectroscopy

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Keywords

DXR3 Raman microscope,
polyethylene (PE), density, Raman
spectroscopy, Raman microscopy,
classification, discriminant analysis

Application benefits

Raman spectroscopy provides molecular level structural information, and is advantageous in classifying polyethylene (PE). Sample preparation is minimal. The method is non-destructive, and the analysis is fast (once the TQ methods are established).

Introduction

Polyethylene (PE) is one of the most common plastics in the world with annual global production of around 80 million tons.¹ Based on density, polyethylene is generally classified as high-density polyethylene (HDPE, $> 0.940 \text{ g/cm}^3$) or low-density polyethylene (LDPE, $< 0.930 \text{ g/cm}^3$).² These different density polyethylene's have vastly different physical, chemical, and mechanical properties, and hence are used in different applications. For example, HDPE is primarily used for milk jugs, detergent bottles, garbage containers, and water pipes, due to its high tensile strength; LDPE, on the other hand, has a lower tensile strength and is used mainly for plastic bags and wraps. Therefore, density is one the most important properties of polyethylene, and classifying them according to their density is essential for proper PE specification.

Bulk PEs are manufactured as pellets (resins, granules), and later converted to other forms (such as films and pipes) using extrusion or molding processes. They are also made into multilayer films for a wide range of industrial applications like food and consumer product packaging. The density of bulk PE pellets and single-layer PE films can be measured and classified with relative ease using several standard techniques: ISO 1183-1/ASTM D792 (immersion method),³ ISO 1183-2/ASTM D1505 (density gradient method),⁴ and ASTM D4883 (ultrasound method).⁵ However, all these techniques require the PE in its "pure" form, which can be challenging in the case of PE in multilayer films. Extensive sample preparations (microtoming, separation of layers by dissolving in solvents) are often required⁶ to isolate the PE layer before analysis, which can be labor-intensive and time-consuming.

Raman spectroscopy is sensitive to changes in the molecular structure level of PE, such as the degree of crystallinity, which is the key determining factor of PE density.^{7,8} More importantly, the confocal capability of Raman microscopy allows for facile *in situ* analysis of individual PE layers in multilayer films without the need to isolate the PE layer. To our best knowledge, PE density measurement using Raman has been limited to PE pellets.^{7,8} In this work, we want to systematically explore the feasibility of using



Thermo Scientific™ DXR3 Raman Microscope.

confocal Raman microscopy for PE film density analysis, both qualitatively and quantitatively. We demonstrate that Raman microscopy in combination with the discriminant analysis method can be successfully applied to distinguish HDPE and LDPE in both pellet and film forms. In a subsequent application note, we will detail the quantitative determination of PE density using a confocal Raman microscope.

Experimental

Sample description

A total of 16 PE samples (10 pellets and 6 films) with known densities were used for the classification studies. All samples were used as received.

Method description

A Thermo Scientific™ DXR2 Raman Microscope was used for the collection of Raman data. For each type/class of the pellet samples, Raman spectra were collected from 3 different pellets and averaged. For each film sample, Raman spectra were collected from 3-4 locations across the surface of the sample. An averaged spectrum was then used for final analysis.

A 532 nm laser was used with a 2 mW laser power at the sample. A 10x objective and a 50 μm slit aperture were used to obtain more representative spectra from the samples. Total acquisition time for each spectrum was 30 seconds (3 second exposure x 10 exposures). Thermo Scientific™ OMNIC™ software was used for operation of the DXR2 Raman Microscope, and collection of Raman spectra; Thermo Scientific™ TQ Analyst™ software was used for chemometric analysis of the Raman data.

Results and discussion

Raman spectra

Representative Raman spectra of HDPE and LDPE samples, in both pellet and film forms, are shown in Figure 1. There are noticeable differences between HDPE and LDPE spectra, for both pellets and films. In the CH_2 bending and the CH_2 twisting

region, the intensity of the CH_2 bending mode at 1416 cm^{-1} (relative to the CH_2 bending mode at 1440 cm^{-1}) is higher for HDPE than for LDPE. This observation agrees with the previous reports that the 1416 cm^{-1} and 1440 cm^{-1} peaks are indicators of crystalline and amorphous PE phases, respectively.⁷⁻¹⁰ The higher the degree of crystallinity, the higher the density. The differences between HDPE and LDPE are also pronounced in the C-H stretching region. The intensity of the symmetric CH_2 stretching mode at 2848 cm^{-1} (relative to the asymmetric CH_2 stretching mode at 2882 cm^{-1}) appears to be higher for LDPE compared to HDPE. Since the C-H stretching ($2825\text{-}2970\text{ cm}^{-1}$) and the CH_2 bending regions ($1398\text{-}1470\text{ cm}^{-1}$) are sensitive to the density of PE, these regions were selected for subsequent discriminant analysis.

Data processing

The raw Raman spectra were processed using Norris 2nd derivative, and the resulting spectra were further processed by standard normal variate (SNV). Examples of the data processing are shown in Figure 2. Norris derivative is effective in removing background drift in Raman spectra caused by fluorescence, whereas SNV is effective in compensating such variations as sample surfaces and laser penetration depths.¹¹⁻¹²

The discriminant analysis classification method with principal component analysis (PCA) algorithm¹³ from the TQ Analyst software package was applied to distinguish HDPE vs. LDPE. A total of 12 samples, a mix of pellets and films, were used as the calibration standards. Four additional samples (one HDPE pellet, one HDPE film, one LDPE pellet, and one LDPE film) were selected as the validation standards (Table 1). PCA derives the principal components (PC) or the significant spectral information from the spectral variance of the calibration sample set. The number of significant PCs represents the number of independent variables affecting spectral responses, including but not limited to: concentration, impurities, opaqueness, and

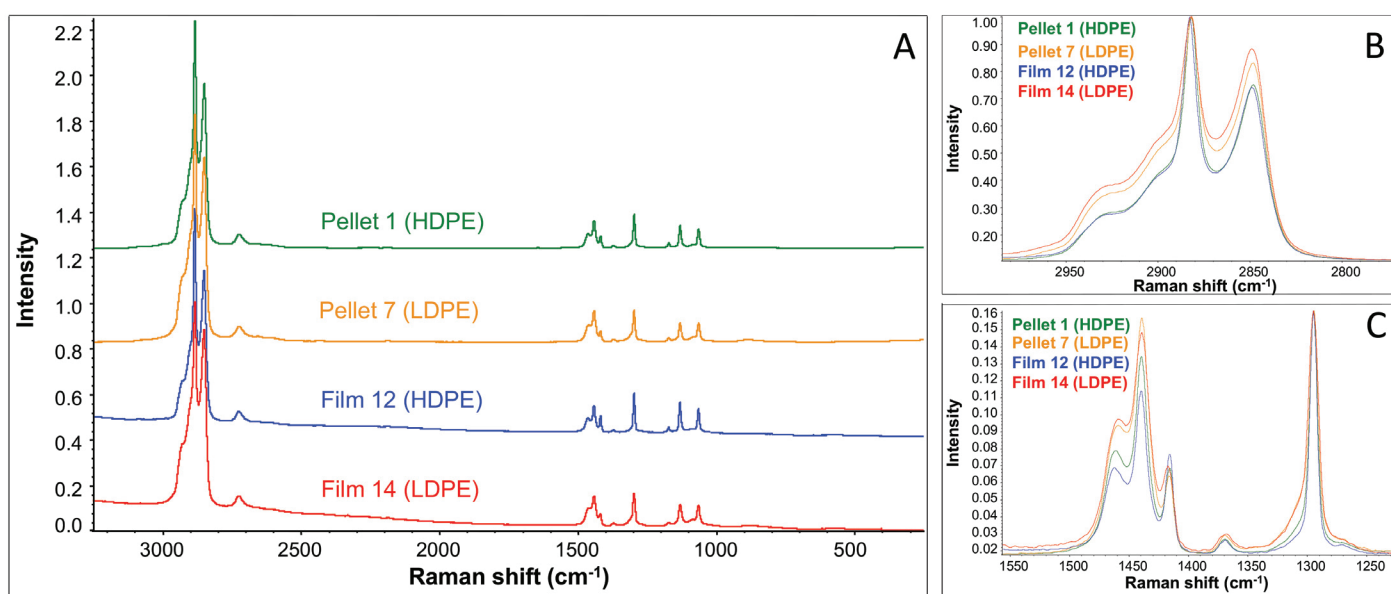


Figure 1. Representative Raman spectra of HDPE and LDPE pellets and films. (A) Full spectral range. (B) C-H stretching region. (C) CH_2 bending and CH_2 twisting region.

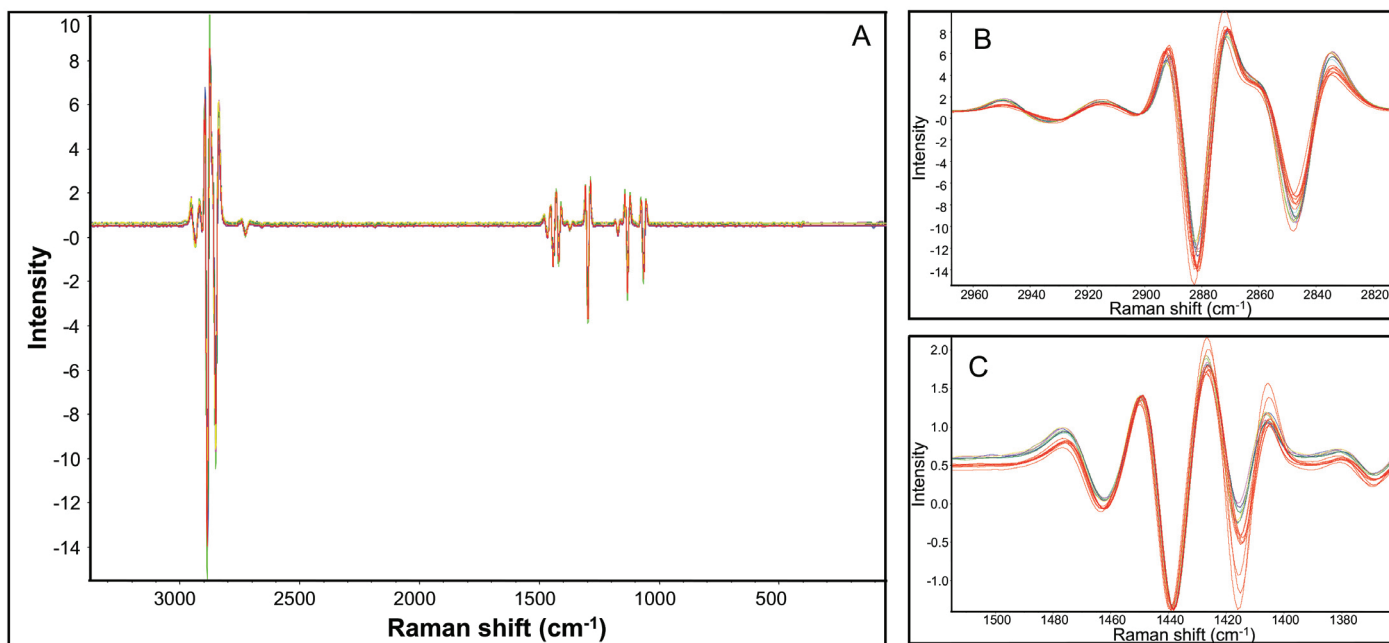


Figure 2. Norris 2nd Derivative and SNV processed sample spectra. (A) Full spectral range. (B) C-H stretching region. (C) CH₂ bending region. HDPE spectra are in red in both B and C Plots.

Classification of PE by discriminant analysis

				Calibration results		
	PE sample	Actual class	Usage	Calculated class	Distance to HDPE	Distance to LDPE
Pellets	1	HDPE	Calibration	HDPE	0.89	4.23
	2	HDPE	Calibration	HDPE	0.77	4.97
	3	HDPE	Calibration	HDPE	0.67	4.05
	4	HDPE	Validation	HDPE	1.33	3.69
	5	HDPE	Calibration	HDPE	0.68	5.14
	6	HDPE	Calibration	HDPE	0.76	4.91
	7	LDPE	Calibration	LDPE	4.01	0.99
	8	LDPE	Calibration	LDPE	5.32	0.78
	9	LDPE	Validation	LDPE	3.79	0.94
	10	LDPE	Calibration	LDPE	4.71	0.77
Films	11	HDPE	Validation	HDPE	1.23	4.79
	12	HDPE	Calibration	HDPE	1.24	4.66
	13	HDPE	Calibration	HDPE	1.30	4.93
	14	LDPE	Validation	LDPE	4.97	0.84
	15	LDPE	Calibration	LDPE	4.84	0.57
	16	LDPE	Calibration	LDPE	4.54	1.19

Table 1. PE sample class types and calibration results.

sample color. Scores of PCs depict the projected sample spectrum in the principal component domain. The PCA-based classification method then calculates the Mahalanobis (M) distance, defined by the distance between the sample and the center of each cluster in the PC domain. The sample is classified as belonging to a class if $M < 3$, and rejected from a class if $M > 3$.

The number of PCs has a direct impact on the robustness of the discriminant analysis. As shown in Table 2, the first several principal components represent the majority of the spectral variation. Five PCA factors, accounting for 99.7% of the total spectral variance, were used in this classification model.

Number of PCs	Cumulative Variance%
0	0
1	80.96
2	98.03
3	98.83
4	99.46
5	99.74

Table 2. Impact of number of PCs on variance coverage.

Figure 3 is a 3-D plot of PCA Clusters of HDPE and LDPE. The HDPE samples (red) and LDPE (blue) samples are located on the opposite ends of the cube. Notwithstanding PC1 accounting for ~81% of the total spectral variation in the data set, the separation between HDPE and LDPE is mainly in the PC2 dimension. In the current case, the PC2 dimension seems to be closely correlated to the PE density. Figure 4 shows the crossvalidation results of the 16 samples, the M distance to its own class vs. the M distance to the other class. The average M distance for each sample to its own class was about 1, but the average distance to the other class is over 4, as listed in Table 1. For both sample classes (HDPE and LDPE), there is no separation between pellets and films, suggesting the sample form (pellet vs. film) has little, if any, impact on the methodology.

The Raman spectrum of a previously unused pellet sample with known density was used to test the established discriminant method, and the result is shown in Figure 5. The sample was successfully classified as HDPE with an M value of 0.68.

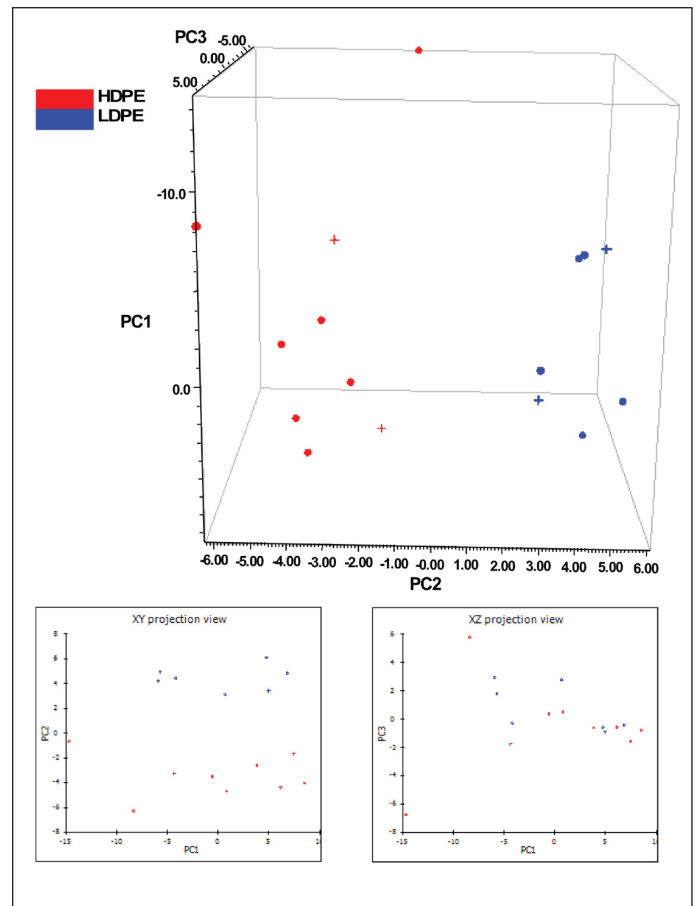


Figure 3. 3-D cluster plot of HDPE and LDPE samples. The • are the calibration samples, and the + are the validation samples.

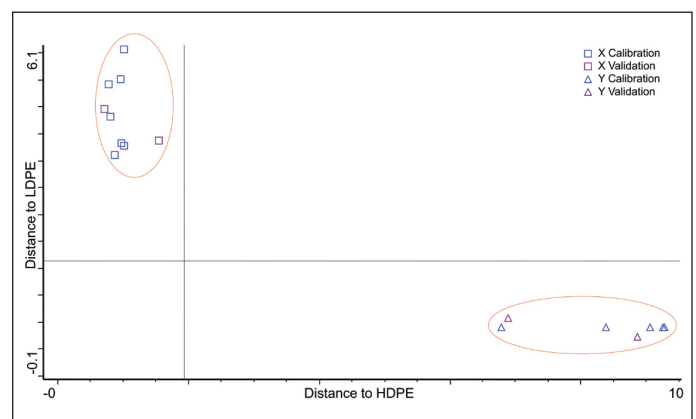


Figure 4. TQ Analyst software discriminant analysis calibration output for PEs with different densities. The two different types of PEs: HDPE and LDPE are clearly separated, and correctly classified. The calibration results are also shown in Table 1.

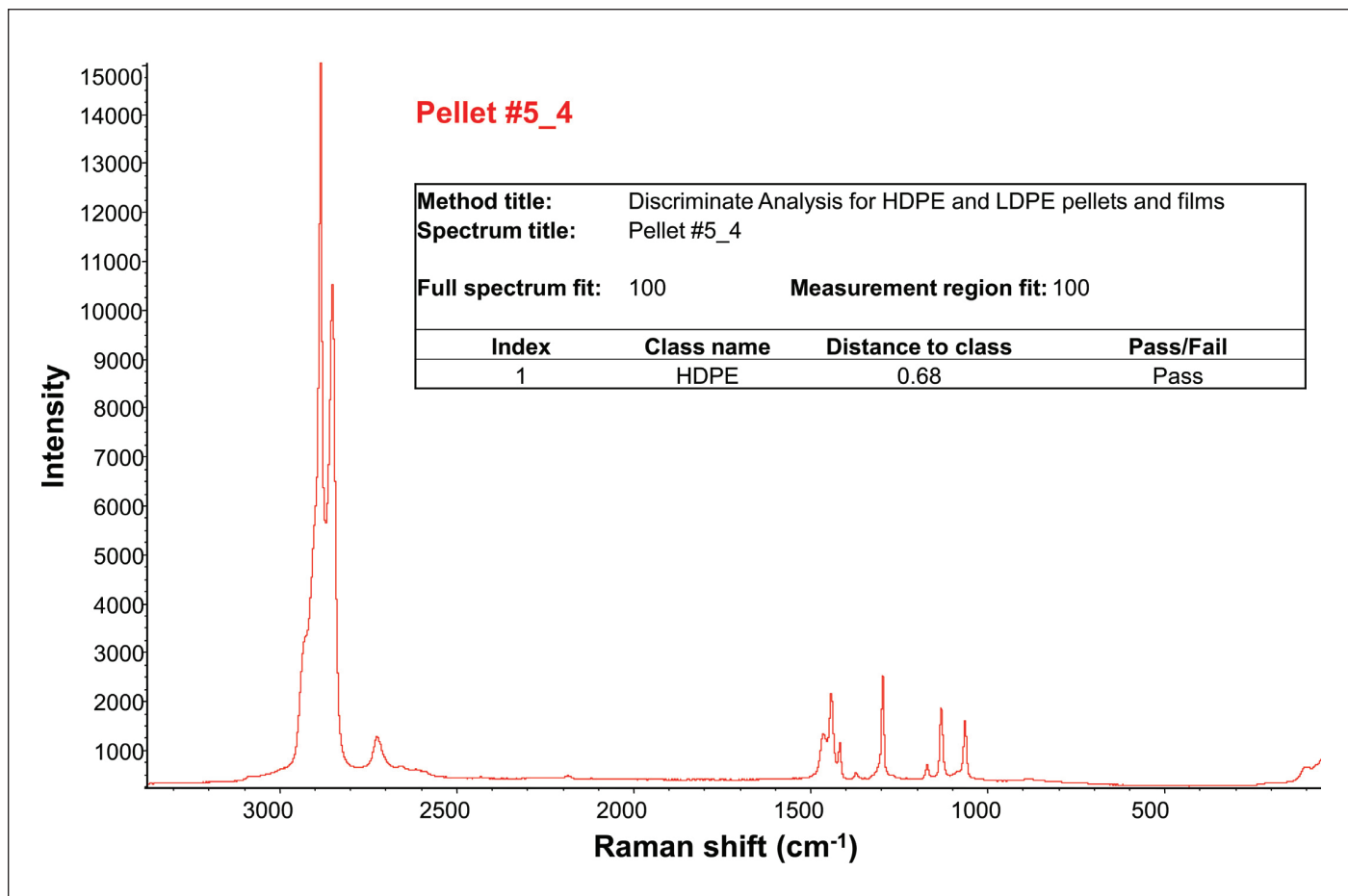


Figure 5. Classification of a PE sample by using its Raman spectrum and the discriminant method created by the TQ Analyst software.

Conclusion

In this application note, we have successfully demonstrated the use of a Thermo Scientific DXR2 Raman Microscope, in combination with the TQ Analyst software, to classify polyethylene's of different density classes in both pellet and film forms. Raman spectroscopy is nondestructive and requires minimal sample preparation. The classification method was created solely based on the Raman spectral features of LDPE and HDPE and was indifferent to the sample forms. Once the method is established, PE samples, pellets or films, can be correctly classified within minutes. Moreover, this work expands the scope of the previously reported study on PE pellets to include PE films, which broadens its applicability in the plastic/polymer industry as well as many downstream industries. The described methodology should be applicable for in situ classification of thin PE layer(s) in multilayer films.

The data were collected using an older model instrument DXR2 Raman microscope. Currently, Thermo Fisher Scientific offers an improved model, the DXR3 Raman Microscope, which offers superior speed and performance over its predecessor model.

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