

In situ density determination of polyethylene in multilayer polymer films using Raman microscopy

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Keywords

Polyethylene (PE), density,
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Application benefits

Polyethylene density determination based on Raman microscopy and Partial Least Squares (PLS) regression is applicable for both pellet and film samples. The confocal capability of Raman microscopy allows for *in situ* density determination of PE layers within multilayer polymer films, without the need for tedious and challenging sample preparations.

Thermo Fisher Scientific solutions

- DXR2 Raman Microscope
- OMNIC software
- TQ Analyst software

Introduction

Polyethylene (PE) is one of the most common plastics in the world with an annual global production of around 80 million tons.¹ Unlike other commercial polymers, PE can be manufactured across a range of densities that are related to the spacing between the polymer chains.² For examples, High-Density PE (HDPE, 0.941-0.965 g/cm³) is mainly comprised of linear PE chains that can closely approach each other, thus creating very densely packed networks. Conversely, Low-Density PE (LDPE, 0.910-0.940 g/cm³) has excessive branching that causes a less compact molecular structure. Linear Low-Density PE (LLDPE, <0.940 g/cm³), too, has a large number of branches, but the branches are shorter than those in LDPE. Because the density of PE can be controlled and varied, it provides an important mechanism to control its properties to suit different applications. PE density is therefore a vital part of the material characterization and selection process.

There are several standard methods for PE density measurement, such as ISO 1183-1/ASTM D792 (immersion method)³, ISO 1183-2/ASTM D1505 (density gradient method),⁴ and ASTM D4883 (ultrasound method)⁵. These methods, however, are primarily geared towards PE samples in a “pure” form such as pellets and single-layer films. Challenges arise when PE is present in multilayer films, which are widely used in food, pharmaceutical and consumer product packaging. Extensive sample preparations, including microtoming and separation of layers using solvents, are required to isolate the PE layer(s) before analysis, which can be labor-intensive and time-consuming.⁶



Thermo Scientific DXR2
Raman Microscope

To that end, Raman microscopy could offer an *in situ* density determination of PE layers in multilayer films by leveraging its confocal capability. Raman spectroscopy has long been utilized to investigate the structure of polymers, including molecular conformation, orientation, and crystal structure.⁷⁻⁹ Combined with multivariate analyses such as principal component analysis (PCA) and partial least squares (PLS) regression whereby statistically observed spectral variations are correlated with known sample properties, crystallinity, density and melting point can be predicted.⁷ Existing literature, however, has also been limited to bulk PE pellets. In our previous report,¹⁰ we expanded the scope of the methodology to include PE films. It is demonstrated that Raman microscopy in combination with a PCA based discriminant analysis can qualitatively distinguish HDPE and LDPE in both pellet and film forms. In this application note, we will describe the development of a Partial Least Squares (PLS) model to quantitatively determine the density of PE layers in both single-layer and multilayer films using Raman microscopy.

Experimental

A total of 25 PE samples (12 pellets and 13 films) with different known densities (Table 1) were used for developing a PLS model for density determination. All samples were used as received. A clear transdermal nicotine patch sample was used for identifying the PE layers and *in situ* determination of PE layer densities. The sample was mounted onto a gold-coated microscope slide with the backing layer facing the microscope objective, and the release liner at the bottom.

A Thermo Scientific™ DXR2™ Raman Microscope was used for collecting Raman data. For each of the pellet samples, Raman spectra were collected from 3 different pellets and averaged. For each of the film samples, 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 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). For the transdermal nicotine patch sample, Raman confocal line depth profiling was performed using a 532 nm laser, 5 mW laser power at the sample, 50x objective, 25 μm confocal pinhole aperture, and with auto exposure (S/N = 200). A depth of 220 μm was probed by using a 5 μm step size (containing 45 points or spectra).

Thermo Scientific™ OMNIC™ software was used for instrument control and data acquisition. Thermo Scientific™ TQ Analyst™ software was used for chemometric analysis of the Raman data.

Results and discussion

Raman spectra of HDPE, LDPE, and LLDPE

Representative Raman spectra of HDPE, LDPE, and LLDPE samples are shown in Figure 1. There are noticeable differences among three types of PE samples in both CH stretching (2900-3100 cm^{-1}) and CH₂ bending and twisting (1250-1500 cm^{-1}) regions. The intensity of the symmetric CH₂ stretching mode at 2848 cm^{-1} (relative to the asymmetric CH₂ stretching mode at 2882 cm^{-1}) decreases in the order of LLDPE > LDPE > HDPE (Figure 1A). In the CH₂ bending and the CH₂ twisting region (Figure 1B), the intensity of the CH₂ bending mode at 1416 cm^{-1} (relative to the CH₂ bending mode at 1440 cm^{-1}) is higher for HDPE than for LDPE. The 1416 cm^{-1} peak is completely absent for the LLDPE film sample (#19). 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.^{7,8} The higher the crystallinity, the higher the density. Since the CH₂ bending region (1400-1500 cm^{-1}) is sensitive to the density of PE, it was selected for subsequent quantitative analysis.

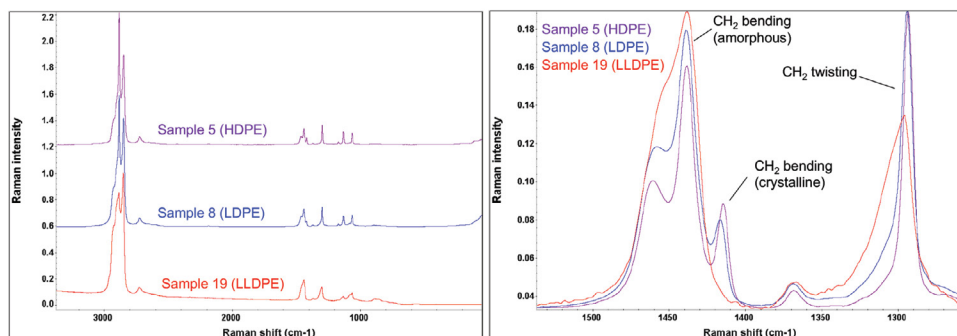


Figure 1: Representative Raman spectra of HDPE, LDPE, and LLDPE samples. **(A)** Full spectral range in stack view. **(B)** CH₂ bending and CH₂ twisting region in overlay view.

Data processing

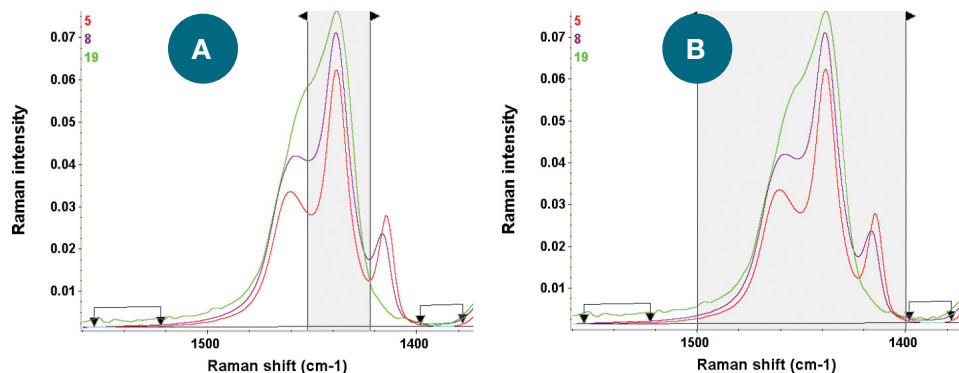
Peak area for pathlength correction option in the TQ Analyst software was used to normalize Raman spectral intensities. The peak area of the CH₂ bending mode at 1440 cm⁻¹ was used for the normalization (1422-1452 cm⁻¹ range, Figure 2A). An averaged two-point baseline correction was used to account for baseline shifts/noise.

Developing a PLS model for PE density determination

Partial Least Squares (PLS) algorithm¹¹ from the TQ Analyst software was used to develop a model for PE density determination. PLS is a quantitative regression algorithm

through statistical analysis. It uses spectral covariance and factorial analysis to extract significant and relevant chemical information from sample spectra as factors, then correlate them with sample properties such as concentration, crystallinity and density. A total of 20 samples, a mix of pellets and films, were used as the calibration standards. Five additional pellet and film samples with density values spread across the density range of the samples were selected as the validation standards (Table 1). A spectral range of 1400-1500 cm⁻¹ with averaged two-point correction for baseline (Figure 2B) was used in the method.

Figure 2: (A) Peak Area Ratio to normalize Raman spectral intensities, showing the CH₂ bending peak region for normalization. (B) Spectral range used for PLS calibration. In both cases, an averaged two-point option was used for baseline correction.



	Sample #	Actual Density (g/cm ³)	PE Type	Usage	Calculated Density (g/cm ³)	Difference (g/cm ³)	% Difference
Pellets	1	0.9460	HDPE	Calibration	0.9454	0.0006	0.06%
	2	0.9505	HDPE	Calibration	0.9486	0.0019	0.20%
	3	0.9510	HDPE	Calibration	0.9509	0.0001	0.01%
	4	0.9470	HDPE	Validation	0.9523	-0.0053	-0.56%
	5	0.9620	HDPE	Calibration	0.9564	0.0056	0.58%
	6	0.9600	HDPE	Calibration	0.9594	0.0006	0.06%
	7	0.9195	LDPE	Calibration	0.9236	-0.0041	-0.45%
	8	0.9170	LDPE	Calibration	0.9183	-0.0013	-0.14%
	9	0.9235	LDPE	Calibration	0.9250	-0.0015	-0.16%
	10	0.9300	LDPE	Calibration	0.9264	0.0036	0.39%
	11	0.9235	LLDPE	Calibration	0.9295	-0.0060	-0.65%
	12	0.9185	LLDPE	Calibration	0.9259	-0.0074	-0.81%
Films	13	0.9496	HDPE	Calibration	0.9568	-0.0072	-0.76%
	14	0.9606	HDPE	Calibration	0.9556	0.0050	0.52%
	15	0.9460	HDPE	Calibration	0.9456	0.0004	0.04%
	16	0.9247	LDPE	Calibration	0.9225	0.0022	0.24%
	17	0.9258	LDPE	Calibration	0.9241	0.0017	0.18%
	18	0.9297	LDPE	Calibration	0.9276	0.0021	0.23%
	19	0.8598	LLDPE	Calibration	0.8604	-0.0006	-0.07%
	20	0.8650	LLDPE	Calibration	0.8623	0.0027	0.31%
	21	0.8881	LLDPE	Validation	0.8812	0.0069	0.78%
	22	0.9008	LLDPE	Calibration	0.8993	0.0015	0.17%
	23	0.9040	LLDPE	Validation	0.9072	-0.0032	-0.35%
	24	0.9236	LLDPE	Validation	0.9215	0.0021	0.23%
	25	0.9367	LLDPE	Validation	0.9349	0.0018	0.19%

Table 1: PE samples and their densities.

*Rows highlighted in green are the samples used for validation.

Figure 3 shows the calibration results for PE densities obtained with the 3-factor PLS model. The inset is the Predicted Residual Error Sum of Squares (PRESS) plot. In the current case, a 3-factor model suffices as the contribution from the 4th and 5th factors are negligible. The calibration curve has a correlation coefficient of 0.9914. The RMSE (Root Mean Square Error) values are 0.00360 for the calibration samples and 0.00432 for the validation samples, respectively. The results are also summarized in Table 1. For all 25 samples, the calculated densities are within $\pm 0.81\%$ of the actual values. It is

important to note that the percent differences do not exhibit any bias between pellets and films, indicating that the sample form (pellets vs. films) has no bearing on the model performance.

Density Determination of PE films

Figure 4 demonstrates an example of applying the Raman spectrum and the PLS model to predict the density of a PE film sample. The predicted density is 0.9014 g/cm³, showing a good agreement with the actual density of 0.9008 g/cm³.

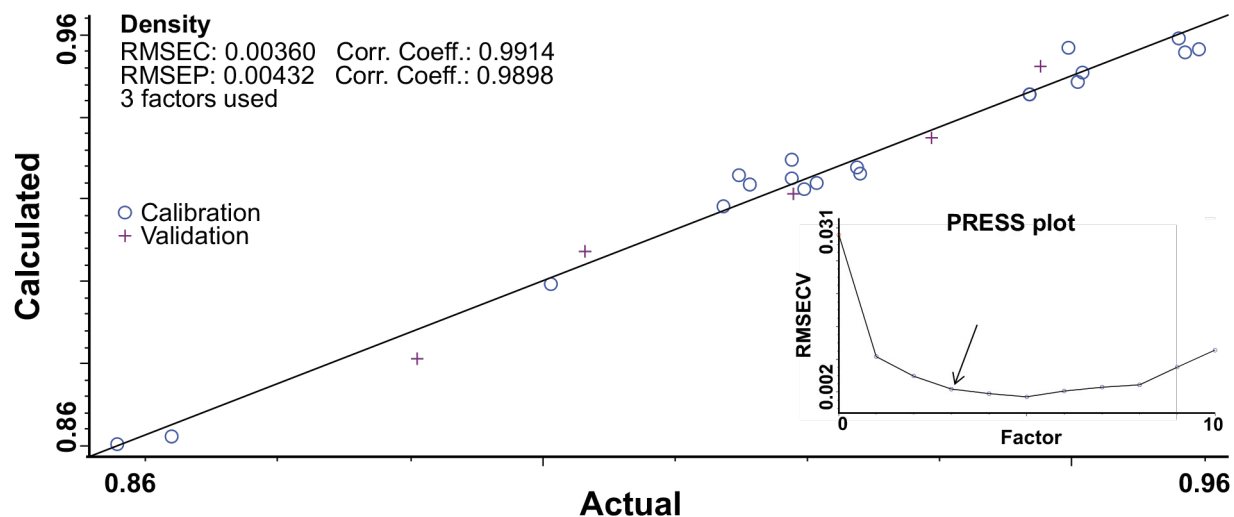


Figure 3: Calibration results for PEs of different densities using a PLS quantitative analysis. The ○ denotes calibration standards and the + denotes validation standards. Inset is the PRESS plot for the PLS calibration. Three factors were used in the current PLS calibration model.

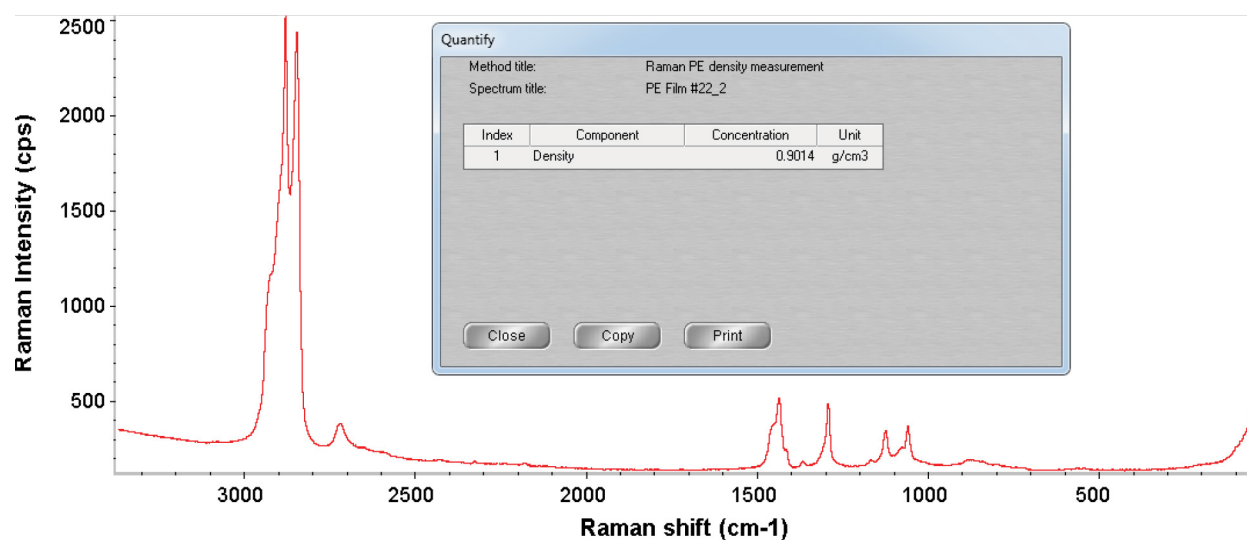


Figure 4: Prediction of the density of a PE film sample using its Raman spectrum and the PLS model. The known density of the film is 0.9008 g/cm³ and the predicted density is 0.9014 g/cm³.

Figure 5A shows the Raman confocal depth profile of a clear transdermal nicotine patch. A total of 6 polymer layers were identified, including two PE layers – PE layer 1 (part of the backing layer) and PE layer 2 (closer to the release liner). There are perceptible differences in the Raman spectra between the two PE layers (Figure 5B and 5C). Applying the PLS model, the densities are determined to be 0.9150 g/cm³ for PE Layer 1 and 0.9583 g/cm³ for PE Layer 2, placing PE layer 1 in the LDPE /LLDPE class and the PE Layer 2 in the HDPE class. The classification of the PE layers based on the predicted densities conforms to other reports: LDPE/LLDPE is used in the occlusive backing layer for its flexibility whereas HDPE is used as the rate-controlling membrane as an integral part of the reservoir diffusion control mechanism.¹²⁻¹³ While the exact densities of the two PE layers are not available, the results presented here nonetheless demonstrates the advantage of using Raman microscopy combined with the PLS method for density determination. The confocal capability of Raman microscopy allows for *in situ* PE density determination in multi-layer films without the need to isolate the individual PE layers.

Conclusions

Raman microscopy is a powerful analytical tool for PE density determination. Since PE chains in crystalline and amorphous domains exhibit unique Raman features in the CH₂ bending region, a PLS model based on the Raman features in the 1400-1500 cm⁻¹ region was successfully developed. The model is applicable for both pellet and film samples, showing a good agreement between actual and predicted density values. Applying the model to a real-world multilayer film containing two PE layers, the predicted density values correctly place the two layers into their respective PE classes. More importantly, the confocal capability of Raman microscopy allows for *in situ* density determination of PE layers within multilayer polymer films, without the need for tedious and challenging sample preparations required by many other techniques. The presented methodology should be of interest for PE manufacturers as well those who perform failure analysis, reverse engineering, and polymer composites development.

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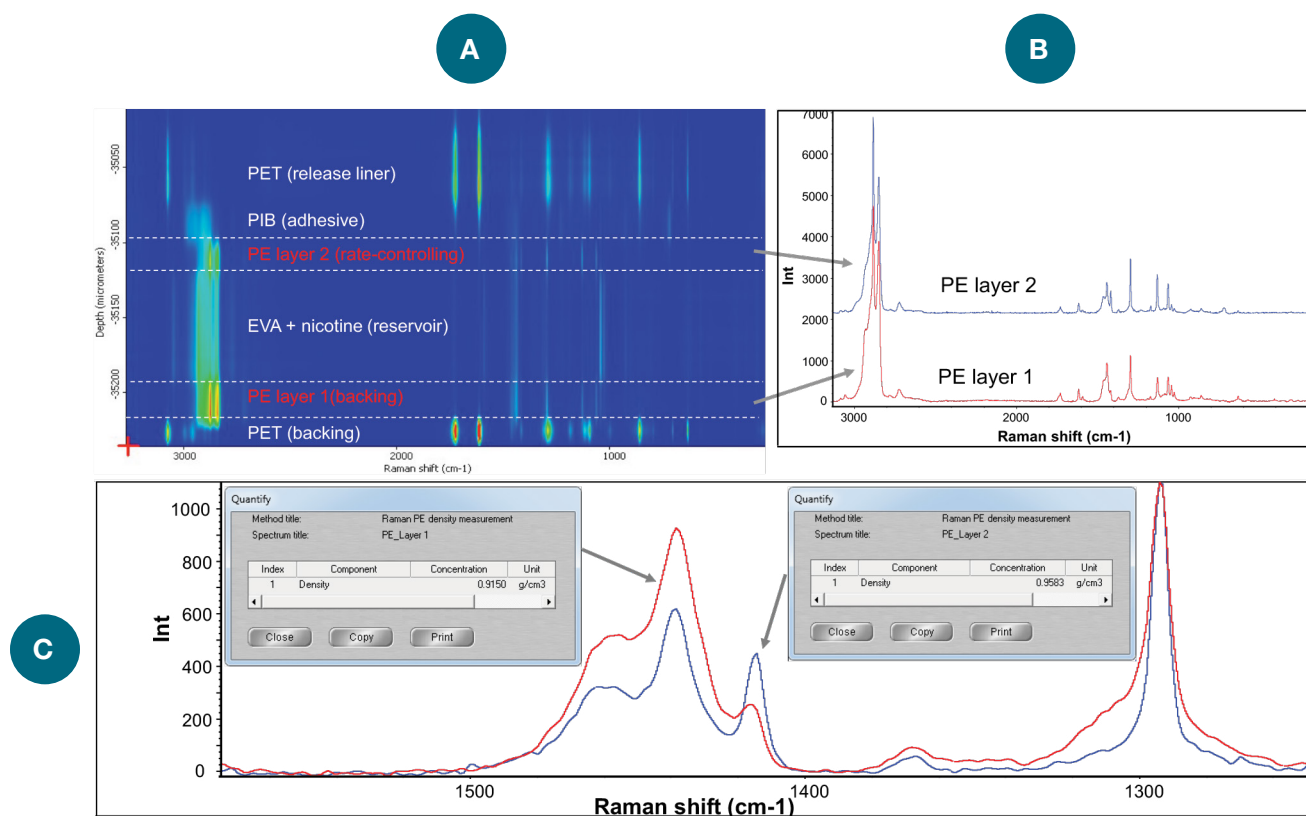


Figure 5: (A) Confocal Raman line depth map of a multilayer polymer patch, showing the presence of two types of PE layers. (B) Raman spectra of the two PE layers in full spectral range. (C) Raman spectra of the two PE layers in the CH₂ bending and CH₂ twisting region. The insets in (C) show the calculated densities of the two PE layers using the 3-factor PLS model. PET = poly(ethylene terephthalate), EVA = ethylene/vinyl acetate copolymer, PIB = polyisobutylene.

References

1. Piringer O.G. and Baner A.L., ed. *Plastic Packaging: Interactions with Food and Pharmaceuticals*. 2nd ed. Weinheim: Wiley-VCH; 2008.
2. Polyethylene, The Essential Chemical Industry – online, <http://www.essentialchemicalindustry.org/polymers/polyethene.html>, retrieved on 11/27/2017.
3. (a) ISO 1183-1:2012, *Plastics – Methods for determining the density of non-cellular plastics – Part 1: Immersion method, liquid pycnometer method and titration method*; ANSI New York, NY. (b) ASTM D792-13, *Standard test methods for density and specific gravity (relative density) of plastics by displacement*; ASTM International, West Conshohocken, PA, 2013.
4. (a) ISO 1183-2:2004, *Plastics – Methods for determining the density of non-cellular plastics – Part 2: Density gradient column method*. ANSI New York, NY. (b) ASTM D1505-10, *Standard test method for density of plastics by the density-gradient technique*; ASTM International, West Conshohocken, PA, 2010.
5. ASTM D4883-08, *Standard test method for density of polyethylene by the ultrasound technique*; ASTM International, West Conshohocken, PA, 2008.
6. Mieth A., Hoekstra E., and Simoneau C. *Guidance for the identification of polymers in multilayer films used in food contact materials: User guide of selected practices to determine the nature of layers*, EUR 27816 EN, 2016; doi: 10.2788/10593.
7. Sato H., Shimoyama M., Kamiya T., Amari T., Sasic S., Ninomiya T., Siesler H.W., and Ozaki Y. *Raman spectra of high-density, low-density, and linear low-density polyethylene pellets and prediction of their physical properties by multivariate data analysis*, J. Appl. Polym. Sci., 2002, 86, 443–448.
8. Strobl G.R. and Hagedorn W. *Raman spectroscopic method for determining the crystallinity of polyethylene*, J. Polym. Sci. B Polym. Phys., 1978, 16, 1181-1193.
9. Williams K.P.J. and Everall, N. J. *Use of micro Raman spectroscopy for the quantitative determination of polyethylene density using partial least-squares calibration*, J. Raman Spectrosc. 1995, 26, 427-433.
10. Ibrahim M. and He H. *Classification of polyethylene by Raman spectroscopy*, Thermo Scientific Application Note AN52301, 2017.
11. Thermo Scientific Product Overview. *TQ Analyst Software Chemometric Algorithms*, 2009.
12. Kearney C. J. and Mooney D.J. *Macroscale delivery systems for molecular and cellular payloads*, Nat. Mater., 2013, 12, 1004-1017
13. Allen L. V. and Ansel H. C., ed. *Ansel's Pharmaceutical Dosage Forms and Drug Delivery Systems*, 10th ed. Lippincott Williams & Wilkins; 2013.

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