Application Note: 51663

Density and Copolymer Content in Polyethylene Samples by FT-NIR Spectroscopy

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Key Words

- Antaris
- FT-NIR Spectroscopy
- Plastic
- Polyethylene
- Polymer

Introduction

Polymer plastics have become ubiquitous worldwide and include some of the most important and useful materials available. The plastics industry is one of the largest manufacturing segments in the U.S. accounting for almost $4 billion in shipments and employing over 1 million people. Common synthetic polymers include polypropylene, polyethylene, polyvinyl chloride, polyamide and polyester. However, in addition to their advancing use and value, increasing awareness has been given to their environmental impact, both in regard to manufacture as well as post-use. Significant attention is being directed to recycling these plastics in order to minimize their environmental impact and to reduce the need for petrochemical raw materials used in their manufacture.

The most important of these polymers both in volume of material produced as well as environmental impact may be polyethylene. Polyethylene is a thermoplastic made through the polymerization of ethene (Figure 1) and is used in packaging films, toys, barrels, plumbing pipes, molded housewares, and trash and grocery bags. A variety of different polyethylene types has been developed based mostly on density of the material and branching of the intrinsic molecular chains.

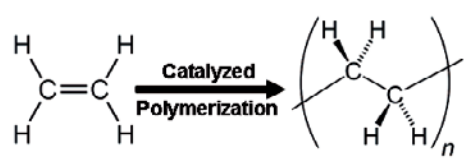

Figure 1: Catalyzed polymerization of ethene to form polyethylene

The unequivocal identification of the feedstock is of key importance in manufacturing items as well as proper recycling of these materials. Properly identifying and separating different recyclable plastics from each other so that they are processed correctly requires a great deal of effort. In addition to separating polyethylene items from other plastics, different types (densities) of polyethylene need to be separated as do items co-polymerized with other types of plastics. Unfortunately, this is often difficult to do without complex chemical analysis.

Figure 2: Antaris MDS with sample cup spinner

Fourier transform near infrared provides a means to identify and analyze various polyethylenes. The Thermo Scientific Antaris™ line of FT-NIR analyzers has proven to be useful for identifying and measuring a wide range of materials quickly and easily with no sample preparation. The Antaris II Method Development Sampling (MDS) system (Figure 2) was used to perform in-depth analyses of different densities of polyethylene as well as the amount of ethylene present in polypropylene samples.

Experimental

Two separate studies on different polyethylene materials were performed. The first focuses on classifying polyethylene samples of different densities, and development of a quantitative prediction of polyethylene densities. The second illustrates the ability of the Antaris II to quantify the amount of polyethylene in polypropylene copolymers.

Study 1

Three sets of polyethylene samples with distinct density ranges (Table 1) were analyzed using the Antaris II MDS system's integrating sphere module with a spinning sample cup. The materials were classified as either linear low density polyethylene (LLDPE, density 0.9170-0.9200 g/cm^3); medium density polyethylene (MDPE, density 0.9260-0.9400g/cm^3); or high density polyethylene (HDPE, density range >0.941g/cm^3). Each of the samples was scanned in the range between 10,000 and 4000 cm^{-1}. A discriminant analysis chemometric model was developed using TQ Analyst™ software. The first derivative spectra were analyzed between 6000 and 5700 cm^{-1} (Figure 3) where there was clear spectral difference between the three groups of materials. A Norris derivative smoothing filter was applied to the spectra before the chemometric modeling.

Sample Number	Density (g/cm³)	Actual Class	Predicted Class
1	0.9170	LLDPE	LLDPE
2	0.9170	LLDPE	LLDPE
3	0.9173	LLDPE	LLDPE
4	0.9178	LLDPE	LLDPE
5	0.9179	LLDPE	LLDPE
6	0.9180	LLDPE	LLDPE
7	0.9180	LLDPE	LLDPE
8	0.9182	LLDPE	LLDPE
9	0.9287	LLDPE	LLDPE
10	0.9192	LLDPE	LLDPE
11	0.9200	LLDPE	LLDPE
12	0.9340	MDPE	MDPE
13	0.9340	MDPE	MDPE
14	0.9348	MDPE	MDPE
15	0.9350	MDPE	MDPE
16	0.9360	MDPE	MDPE
17	0.9360	MDPE	MDPE
18	0.9360	MDPE	MDPE
19	0.9365	MDPE	MDPE
20	0.9370	MDPE	MDPE
21	0.9376	MDPE	MDPE
22	0.9380	MDPE	MDPE
23	0.9386	MDPE	MDPE
24	0.9388	MDPE	MDPE
25	0.9395	MDPE	MDPE
26	0.9590	HDPE	HDPE
27	0.9590	HDPE	HDPE
28	0.9590	HDPE	HDPE
29	0.9595	HDPE	HDPE
30	0.9595	HDPE	HDPE
31	0.9595	HDPE	HDPE
32	0.9597	HDPE	HDPE
33	0.9598	HDPE	HDPE
34	0.9600	HDPE	HDPE

Table 1: Density and classification of polyethylene materials analyzed. All samples were correctly predicted.

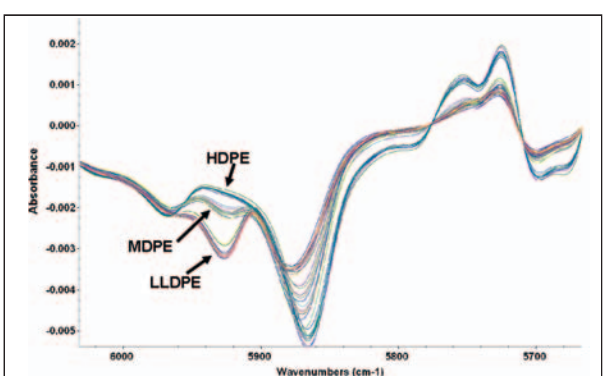

Figure 3: First derivative spectral range analyzed for discriminant analysis of the different polyethylene density classes.

The principal component scores plot (Figure 4) shows excellent separation of the different density classes. Principal components describe the spectral variation in a discriminant analysis. The first principal component describes most of the variation within the standard spectra and each subsequent principal component describes the remaining variation. Figure 4 plots the spectra against the first and second principal component. The separation between the different density classes of polyethylene indicate these materials can be successfully classified with the Antaris NIR analyzer.

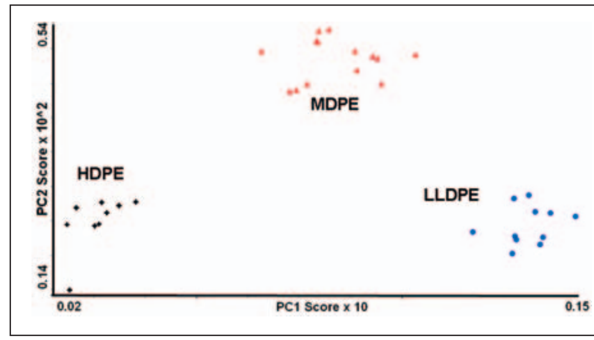

Figure 4: Principal component scores plot demonstrating clear spectral separation between the different density classes of polyethylene.

In addition to qualitatively classifying different polyethylene materials, a quantitative analysis was performed on the MDPE samples. The 11 samples of MDPE ranging in density from 0.9340 to 0.9395 g/cm³ were re-analyzed using a partial least squares (PLS) chemometric model. The unprocessed spectra were analyzed in the range from 10,000 to 6200 cm^{-1} using a 1 point baseline correction at 8840 cm^{-1}. A plot of the chemometric model's calculated values vs. actual values indicates that density can be accurately predicted (Figure 5). Selected validation spectra provide a root mean standard error of prediction (RMSEP) of 0.0005 g/cm³ with a correlation coefficient of 0.97699.

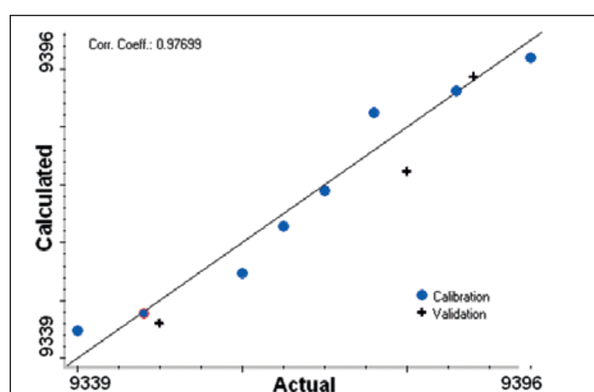

Figure 5: Regression plot showing the fit of the chemometric model for the MDPE samples. Root Mean Square Error of Prediction (RMSEP) = 0.0005.

Study 2

Polypropylene films containing ethylene as a copolymer have better clarity and lower melting points than polypropylene alone. These characteristics make such materials useful in low temperature heat-sealable applications. Melting points are linearly related to ethylene content, which makes ethylene an important measurable component. For this study, a series of 28 random and impact ethylene-polypropylene copolymer samples containing various amounts of ethylene (2% to 16%) were scanned with the Antaris II MDS system. A PLS method of analysis was selected using TQ Analyst software. The unsmoothed unprocessed spectra were analyzed between 9000 and 4500 cm^{-1} using a one point baseline correction at 9029 cm^{-1}. Figure 6 shows the spectra used in the analysis. A plot of the predicted vs. actual values of ethylene concentration in polypropylene is shown in Figure 7 and demonstrates an excellent fit. The model produces a RMSEP of less than 0.4% ethylene with a correlation coefficient of 0.99764.

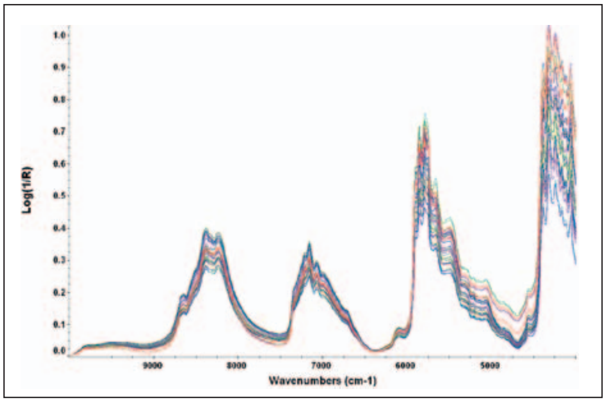

Figure 6: Spectra of ethylene-polypropylene copolymer samples. Concentration of polyethylene ranged from 2% to 16%.

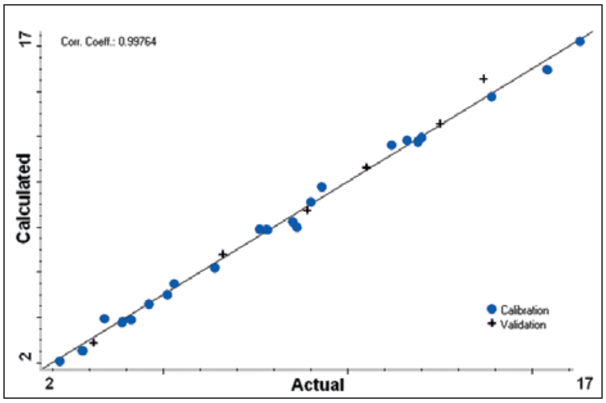

Figure 7: Regression plot of the calculated vs. actual values for the ethylene-polypropylene copolymer samples. RMSEP = 0.386.

Conclusion

The feasibility of both qualitative and quantitative analysis of polymeric materials using the Antaris FT-NIR analyzer has been clearly demonstrated. Specifically, polyethylene is correctly separated into different groups. Additionally, the density of MDPE is accurately predicted, and the levels of blends in an ethylene-polypropylene copolymer are accurately predicted.

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AN51663_E_05/08M