

Determination of Plasticizer Content in PVC by FT-NIR Spectroscopy

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KEY WORDS

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ABSTRACT

Fourier transform near-infrared spectroscopy (FT-NIR) was used to determine the dioctyl phthalate (DOP) plasticizer content in polyvinyl chloride (PVC). The FT-NIR spectra for PVC plates were collected in the reflectance mode using the Integrating Sphere module. Data was collected for PVC films using the transmittance mode. Partial Least Squares (PLS) methods were developed for the measurement of DOP in these materials. The results of this study showed that FT-NIR spectroscopy is a suitable technique for the measurement of polymer composition.

INTRODUCTION

FT-NIR spectroscopy has many advantages in comparison with traditional analytical methods. Noninvasive and nondestructive analyses can be performed. Reagents are not typically required and samples can be analyzed in situ through glass or polymer containers. Minimal sample preparation is generally needed. Simultaneous multicomponent analysis is possible in a very short time. In most cases, the analysis time is typically less than one minute. This allows high sample throughput and quick feedback of critical analytical information to production personnel.

Since FT-NIR measurements are simple and rapid, the technique is an ideal tool for quality control. It is also a convenient tool for at-line or near-line process control analyses because of the rapidity in which results are obtained.

The near-infrared (NIR) region is usually considered to include wave numbers between 14400 and 4000 cm^{-1} . Absorption bands originate from overtones and combinations of the fundamental (mid-IR) bands (mostly from C-H, N-H and O-H bonds). Broad, overlapping and low intensity peaks usually dominate the NIR spectrum.

The purpose of this work was to develop an FT-NIR method for the determination of the plasticizer content in polyvinyl chloride (PVC). PVC is used for many products such as toys, cables and foils. The plasticizer content differs depending on the commercial use of the material since the level of plasticizer determines the physical properties of the PVC. The plasticizer used for the material in this study was dioctyl phthalate (DOP).

The amount of DOP present in PVC is typically determined by gravimetry after Soxhlet extraction. This technique is time-consuming, tedious and requires the use of organic solvents. Furthermore, the extract contains small amounts of antioxidants that can interfere with the gravimetric determination.

Replacement of this procedure with a faster, easier and more specific FT-NIR method would clearly be advantageous. Mid-IR could also be used but it requires sample preparation making FT-NIR more attractive for routine analyses.

EXPERIMENTAL

Calibration Samples

Two sets of samples were obtained for this work. The first sample set contained 22 samples of PVC plates with known thicknesses. These plates contained different levels of DOP in the range of 5-50%. The sample thicknesses were confirmed using a digital micrometer. The PVC contents of these samples were calculated based on the weight percentage of DOP added to each. Ten translucent PVC (Neralit™ N702) plates with the stabilizer Naftomix™ MCS 20 (2.8%) and twelve (12) transparent PVC plates with the stabilizer Interlite™ ZP 7,003 (1.4%) were produced for this study. The content of DOP and the thickness of individual plates are presented in Table 1. The plates were kept separate from each other due to the known tendency of DOP to migrate between samples.

Table 1: DOP content in PVC (Neralit N702) plates

TRANSLUCENT PLATES			TRANSPARENT PLATES		
SAMPLE #	% DOP	THICKNESS mm	SAMPLE #	% DOP	THICKNESS mm
1	10	1.06	11	5	1.06
2	20	1.16	12	10	1.25
3	30	1.07	13	20	1.24
4	40	1.10	14	30	1.14
5	50	1.04	15	40	1.05
6	10	0.80	16	50	0.91
7	20	0.61	17	5	1.18
8	30	0.64	18	10	1.00
9	40	0.60	19	20	0.82
10	50	0.57	20	30	0.72
			21	40	0.62
			22	50	0.57

The second sample set was comprised of 11 PVC transparent films with different contents of DOP and with known thicknesses (Table 2). The thicknesses of all of the samples were confirmed using a digital micrometer. As with the previous samples, the DOP contents were calculated from the amount used to prepare the formulations. The PVC (Neralit 652) films contained the stabilizer Landromark™ LZB 968.

Table 2: DOP content in PVC (Neralit 652) films

TRANSPARENT FILMS		
SAMPLE #	% DOP	THICKNESS mm
1	9	0.286
2	13	0.364
3	16	0.286
4	19	0.234
5	22	0.314
6	25	0.353
7	28	0.324
8	31	0.334
9	34	0.369
10	37	0.330
11	40	0.337

Spectral Data Collection

Spectra for each of the samples were collected from 12000 to 3800 cm^{-1} on the Thermo Nicolet Industrial Solutions Antaris™ FT-NIR analyzer (Figure 1), equipped with a CaF_2 beam splitter and an InGaAs detector. Ninety scans were collected at 4 cm^{-1} resolution. The plates were analyzed as is without sample preparation.

The reflectance spectra of PVC plates were collected

using the integrating sphere module. The plates were placed directly onto the window of the sphere. In this case, it was not convenient to analyze these samples using transmission. It was necessary to optimize the procedure for the reflectance measurements. The internal gold flag of the integrating sphere was used as the background reference.

The spectra of PVC films were collected in the transmission mode. Samples in paper cards were placed in a transmission sample holder. The central reference position was used to collect an air background for these measurements.

Thermo Nicolet TQ Analyst™ software was used for all chemometric modeling. Multiplicative signal correction (MSC) and a Norris second derivative procedure were used to pretreat the data. The Norris derivative procedure uses segments and gaps to calculate the derivative, thus smoothing the data. This counteracts the tendency of derivative pretreatments to enhance the spectral noise. The PLS regression technique was used to develop the calibrations. The spectral regions used for each calibration were selected with the aid of the TQ Analyst region selection algorithm.



Figure 1: Antaris Method Development Sampling System

RESULTS

The examples of FT-NIR spectra of PVC translucent plates, PVC transparent plates and PVC films are shown in Figures 2, 3 and 4, respectively.

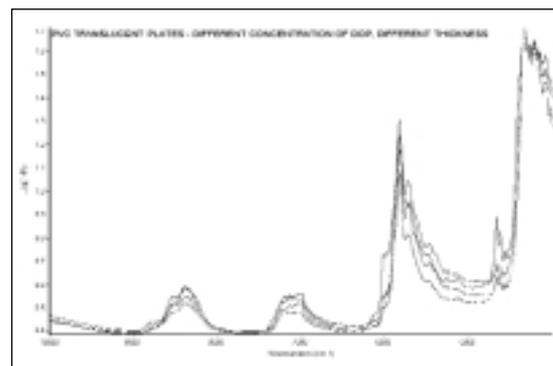


Figure 2: FT-NIR spectra of PVC translucent plates – integrating sphere (full scale)

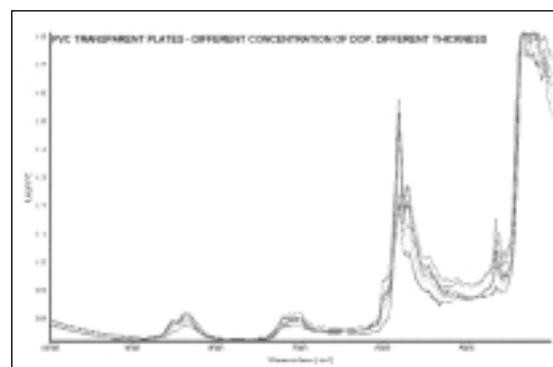


Figure 3: FT-NIR spectra of PVC transparent plates – integrating sphere (full scale)

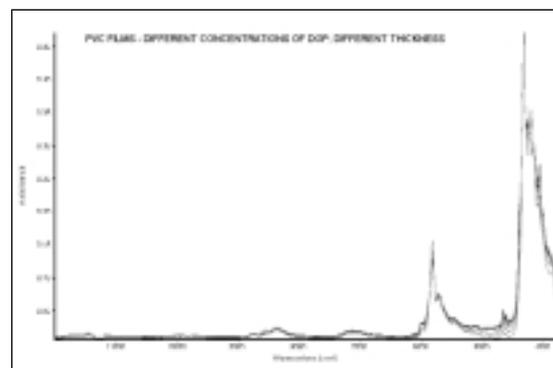


Figure 4: FT-NIR spectra of PVC films – transmission (common scale)

The PLS regression technique was used for all three calibrations developed. This calibration technique should be used when the relationship between the concentration and absorbance is complex. This is true in cases, for example, when chemical interactions between components cause peaks in the spectrum to shift or broaden. It is also useful when several sample properties co-vary. The best results were obtained using the parameters summarized in Table 3.

Table 3: PLS model parameters

MATERIAL	NUMBER OF FACTORS	DATA FORMAT	REGION cm^{-1}	PATHLENGTH TYPE
Translucent plates	4	Norris second derivative Segment = 9, Gap = 0	8982-3920	MSC
Transparent plates	4	Norris second derivative Segment = 5, Gap = 5	4772-4520, 5935-5322	MSC
Films	3	Norris second derivative Segment = 5, Gap = 5	4125-3946, 4296-4263	MSC

The calibration plots (FT-NIR results vs. weight percentage) are shown in Figures 5-7 for each case. The correlation coefficient, the Root Mean Square Error of Calibration (RMSEC), cross validation correlation coefficient and the Root Mean Square Error of Cross Validation (RMSECV) values are summarized in Table 4.

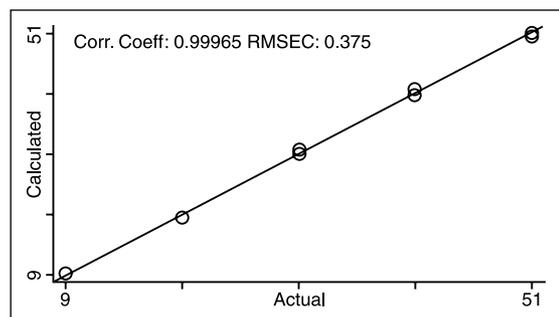


Figure 5: PLS calibration result for PVC translucent plates

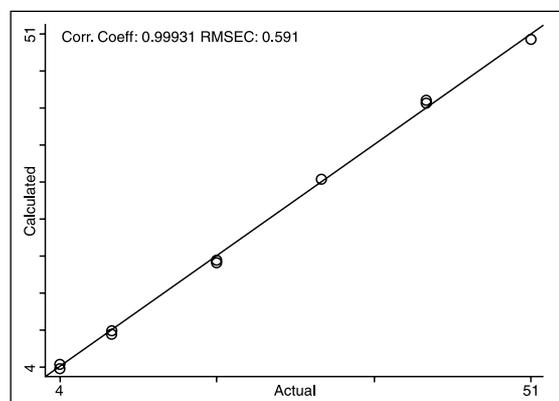


Figure 6: PLS calibration result for PVC transparent plates

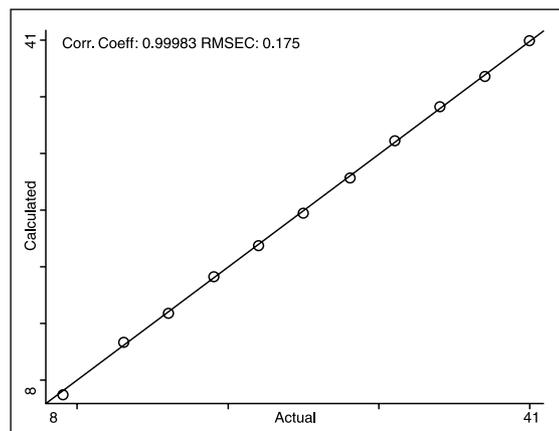


Figure 7: PLS calibration result for PVC films

Table 4: PLS results for the determination of the plasticizer content in PVC

	CALIBRATION		CROSS VALIDATION	
	Correlation coefficient	RMSEC	Correlation coefficient	RMSECV
Translucent plates	0.99965	0.375	0.995	1.490
Transparent plates	0.99931	0.591	0.996	1.450
Films	0.99983	0.175	0.999	0.407

CONCLUSION

FT-NIR methods were developed for the determination of the content of the plasticizer DOP in three different forms of PVC (translucent plates, transparent plates and films). The results of the PLS regression models confirmed that FT-NIR spectroscopy is a suitable technique for this purpose because the calibrations are of high quality.

The data presented in this paper proves that FT-NIR can be used to predict polymer composition quickly and with minimal or no sample preparation. The total spectral analysis time is typically shorter than one minute per sample. Implementation of FT-NIR methods similar to those reported here can lead to improved efficiency and better process and quality control for polymer applications.



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