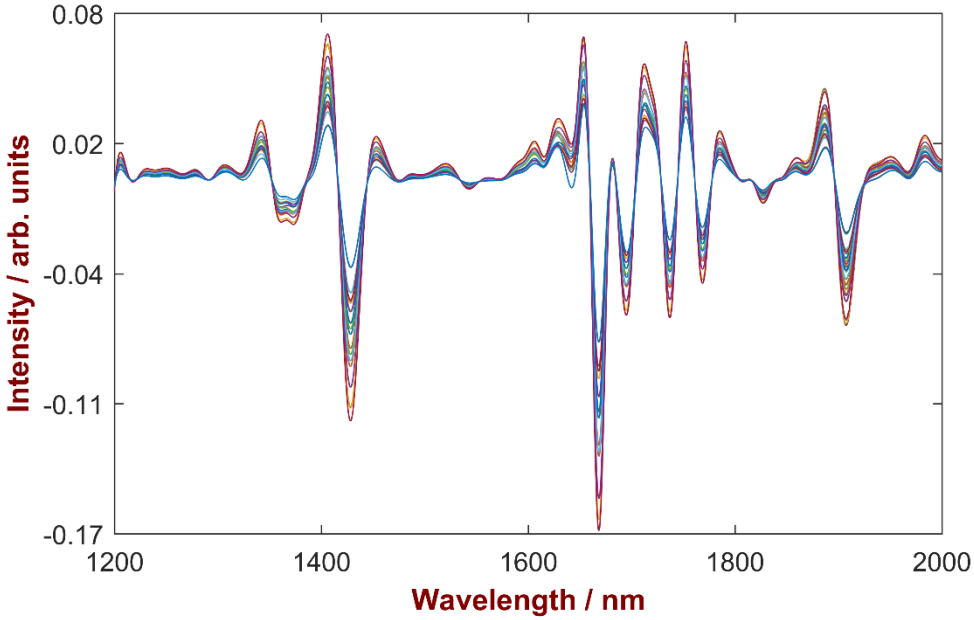
NIR Application Note NIR–067

Simultaneous determination of multiple quality parameters in epoxy resins using Vis-NIR spectroscopy



This Application Note demonstrates the feasibility of Vis-NIRS for the simultaneous determination of multiple chemical and physical parameters in epoxy resins. Vis-NIRS is a fast alternative to conventional lab methods: it accelerates raw material inspection, process monitoring, and final product control.

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Method description

Introduction

Epoxy resins are a class of polymers containing epoxy groups and they are used in a wide range of application, e.g., as adhesives, surface coating or insulators. Their use is based on their affinity to build thermosetting polymers. This means that after curing the material cannot be modified anymore. The building process of almost all thermosetting polymers has some common characteristics. Highly reactive raw components such as epoxy resins form chemical bonds with themselves or are linked with co-reactants (hardener) to a polymer. The reactivity of epoxy resins is caused through the presence of highly reactive epoxy groups. Therefore, in order to ensure the right reactivity, it indispensable to determine the amount of epoxy groups in the raw material. This parameter is called weight per epoxy equivalent (WPE) or epoxy equivalent weight (EEW). This important parameter provides information about the reactivity of the epoxy resin and is used for the calculation of the required ratio of the curing agent. The classical way of determination is based on titration, which involves, sample preparation and consumes chemicals. Additionally, he building of thermosetting polymers can occur at room temperature but it also can be realized at high temperatures. The advantage of heating is the increased fluidity caused by a decrease of viscosity. Therefore, dependent on the physical state of the raw material is it also important to determine viscosity of the sample at normal conditions, usually at 25 °C, as well as at high temperature, usually at 150 or 200 °C. This if often realized through rheological analysis at different conditions.

On the other hand, near-infrared spectroscopy (NIR) can be used for the simultaneous determination of WPE as well as rheological properties of the sample. When using NIR, the sample can be analyzed without any sample preparation and also without cost intensive chemicals. This enables significant time and cost savings. Furthermore, the duration of analysis is less than one minute, which shortens significantly the duration of quality control. Such application possibilities of NIR for the determination of chemical and physical properties are demonstrated in the present Application Note.

Experimental

175 samples provided by a customer were used in the present study. Reference values were determined using reference methods. The number of samples as well as the corresponding reference method are summarized in **Tab. 1**.

Tab. 1: Number of samples as well as reference methods.

Parameter	No. of samples	Reference method
WPE	104	ASTM D1652
Viscosity at 25 °C	23	ISO 10258-1
Viscosity at 150 °C	22	ASTM D4440
Viscosity at 175 °C	10	ASTM D4440
Viscosity at 200 °C	16	ASTM D4440

The spectra were collected in reflection mode on a Metrohm NIRS DS2500 Analyzer over the full wavelength range (400–2500 nm). The sample was placed into large sample cup and analyzed in moving mode in order to minimize the impact of sample inhomogeneity. Four spectra were acquired for each sample. The software package Vision Air 2.0 Complete was used for data acquisition, data management and development of the quantification method. **Tab. 2/ Fig. 1** lists the used equipment.

Tab. *2*: Used equipment and software.

Equipment	Metrohm number
NIRS DS2500 Analyzer	2.922.0010
DS2500 large sample cup	6.7402.050
Vision Air 2.0 Complete	6.6072.208

Fig. 1: The NIRS DS2500 Analyzer was used for spectral data acquisition over the full range from 400 to 2500 nm.

Results

Fig. 2 shows Vis-NIR spectra of epoxy resins. Redundant spectral information was excluded from the method development by the selection of analyte specific wavelength ranges combined with dedicated spectral pre-treatments. Example of such procedure is shown in

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Fig. 3, which demonstrates spectra pretreated with a 2nd derivative over the full wavelength range.

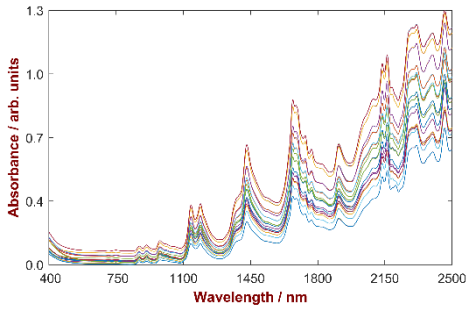

Fig. 2: Raw Vis-NIR spectra of epoxy resins over the full wavelength range.

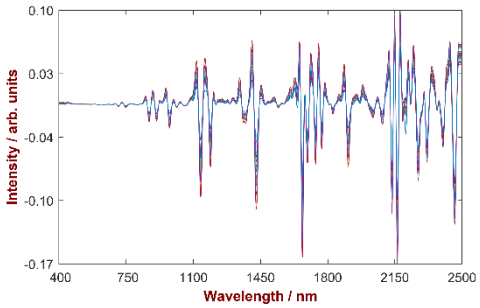

Fig. 3: Spectra pretreated with 2nd derivative over the full wavelength range.

The correlation plots, see **Fig. 4–8**, show high correlation between the parameters determined by reference analytical method (x-axis) and the predicted values (y-axis) from Vis-NIR spectroscopy. The good correlation results are confirmed by the analytical figures of merit shown in **Tab. 3–7**.

WPE:

Tab. 3: Results of the quantitative method development for WPE.

Range	650–770 g/Eq
Regression model	PLS, 10 factors
Pre-treatment	2nd derivative
Wavelength ranges	816–1044 nm 1120–1210 nm 1290–1490 nm 1570–2100 nm
R^2	0.989
SEC	3.2 g/Eq
SECV	3.4 g/Eq

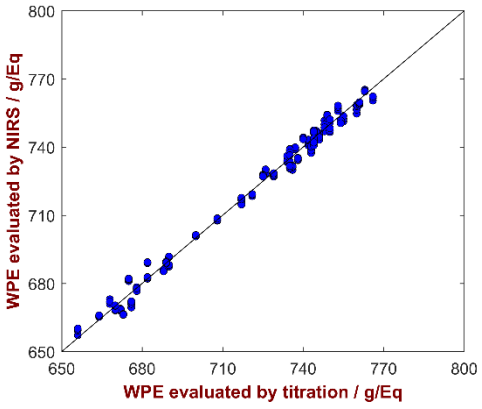

Fig. 4: Correlation plot of the WPE predicted by NIRS versus the reference values. A high correlation is observable.

Viscosity at 25 °C:

Tab. 4: Results of the quantitative method development for viscosity at 25 °C.

Range	402–670 mPa s
Regression model	PLS, 10 factors
Pre-treatment	2nd derivative
Wavelength ranges	816–1044 nm 1120–1210 nm 1290–1490 nm 1570–2100 nm
R^2	0.973
SEC	12.5 mPa s
SECV	13.9 mPa s

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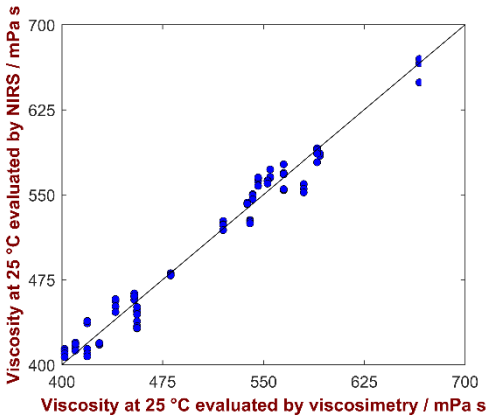

Fig. 5: Correlation plot of the viscosity at 25 °C predicted by NIRS versus the reference values. A high correlation is observable.

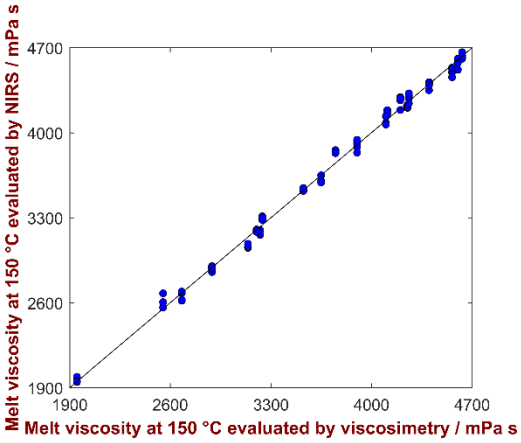

Fig. 6: Correlation plot of the viscosity at 150 °C predicted by NIRS versus the reference values. A high correlation is observable.

Viscosity at 150 °C:

Tab. 5: Results of the quantitative method development for viscosity at 150 °C.

Range	1950–4630 mPa s
Regression model	PLS, 8 factors
Pre-treatment	2nd derivative + SNV
Wavelength ranges	416–1080 nm 1120–2484 nm
R^2	0.995
SEC	51.8 mPa s
SECV	58.6 mPa s

Viscosity at 175 °C:

Tab. 6: Results of the quantitative method development for viscosity at 175 °C.

Range	2125–4733 mPa s
Regression model	PLS, 7 factors
Pre-treatment	2nd derivative + SNV
Wavelength ranges	416–1080 nm 1120–2484 nm
R^2	0.991
SEC	101.4 mPa s
SECV	143.5 mPa s

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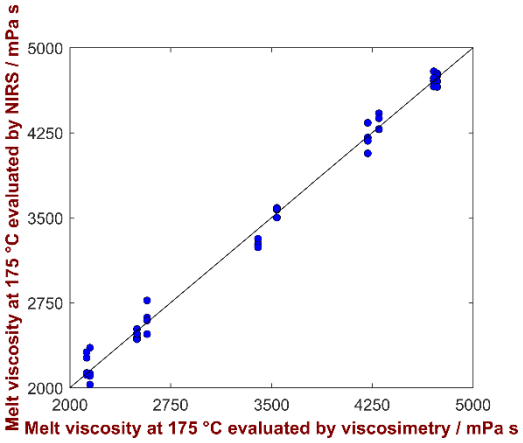

Fig. 7: Correlation plot of the viscosity at 175 °C predicted by NIRS versus the reference values. A high correlation is observable.

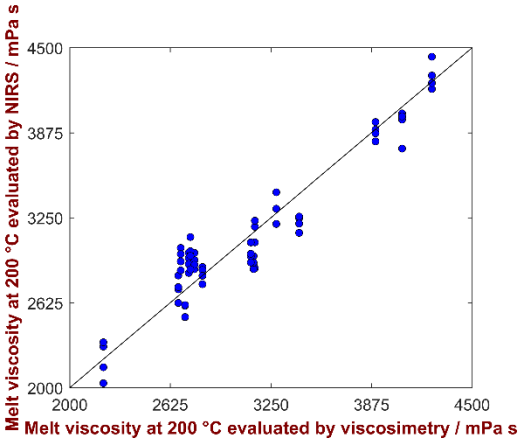

Fig. 8: Correlation plot of the viscosity at 200 °C predicted by NIRS versus the reference values. A high correlation is observable

Viscosity at 200 °C:

Tab. 7: Results of the quantitative method development for viscosity at 200 °C.

Range	2210–4250 mPa s
Regression model	PLS, 10 factors
Pre-treatment	1st derivative
Wavelength ranges	416–1080 nm 1120–2484 nm
R^2	0.907
SEC	182.6 mPa s
SECV	196.3 mPa s

Summary

The results presented in this application note shows the feasibility of using Vis-NIR spectroscopy for quality control of epoxy resins. It was successfully demonstrated, that this technique enables simultaneous determination of WPE and different viscosities. The error of calibration can be further improved, when improving the accuracy and precision of the reference method.

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