

Application Note AN M115

UV curing

Introduction

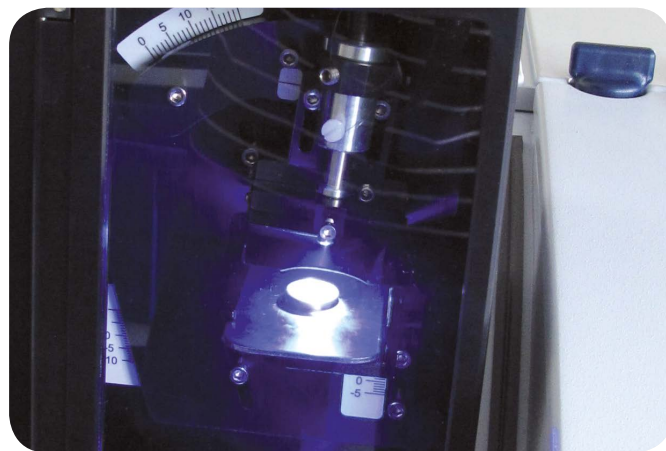
Photocurable polymers cover a wide field of applications due to their multifunctional properties. Mainly the automotive industry, consumer electronics, printing and the coating industry make use of them. The properties of UV cured polymers depend not only on their composition but also on their reaction kinetics. FTIR spectroscopy is an excellent analytical method for monitoring kinetics of photo initiated curing processes.

The principle of photoinitiated curing processes is based on irradiating the sample with UV-light (or visible light), which activates so called photoinitiators. They form reactive substances which start the polymerization. UV curable acrylates form radicals as reactive substances and UV curable epoxy adhesives form cationics.

Four steps are characteristic for the basic kinetics of radical polymerization.

The reaction is initiated by energy induced radical formation (e.g. via UV-radiation).

The radicals react with monomers and form monomer-radicals. After the reaction has been initiated the propagation step takes place; monomer-radicals react with monomers and the polymer chain grows. The last step is the termination, where different reactions can occur (for example combination of two active chain ends).



Keywords	Instrumentation and Software
FTIR	INVENIO, VERTEX
VERTEX 80	ATR accessory A225/Q
Curing	Transmittance accessory A043-N/Q
Rapid Scan	UV-radiation source
Kinetic	Triggerbox E525/Z
Molecular reaction	OPUS 3D Software

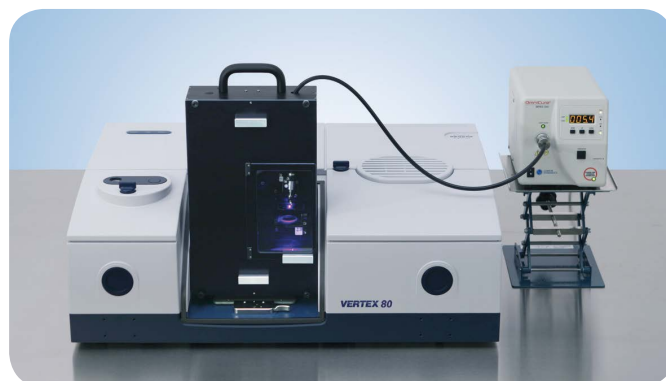


Figure 1: Bruker VERTEX 80 FTIR spectrometer with UV-irradiation source on the right side and transmittance accessory with horizontal sample mount in the sample compartment.

- Initiation: R → R•
- Start: R• + M → R-M•
- Propagation: R-M• + nM → R-(M)_n-M•
- Termination: e.g. R-(M)_n-M• + R-(M)_n-M• → R-(M)_n-M-M-(M)_n-R

Experimental

The Bruker FTIR spectrometers of the INVENIO and VERTEX series provide very high spectral collection rates in combination with the Rapid Scan functionality and are ideally suited for monitoring fast irreversible reaction kinetics. The achievable temporal resolution for the INVENIO and VERTEX research spectrometer systems is different and depends on the used spectral resolution. The appropriate spectral collection rates are listed in table 1.

Rapid Scan Spectra rate

Spectral resolution	Spectra rate (Spectra/sec) temporal resolution VERTEX 80/80v	Spectra rate (Spectra/sec) temporal resolution INVENIO R and VERTEX 70v
16 cm ⁻¹	>110; ca. 9 msec	>70; ca. 14 msec
12 cm ⁻¹	95; ca. 10 msec	60; ca. 16 msec
8 cm ⁻¹	85; ca. 12 msec	50; ca. 20 msec
4 cm ⁻¹	55; ca. 18 msec	32; ca. 31 msec
2 cm ⁻¹	32; ca. 31 msec	18; ca. 55 msec

Table 1: Achievable temporal resolution in dependence of spectral resolution with spectrometer systems VERTEX 80/80v, VERTEX 70v and INVENIO R in Rapid Scan measurement mode (option S129)

Bruker offers the option of an external UV-source including trigger functionality. For that purpose two possibilities of triggering are available: the sample is irradiated during the complete measurement time or the sample is irradiated at the start of the measurement but only for a predefined time. The UV-radiation is coupled to the measurement area via fiber optics.

Figure 2 shows a VERTEX 80 spectrometer with heatable ATR accessory in the sample compartment and the fiber-optic of the external UV-source is fixed by an adjustable mount at the ATR accessory. A suitable single reflection diamond ATR accessory is the Platinum ATR from Bruker, which can also be used for far IR-range.

Besides the ATR technique also transmittance measurements are used as an analytical tool. The Bruker Optics transmittance accessory A043-N/Q with horizontal sample mount is shown in figure 1. Of course, the sample mount can be adjusted in height and the mount for the UV fiber-optic is adjustable too.



Figure 2: Bruker VERTEX 80 FTIR spectrometer with UV-irradiation source on the right side and heatable ATR accessory in the sample compartment.

Spectra were collected every 120 msec with a spectral resolution of 4 cm⁻¹. Due to its fast responsivity a liquid nitrogen cooled mid-band MCT detector was used. The OPUS spectroscopy software was used for data acquisition and the additional package OPUS/3D was used for data visualization and data evaluation.

A photocurable acrylate adhesive was placed on the surface of the Diamond ATR crystal. After collecting 10 spectra the sample was irradiated with defined UV radiation power during the complete measurement time by use of a trigger signal.

Assignment table for some observed absorption bands

Absorption band @ [cm ⁻¹]	Functional group	Vibration
1620	C=C	Stretching
1147	C-O-C	Stretching
810	H-C=C	Deformation

Table 2: Band assignment of selected functional groups

Results

Figure 3 shows a 3D-plot which is used in the OPUS software to present time-resolved measurement data.

The band at 810 cm⁻¹ is assigned to the C-H deformation vibration located at the C=C double bond and the band at 1620 cm⁻¹ is assigned to the stretching vibration of the C=C double bond. The elimination of C=C double bonds can be seen from the disappearance of these absorption bands. The increase at 1147 cm⁻¹ is assigned to the C-O-C group. The carbonyl band shifts from 1721 cm⁻¹ to 1727 cm⁻¹. Temporal progression of absorption band intensities is displayed in the trace view, which simplifies the evaluation of reaction kinetics.

A detailed view of selected normalized traces is presented in figure 4 and a detailed view of spectra is shown in figure 5.

In this example of a radical polymerization C=C double bonds were eliminated while C-O-C bonds were formed. The adhesive is completely cured after 18 seconds.

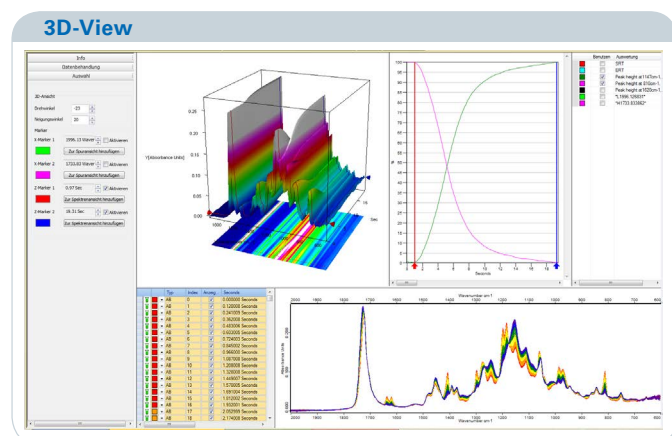


Figure 3: Evaluation view for time-resolved Rapid Scan measurement in the OPUS spectroscopy software. The upper left field shows progression of recorded FTIR spectra over the time course of the reaction as a 3D-plot. The upper right field presents the peak heights of the C-O and C-H bands from the FTIR spectra versus time which monitor the reaction rate. The lower right field shows the progression of FTIR spectra.

Conclusion

FTIR spectroscopy is an ideal analytical tool for studying photoinitiated polymerization reactions. Curing times of various adhesives can be easily and rapidly analyzed. Furthermore the reaction rates of functional groups can be determined and these provide a very useful insight into the reaction mechanism.

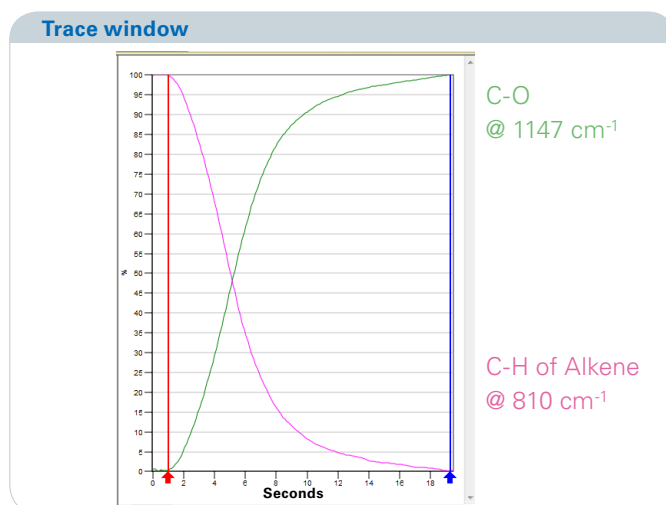


Figure 4: Trace view displaying the temporal progression of normalized intensity of the C-O-C group (green curve) and the C-H group at the C=C double bond (pink curve)

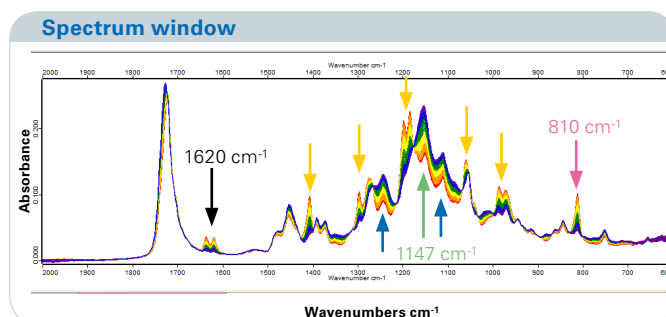


Figure 5: Progressive FTIR spectra of the Rapid Scan measurement.

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