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Application News

IRXross™ Fourier Transform Infrared Spectrophotometer

Monitoring of Adhesive Curing using Time Course Measurement with FTIR Spectroscopy

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User Benefits

- Time-course measurement software allows detailed observation of curing reaction processes.
- QATR™ 10 accessory equipped with Specac Arrow enables measurement of tough adhesives without the need of cleaning ATR prism.

■ Introduction

Reactive adhesives, which are used for binding two surfaces, involve a chemical reaction converting them from liquid to solid state. The duration of the chemical reaction or curing process may take a few seconds to a few hours for a complete curing, depending on various factors such as type of monomer used and initiation conditions.

One example of such adhesives is cyanoacrylate adhesive, which is commonly used for its ability to adhere to a wide range of substrates. It is also known as “superglue” or “instant glue” due to its rapid curing process. The acryl group containing an unsaturated carbon-carbon bond in the cyanoacrylate ester monomer would undergo polymerization in the presence of atmospheric moisture [1]. As the monomer undergoes polymerization, the unsaturated carbon bond would be consumed, as shown in Figure 1. This would lead to a change in molecular structure during the curing process.

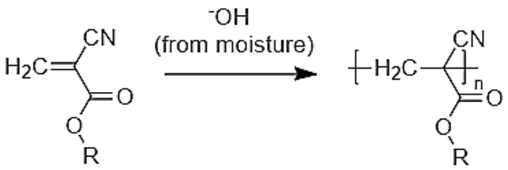

Fig. 1 Polymerization of cyanoacrylate

In order to monitor the curing process and evaluate the reaction rate of the adhesive, Fourier transform infrared spectrophotometer (FTIR) could be used as it can detect any spectral changes during the curing process. This application news introduces the measurement of the curing process for cyanoacrylate adhesive using time course measurement software with IRXross FTIR instrument.

■ Experimental

For this analysis, a commercially available cyanoacrylate adhesive was used as sample. The adhesive was measured using QATR 10 ATR accessory equipped with Specac Arrow (Figure 2). In this configuration, the default puck from QATR 10 accessory is replaced with Arrow puck and Arrow Si ATR slide. The cyanoacrylate adhesive cures rapidly in the presence of moisture and forms strong bonds, therefore if the curing analysis is performed directly on the default QATR 10 puck, an adhesive coating would form on the surface of the crystal prism. This would require rigorous cleaning after measurement and may damage the expensive crystal prism, which is undesirable. The disposable Arrow Si ATR slides would be a great alternative as they are low-cost and omit the need to clean the crystal prism.

On the silicon wafer of the Arrow Si ATR slide, a small drop of the adhesive was added and spread into a thin layer. The measurement was started immediately after. The measurement conditions are shown in Table 1. To monitor the curing process of the adhesive, spectrum measurement was pre-set to collect at every 30 seconds for 1 hour using time-course measurement software (Figure 3).

Fig. 2 Specac Arrow accessory on QATR™ 10 ATR accessory

Table 1 Measurement conditions

Instruments	: IRXross Fourier transform infrared spectrophotometer (KRS-5 window) QATR 10 ATR accessory Specac Arrow accessory (Silicon slide)
Wavenumber range	: 4000 - 650 cm^{-1}
Resolution	: 4 cm^{-1}
Accumulation	: 10 times
Apodization function	: SqrTriangle
Detector	: DLATGS

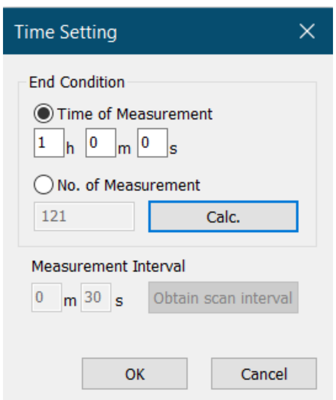

Fig. 3 Time Setting Window

Results and Discussion

Figure 4 displays the overlay ATR spectra in 3D graph obtained using the time-course measurement. The spectral changes that occurred during the sample reaction can be observed in wavenumber range of 650 – 2000 cm^{-1} shown in the 3D graph.

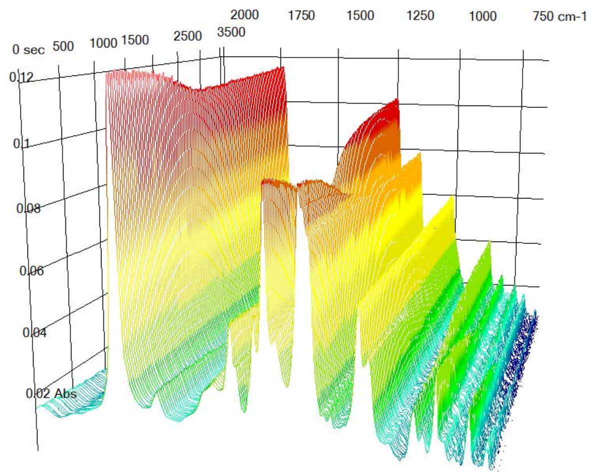

Fig. 4 3D Time-course measurement graph

To visualize the overall spectral changes of the sample, spectra at the start and end of the analysis were extracted from the 3D time-course measurement graph as shown in Figure 5. The peaks in the vicinity of 1288 and 804 cm^{-1} correspond to conjugated C-O-C stretching and C=C vibration modes respectively. The decrease in intensity for both peaks illustrates the consumption of unsaturated carbon-carbon bond during the reaction. In contrast, the peak intensity at around 1252 cm^{-1} due to saturated C-O-C stretching vibration mode has increased, indicating the increase in number of CH_2-C-CH_2 bonds over time.

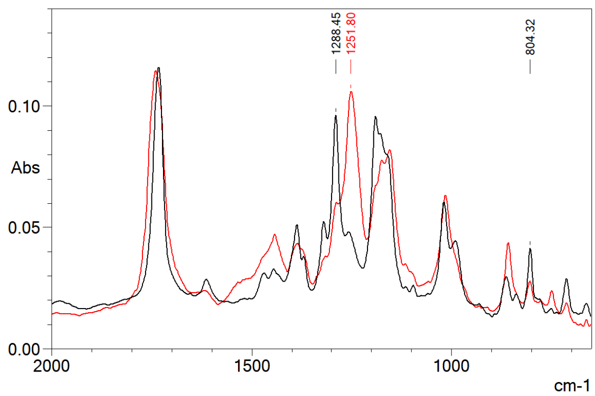

Fig. 5 Overlay spectra of adhesive at the start (black) and end (red) of analysis

During analysis, the absorption profiles for specific peaks or wavenumbers could be displayed as 2D time-course data, which is known as Selected Absorption Curve (SAC). Figure 6 shows the SAC for peaks at 1252 and 1288 cm^{-1}.

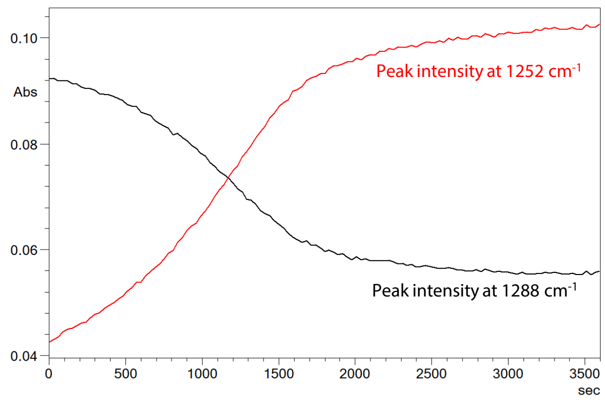

Fig. 6 Selected Absorption Curve (SAC) for peaks at 1252 and 1288 cm^{-1}

The curing reaction rate could be calculated based on the information from SAC. In this example, the rate could be calculated using peak intensity value of the 1252 cm^{-1} peak, assuming the start of the measurement as a reaction rate of 0% and end of measurement as completion of the curing process. The curing reaction rate can be calculated using the following equation:

$$\text{Curing reaction rate (\%)} = (A_t - A_0) / (A_E - A_0) \times 100$$

where A_t is the absorbance value at t time, A_0 is the absorbance value at t = 0 sec and A_E is the absorbance value at the end of reaction, where t = 3600 sec. The calculated curing reaction rate is displayed in Figure 7.

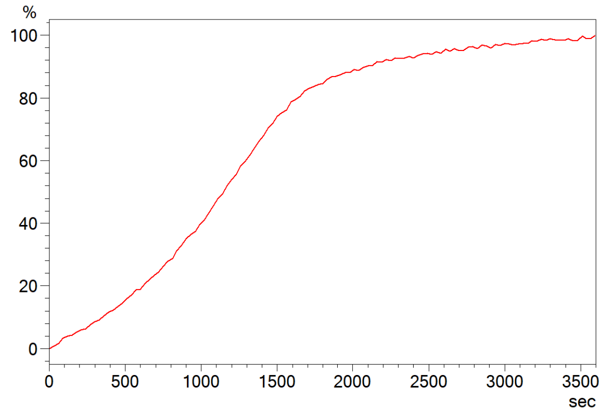

Fig. 7 Curing reaction rate graph

Conclusion

FTIR spectroscopy with time-course measurement software enables the monitoring of curing reaction process of reactive adhesives. The use of low-cost and disposable ATR slides allows analysis of strong adhesives by ATR method and avoids any damage due to rigorous cleaning on crystal prism.

Reference

1. Kwon, Y., and Kennedy, J. P. (2007) Polymerizabiltiy, Copolymerizability, and Properties of Cyanoacrylate. Polym. Adv. Technol. 1: 808-813

04-AD-0294-EN First Edition: Aug. 2023

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