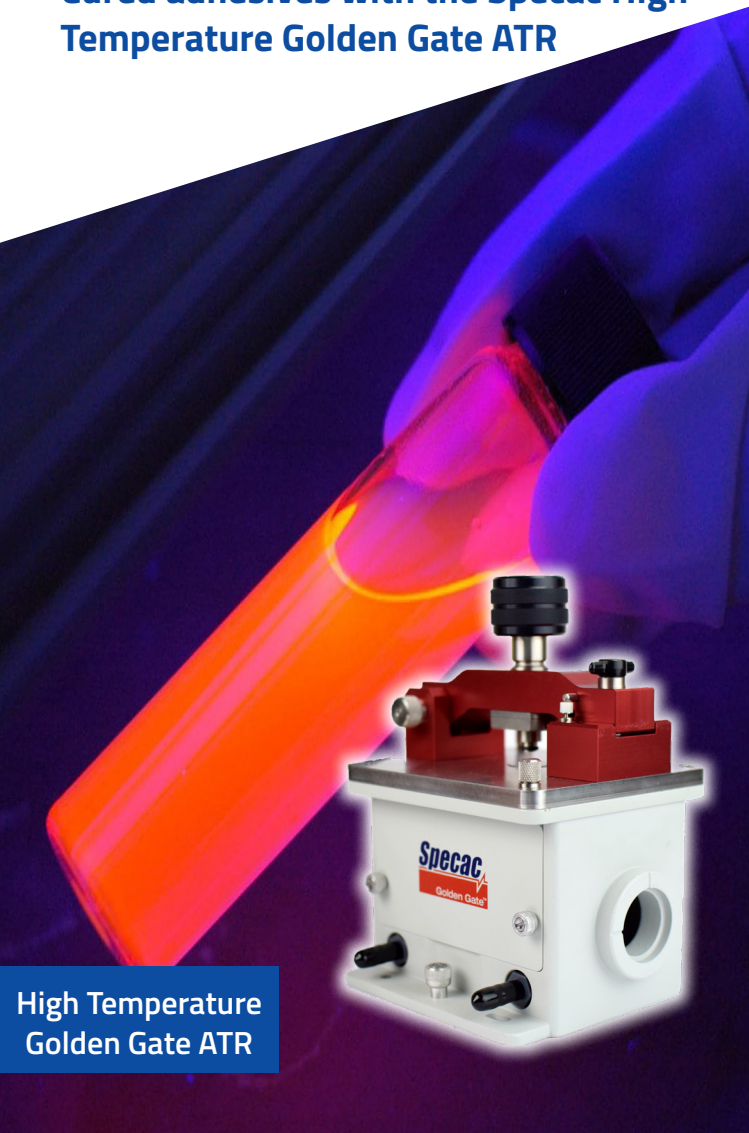
Specac

Application Note

Rapid Reaction Monitoring of UV Cured adhesives with the Specac High Temperature Golden Gate ATR



High Temperature Golden Gate ATR

INSIDE: Learn how the High Temperature Golden Gate ATR has been used with a fast time-resolved IR laser spectrometer to yield important insights into reaction kinetics.

Introduction

Rapid spectroscopic monitoring is a proven tool in R&D and production environments, where it is used to gain insight into chemical reactions. This application note showcases how the Golden Gate ATR accessory can be combined with ultrafast spectroscopic methods to monitor curing reactions, where it can provide invaluable insight on the performance of coatings and adhesives.

Infrared spectroscopy is in many ways an ideal measurement technique for this application as it can perform non-invasive, in-situ measurements that provide direct information about the structure and bonding of the sample. However, many high-performance adhesives have fast curing rates, with the speed of standard infrared spectroscopy techniques becoming the limiting factor in the analysis. A range of laser-based systems, including frequency comb spectrometer systems, now exist that can be combined with the Golden Gate ATR to measure fast chemical reactions.

Investigate the temperature response of solid and liquid samples with controlled temperatures up to 300 °C.

- Multiple sampling top-plates and sampling aids
- Monolithic diamond with brazed tungsten carbide mounting
- Extremely robust construction
- Signature bridge design allows up to 80 lbs force to be applied to solid samples for optimal sample contact
- Benchmark™ baseplate maintains alignment in the spectrometer
- Purgeable optics to reduce atmospheric interference

Acknowledgement: Specac thanks IRsweep for providing the text and figures that this application note was adapted from.

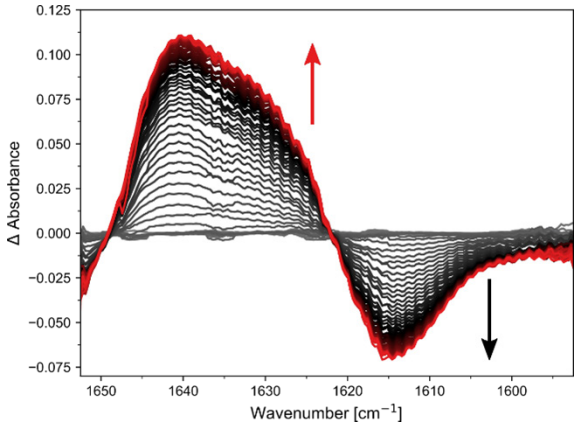


Figure 1: *Time Resolved difference IR spectra, with 25 ms resolution, showing a bleach of the reactant (black arrow) and growth of the product (red arrow) carbonyl bands.*

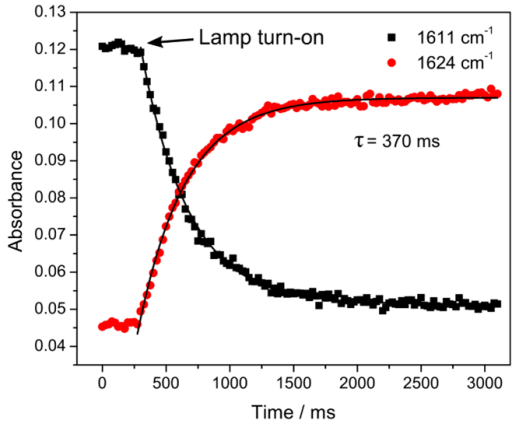


Figure 2: *Kinetic traces showing the change over time at 1611 and 1624 cm^{-1}. Fit lines are an exponential decay, indicative of a first order process.*

Rates of reaction and temperature control

Rates of reaction can be studied by IR spectroscopic methods if the measurement is fast enough to observe the reaction. For a first order process A → B the decay of the peaks associated with [A] fits an exponential decay, with the exponential factor equal to t/τ, where t is time and τ is lifetime.

When studying rates of reaction, it is important to consider the Arrhenius equation. This equation describes the relationship between the rate constant, k (for a first order process: equal to

the inverse of τ) with absolute temperature, T as described by the formula:

$$k=\frac{1}{\tau}=Ae^{\frac{-E_a}{RT}}$$

Where A is a pre-exponential constant, E_a is the activation energy, and R is the universal gas constant. Thus, it can be observed that it is important to tightly control temperature when studying rates of reaction to be able to accurately reproduce such studies. By conducting multiple experiments on a first order process at a range of temperatures it is possible to determine the E_a of a reaction (by plotting ln(k) against 1/T to give a straight-line plot with gradient R/E_a and intercept of ln(A). The High Temperature Golden Gate combined with a rapid spectroscopic method is therefore ideal for such studies.

Experimental

Measurements were conducted with a single-reflection diamond High Temperature Golden Gate ATR accessory (Specac), on an IRis-F1 dual-comb spectrometer (IRsweep). The sample is a UV-activated adhesive, which was kindly provided by DELO Industrial Adhesives (Germany). When uncured it has an infrared band at 1613 cm^{-1} and a new band at 1638 cm^{-1} after curing. For each measurement a background file was initially acquired after cleaning the ATR crystal, followed by a rapid series of measurements spanning before, during, and after curing.

The QCL used operates at 1593–1653 cm^{-1}. The spectrometer was set to a resolution of 4 cm^{-1} and the acquisition time was 1 ms, with a repetition rate of 40 Hz. Curing was triggered using a mercury lamp, via an optical fiber. After starting the measurement, the lamp is turned on to initiate the curing reaction and the resulting spectra are recorded as a time-series.

Results and Discussion

The raw spectra exhibit fringing, which is expected when using a laser-based instrument with an ATR prism. They are likely caused by a change in the refractive index of the sample (i.e. glue vs air) changing the penetration depth of the ATR accessory. Thanks to the

well-defined periodicity of the fringes, they could be removed with a simple Fourier transform (FT) filter.

Difference spectra were generated by subtracting a spectrum of the uncured glue (defined as a negative-time spectrum) from each of the subsequent positive-time spectra, as shown in Figure 1. A good signal-to-noise ratio is obtained even at short integration times demonstrating a good compatibility between the accessory and QCL system.

Negative bands show that a feature has disappeared, while positive bands show that a new feature has grown in. Here it is evident that not one, but two new bands grow in, at ***ca.*** 1638 and 1624 cm^{-1}, whilst the reactant band at ***ca.*** 1610 cm^{-1} decays. It should be noted that no FT filtering was applied to these spectra.

The kinetic traces at two points in the spectra (Figure 2), clearly show the time-point where the lamp was turned on. By fitting the growth and decay of these points, the kinetic properties of the curing process can be determined. In this case, a τ = 370 ms was found. The exact nature of the reaction is probably dependent on the sample thickness and irradiation power, which are parameters that were not fully controlled for these measurements.

Conclusion

Rapid measurements with high signal-to-noise ratios were performed on a sample of glue during curing, giving insight into processes that happen on a millisecond timescale. The High Temperature Golden Gate ATR was aligned without difficulty in the laser-based frequency comb spectrometer, providing fantastic spectral quality.

Faster measurements are possible from the point of view of the spectrometer; however, the present setup appears to be limited by the lamp turn-on time and brightness. A different curing source (e.g. a laser) should allow microsecond timescales to be reached. Here the accessory has only been used at room temperature, however further work conducted at higher temperatures would yield further insights into the reaction mechanism.

AN21-10

United Kingdom
sales@specac.co.uk

China
frank.li@specac.com

United States
sales@specac.com

Singapore
kamhar.woo@specac.com

UK: +44 (0)1689 892 902 | US: +1 866 726 1126

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www.specac.com

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