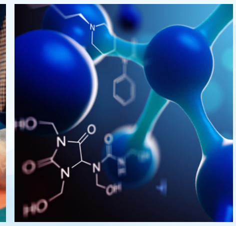
HORIBA

Raman

Macroscopic Raman Spectroscopy to Monitor Chemical Reactions and Polymerization/Curing



Technical Note
Polymers
RA TN-17

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Polymerization is defined as a chemical reaction in which two or more molecules called monomers combine to form larger molecules that contain repeating structural units. Monitoring chemical changes as a function of polymerization is important, as it can give insight into reaction kinetics and mechanisms. In addition, it enables the polymer engineer to confirm that they are manufacturing a material that will meet final chemical and physical requirements. One such technique that is suitable for monitoring polymerization reactions is macroscopic Raman spectroscopy, which is a light scattering technique that can provide real-time chemical information as the reaction is occurring. This technical note will show how the HORIBA MacroRAM™, a macroscopic Raman system, can be used along with the HORIBA Superhead™, to monitor and analyze a simple polymerization-curing reaction of a two-part epoxy.

Commercial, two-part, fast-curing Gorilla™ epoxy was deposited onto a stainless steel slide and mixed thoroughly for 20 seconds. After mixing, Raman measurements were acquired using the HORIBA Superhead, which was fiber-coupled to the HORIBA MacroRAM macroscopic Raman spectrometer. The Superhead is a non-contact probe with a 40 mm working distance, allowing for remote measurements of various samples, or for measurement of samples too large for the MacroRAM sample compartment. Measurements were acquired every 1 second for 14000 seconds using 785 nm excitation. It is important to note that the Superhead has a long (10 meter) fiber for measurements up to 30 feet away from the MacroRAM. The setup used is shown in Figure 1.

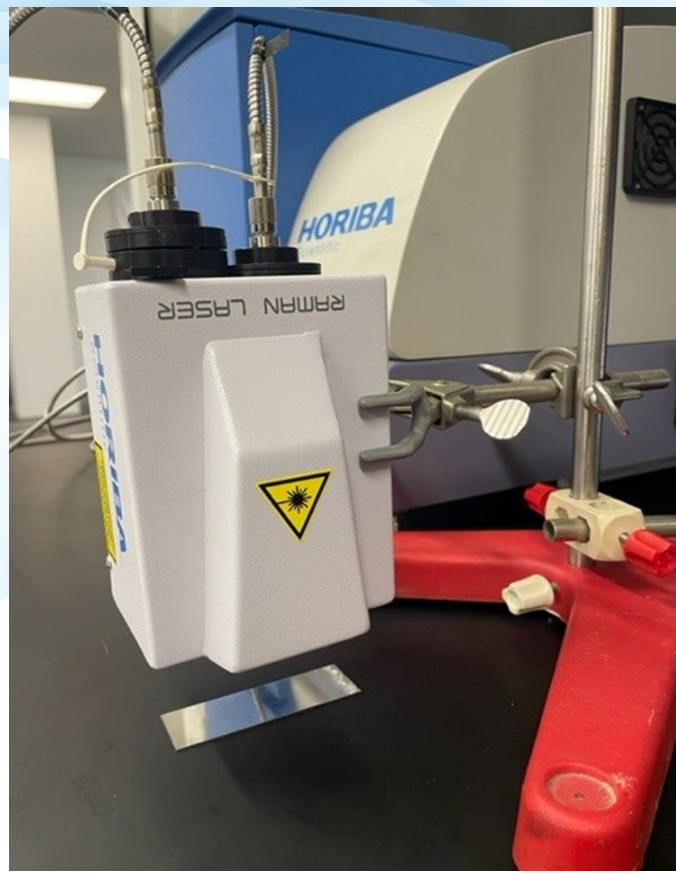

Figure 1: Setup used for acquiring Raman spectra.

After the measurements were complete, the initial spectrum just after mixing, as well as the final spectrum after curing, were extracted and observed for any noticeable differences.

These two spectra are shown below in Figure 2. From observing these spectra, there are clear differences in the relative intensities of the two bands between 1200 and 1300 cm^{-1} between the start and the finish of the reaction. There is also a noticeable drop in the band around 2577 cm^{-1}, which is indicative of the loss of the sulfhydryl group as a function of curing.

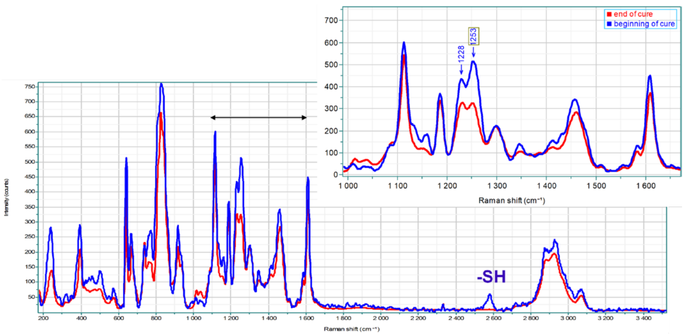

Figure 2: Spectrum acquired just after mixing (blue) and final spectrum acquired after curing (red). Changes are observed in the relative intensities of the bands between 1200 and 1300 cm^{-1}.

For further analysis, a Classical Least Squares (CLS) approach, using the start and end spectra as loadings, was taken in order to follow the reaction and tracked changes in the relative intensities of the two bands between 1200 and 1300 cm^{-1} over time. The results of this analysis are shown in Figure 3 for the entire measurement. The crossover point occurs around 420 seconds, which is about 7 minutes. As mentioned previously, this is a fast-curing epoxy, so 7 minutes is consistent with what is expected for fast curing.

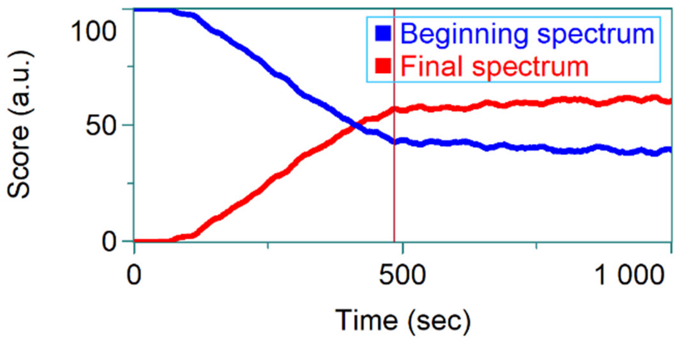

Figure 3: CLS results showing the change in relative intensities of the two bands between 1200 and 1300 cm^{-1} as a function of time. The crossover point, occurring around 7 minutes, is consistent with the fast-curing epoxy used for this measurement.

As shown, macroscopic Raman spectroscopy can easily be used for monitoring chemical changes over time for a polymerization or chemical reaction. These measurements help understand the reaction kinetics and mechanisms and can provide valuable insight into the reaction itself. The HORIBA MacroRAM is an ideal instrument for tracking chemical and polymerization reactions, as it has high sensitivity and spectral resolution. When coupled with a Superhead or other remote probe (e.g. touch/immersion), these measurements are easily made in either contact or non-contact mode outside of the sample measurement compartment.

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