

Real-Time Monitoring of Polymer Heat Curing By Diamond ATR Spectroscopy



Figure 1. The Meridian SplitPea with its Heated Diamond Sampling Plate and Temperature Controller.



Figure 2. The Heated Diamond Sampling Plate.

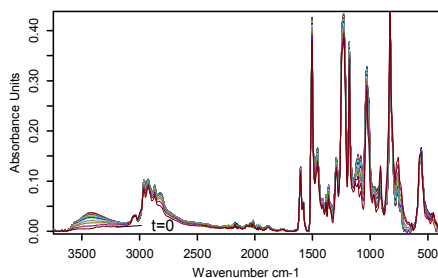


Figure 3. ATR Spectra of Master Bond epoxy while curing at 100°C. Spectra recorded every 30 seconds.

INTRODUCTION

Epoxies were commercially introduced in the early 1950's for the aerospace industry and are now widely used for manufacturing applications including commercial vehicles, electronics, inks and varnishes. Epoxies consist of two components, a resin and a hardener. These are tailored for specific properties such as adhesion, elasticity and hardness. For best performance, the two components are mixed and cured under controlled conditions.

Real-time methods of analyzing curing epoxies are important to determine the optimum conditions for a given epoxy, to ensure quality control and to better understand the underlying chemistry. Spectroscopic methods for these real-time measurements are not common, since many epoxies firmly adhere to the windows or crystals used for transmission or ATR measurements.

The introduction of the diamond ATR crystal now makes feasible the real-time monitoring of epoxy curing. Diamond is extremely hard, so the bonded epoxy can simply be scraped off. This paper examines the curing of an epoxy under controlled elevated temperatures in real-time using a new heated diamond ATR.

EXPERIMENTAL

Two commercial epoxies were examined: Master Bond Polymer System EP41S-4¹ and Araldite® 2014A/B². Each epoxy was cured at three different temperatures: 40°C, 70°C and 100°C. The curing process was spectroscopically monitored using FTIR ATR spectroscopy.

The FTIR measurements were recorded using the Harrick Meridian SplitPea (see Figure 1) installed in a Thermo Nexus spectrometer. The Meridian was equipped with a heated sampling plate with diamond ATR crystal (see Figure 2). The heater and K-type thermocouple of the heated sampling plate were connected to the Harrick Automatic Temperature Controller to regulate the temperature. This configuration is designed for operation up to 200°C.

The spectrometer was configured for data collection at 8 cm⁻¹ resolution and signal averaged over 32 scans. The background spectrum was measured on the clean, heated ATR crystal.

The Master Bond epoxy was mixed in the ratio recommended by the manufacturer. The Araldite epoxy came in a mixing dispenser which ensured the correct resin to hardener ratio. For each measurement, a drop of the mixed epoxy was

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placed on the center of the preheated ATR crystal.

Spectra were collected at even time intervals as the epoxy cured until no visible changes in the spectra were apparent. Time intervals of 15, 30 or 60 seconds were used, depending on the manufacturers' suggested cure times, at 40°C, 70°C and 100°C. When the measurement was complete, the epoxy was allowed to cool and was then scraped off the diamond ATR crystal using a hobby knife. This was done under magnification to view the small sampling area on top of the crystal more easily and to make sure the crystal was clean. The crystal was also rinsed with methyl ethyl ketone prior to the next measurement.

The collected spectra were converted to absorbance units and then baseline corrected. Several wavelengths were selected and the peak intensity as a function of time at those wavelengths was extracted from the collected spectra.

RESULTS AND DISCUSSION

Figures 3 and 4 show the spectra of the two epoxies curing at 100°C as a function of time. From the spectra, it is clear that the two epoxies have different compositions and that both epoxies have functional groups that change during the

curing process.

It is well-known³ that the cross-linking of epoxy resins involves the opening of the epoxy or oxirane ring. When the resin and hardener come in contact with each other, the amine group in the hardener reacts with the epoxy ring in the resin, breaking the ring structure and forming C-N and O-H bonds. The epoxy ring has ring breathing vibrations in the 950-815 cm^{-1} region⁴ which have been used to follow the curing process³. The spectra in Figures 3 and 4 clearly show decreases in the band near 912 cm^{-1} , due to breaking of the ring, and increases in the broad O-H stretching band near 3400 cm^{-1} , as expected.

Figure 5 shows the changes in peak intensities over time as the Araldite epoxy cures at three different temperatures. All three sets of curves clearly show the decreasing absorption due to the epoxy ring vibration at 912 cm^{-1} (in red) and the increasing absorption of the O-H band (blue), as expected. The band at 912 cm^{-1} decreases more quickly than the O-H band increases, indicating that the reaction is a multi-step reaction.

In addition, Figure 5 also clearly shows that the curing reaction proceeds more slowly

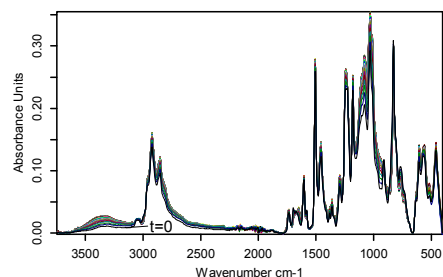


Figure 4. ATR Spectra of Araldite epoxy while curing at 100°C. Spectra recorded every 15 seconds.

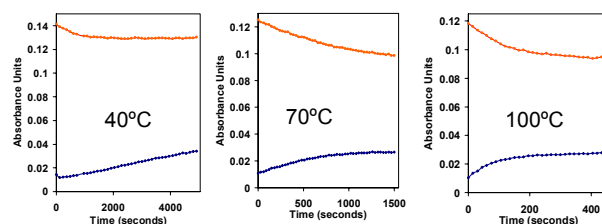


Figure 5. The change in absorbance as a function of cure time for Araldite epoxy at 912.0 cm^{-1} (red) and 3342 cm^{-1} (blue).

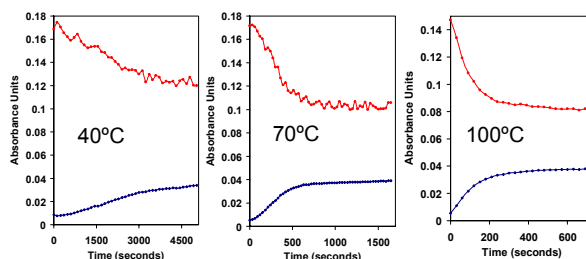


Figure 6. The change in absorbance as a function of cure time for Master Bond Epoxy at 910.6 cm^{-1} (red) and 3421.0 cm^{-1} (blue).



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at lower temperatures. Note that the initial absorbance value for the three measurements is slightly lower with higher temperatures. This indicates that the curing process has begun in the short time interval between placing the sample on the ATR crystal and initiating data collection.

Figure 6 shows the changes in band strength as the Master Bond epoxy is cured at 40°C, 70°C, and 100°C. As with the measurements for the Araldite epoxy, the data clearly show the decreasing absorption due to the epoxy ring vibration (in red) and the increasing absorption of the O-H band (blue). The differing rates of changes of these two bands indicate that the Master Bond curing process is also a multi-step reaction.

Note that the epoxy peaks and O-H peaks are shifted slightly relative to those observed for the Araldite epoxy. This is due to the difference in the rest of the polymer mixture. The Master Bond epoxy also has a stronger initial intensity of the epoxy ring vibration band, indicating either a less constrained vibration or a higher concentration of epoxy rings in the overall structure.

Overall, the 40°C and 70°C data are noisier for the Master Bond epoxy. This may be due to incomplete mixing of the epoxy or a resolution effect from

data collection.

CONCLUSION

FT-IR ATR spectroscopy is a straightforward method for monitoring the curing of epoxies in real-time. The use of a diamond ATR crystal simplifies the removal of the epoxy once curing is complete and a heated crystal holder makes it possible for the curing process to be evaluated at different temperatures as a function of time.

REFERENCES

¹Master Bond Inc., Hackensack NJ 07601, www.masterbond.com.

²Registered trademark of Huntsman Advanced Materials Americas Inc., Los Angeles, CA 90039, www.araldite.com.

³Stuart, Barbara H., *Infrared Spectroscopy: fundamentals and applications* (John Wiley and Sons, 2004).

⁴N. B. Clothup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed. (Academic Press, 1990).



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