

Following Epoxy Cure with Macroscopic Raman Analysis



Application Note
Polymerization
RA92

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Because Raman spectroscopy provides information on molecular composition, it is an ideal tool for studying chemical reactions. In particular, it has been used successfully for studying polymerization where the change often involves the disappearance of a carbon double bond ($>C=C<$) as the polymer chain is lengthened by the addition of a monomeric group. In this note we will be looking at epoxy cure which is a reaction that causes cross-linking during the polymerization process to form a solid with fixed three-dimensional geometry.

The epoxy chemical group is a 3-atom ring, with 2 carbon atoms and one oxygen.

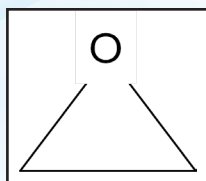


Figure 1: The core epoxy ring that is essential in creating the three-dimensional networks.

During the reaction the ring is opened at the oxygen atom providing a reactive hydroxyl (OH) group. The box below shows the schemes proposed in [1] in which there is also an amine group involved in the reactions. These authors suggest that the three-dimensional network involves reactions with the amine groups.

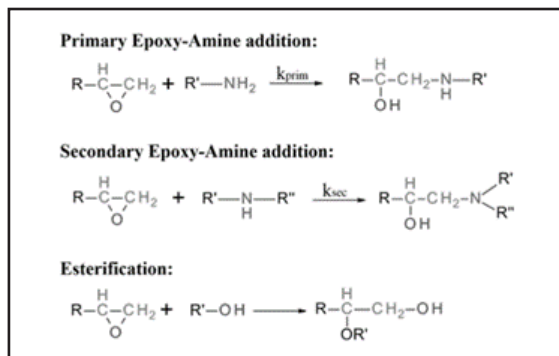


Figure 2: Generic epoxy reactions involving amine groups, as proposed by Kempf, Dippel and Arnolds [1]

In this study we followed the spectral changes of Gorilla Glue™ epoxy as a function of curing time after mixing. On the Gorilla website the epoxy resin is listed as bis-[4-(2,3-epoxipropoxy) phenyl] propane or bisphenol A diglycidyl ether resin (DGEBA), a resin that is common to many commercial epoxy formulations. The structure of DGEBA is shown in Figure 3a.

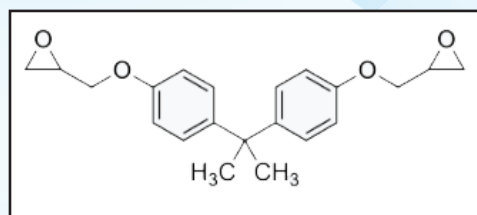


Figure 3a: Structure of bisphenol A diglycidyl ether resin (DGEBA).

The hardener contains an ether of 2-hydroxy-3-mercaptopropyl, and 2,2,4 (or 2,4,4)-trimethylhexane-1,6-diamine (HMP-t-PGE). Their structures are shown in Figure 3b.

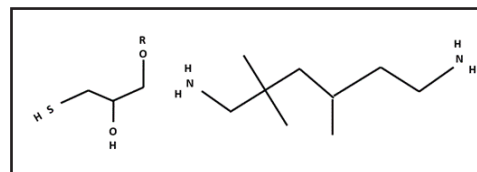


Figure 3b: Structures of 2 components in the hardener, a 2-hydroxy-3-mercaptopropyl ether on the left, and 2,2,4-trimethylhexane-1,6-diamine.

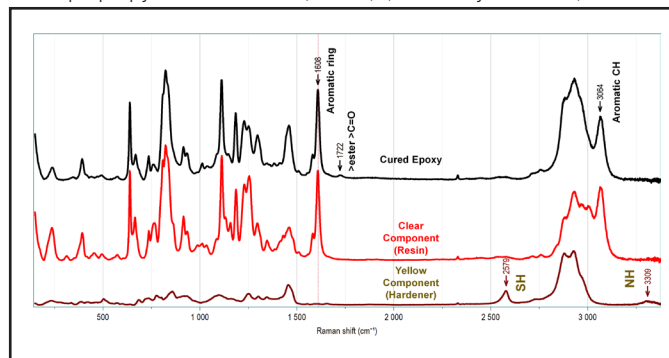


Figure 4: Raman spectra, from top to bottom, of the cured Gorilla epoxy, and the two starting components, the resin and the hardener.

Figure 4 shows the Raman spectra of the resin, the hardener and the cured epoxy. The first thing that you might observe is that the spectrum of the cured epoxy is dominated by the spectrum of the resin. In the figure I have labelled bands that are clearly associated with the aromatic ring and the aromatic CH. The spectral lines of the hardener are substantially broader and relative to the CH region (which is plotted with similar intensities) and the fingerprint bands are ten times weaker than those of the resin/cured epoxy. That, of course, is because the spectrum of the resin and cured epoxy are dominated by the aromatic species which experience pre-resonance enhancement. But there are two features of the hardener that are worthy of note. One is the presence of a band near 2580 cm^{-1} which is assigned to an -SH stretch, and a weak broad band near 3300 cm^{-1} which is assigned to an >NH species. The earlier discussion of the hardener did say that amines are frequently used in the hardener. And the presence of the SH band is consistent with the sulfhydryl group in the hardener. In addition, the final epoxy (measured several days after mixing) shows the presence of a weak band that is assigned to an ester carbonyl ($>\text{C}=\text{O}$), a species that is predicted to be present by the reactions proposed by Figure 2. Note that this spectrum had been taken a few days after the epoxy had been mixed; the carbonyl band is not seen in the early hours after mixing.

In preparation for making the time-series measurements, a small amount of the two components of the commercial epoxy were squeezed out of the dual syringe, mixed for about 20 sec, and then mounted under the SuperHead™, a non-contact Raman fiber probe, for immediate initiation of measurements. The spectra, acquired once per second over a 14,400 sec period (4 hours), are shown in Figure 5. The figure indicates the presence of the sulfhydryl stretch at 2580 cm^{-1} , and also indicates the spectral region between 1230 and 1280 cm^{-1} of the epoxy ring that has been associated with epoxy cure [2]. Curiously, there is little evidence of the amine group that in the pure starting material had about half the intensity of the sulfhydryl.

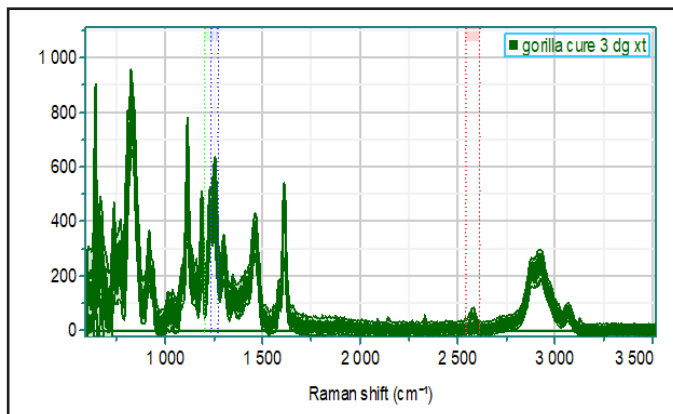


Figure 5: Overlay of all the spectra taken during the 4 hour cure of the Gorilla epoxy, after truncation of the low frequency region, and background subtraction.

Using the simplest multivariate analysis (MVA) technique, one can extract the spectra at the beginning of the

measurements and at the end, and use these spectra to follow the changes with the CLS (Classical Least Squares) algorithm. The results of these operations are shown in the next figures.

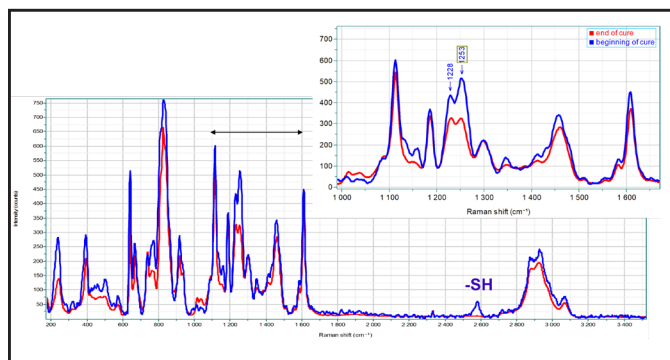


Figure 6: Raman spectra extracted from the 4 hour cure cycle; the blue spectrum with the -SH band was extracted during the beginning of the cure, while the red spectrum was extracted at the end. The bands between 1210 and 1275 cm^{-1} drop intensity during the cure and their relative intensities change because of chemical changes occurring during the cure.

When inspecting the CLS factors, you can see the -SH of the sulfhydryl group, as well as the significant change in the relative intensities of the epoxy bands between 1200 and 1280 cm^{-1} . Each spectrum in the time series is decomposed into a sum of these two spectra and displayed in Figure 7. While the relative contributions of the two component spectra continue to change over the 4 hour period, the biggest changes occur during the first 8.5 min when the sulfhydryl group is consumed in the reaction. These results demonstrate clearly how this epoxy formulation is a “fast cure.”

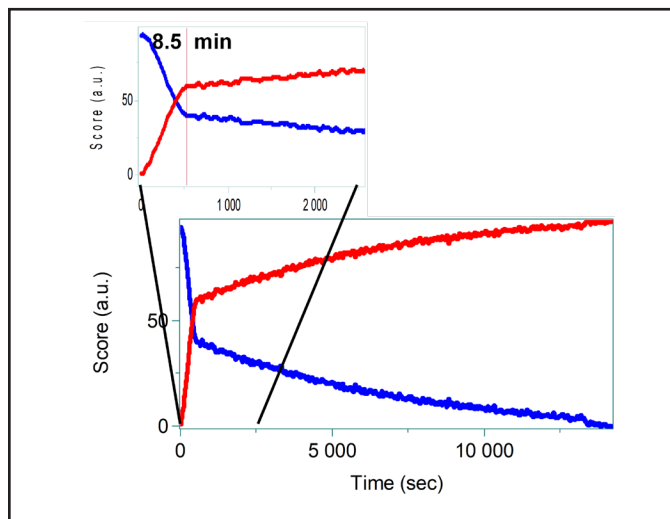


Figure 7: Evolution of the changes of the epoxy during cure, as evidenced by spectral changes documented by CLS modelling.

¹ M. Kempf, B. Dippel and O. Arnolds, Hyphenation of Rheology and Raman Spectroscopy – Investigation of epoxy curing mechanism and polyethylene crystallization, Ann Trans Nordic Rheology Soc 25 181-187 2017
² H. Vaskova and V. Kresalek, Raman spectroscopy of epoxy resin crosslinking, Recent Researches in Automatic Control, conference 2011

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