Analysis of Cured Epoxy Adhesives by ATR / FTIR

Introduction

Epoxy adhesives are available in many different formulations depending upon the application for this important industrial and consumer material. The epoxy adhesive may be designed for maximum adhesion, specialized elasticity, resistance to high temperature or cryogenic usage, as electrical or thermal conductors and for many other applications. If an epoxy adhesive fails to meet specification for its designed application, we will want to determine if the chemical composition of the cured material is correct and then to investigate the source of any differences. Many tools are required for the complete analysis of an epoxy adhesive including measurements of physical and compositional characteristics. One of the instruments which provide a relatively fast and efficient technology for chemical analysis is attenuated total reflectance (ATR) used with a Fourier transform infrared spectrometer (FTIR).

ATR sampling with an FTIR is widely used for this analysis because a sample is readily measured within a minute or less by placing a small chip of the cured epoxy onto the ATR crystal and then applying pressure to achieve full contact with the ATR crystal.

Figure 1. MIRacle ATR Accessory with High Pressure Clamp

Instrumentation

A PIKE MIRacle™ ATR accessory equipped with a single reflection diamond crystal was used for all of the spectra shown in this work[1]. The MIRacle accessory was fitted with a high pressure clamp providing over 10,000 psi of pressure to the cured epoxy samples and ensuring intimate contact with the diamond ATR crystal. The diamond crystal is chosen for this work because of its hardness and scratch resistance. Furthermore, the diamond ATR crystal provides greater depth of penetration of the IR beam to generate a stronger absorbance spectrum[2]. The MIRacle ATR (shown in Figure 1) is a unique optical design providing high throughput (typically 40% or more) of the IR beam and further providing the ability to collect high quality spectral data within a minute or less[3]. The FTIR spectrometer is equipped with KBr beamsplitter, DLaTGS detector and is sealed and desiccated to minimized purge effects. All spectra were collected at 4 cm-1 spectral resolution using 1 minute sample and 1 minute background collection times.

Differentiating Epoxy Samples

A high-performance ATR accessory can easily

differentiate the composition of epoxy samples. This is demonstrated in the spectral data for cured epoxy samples from 3 different manufacturers shown in Figure 2. Samples A and B are 5 minute cure, rigid epoxy samples. As seen in Figure 2, the spectra of these samples are very similar. Sample C is a flexible epoxy and its spectrum is quite different from those of samples A and B.

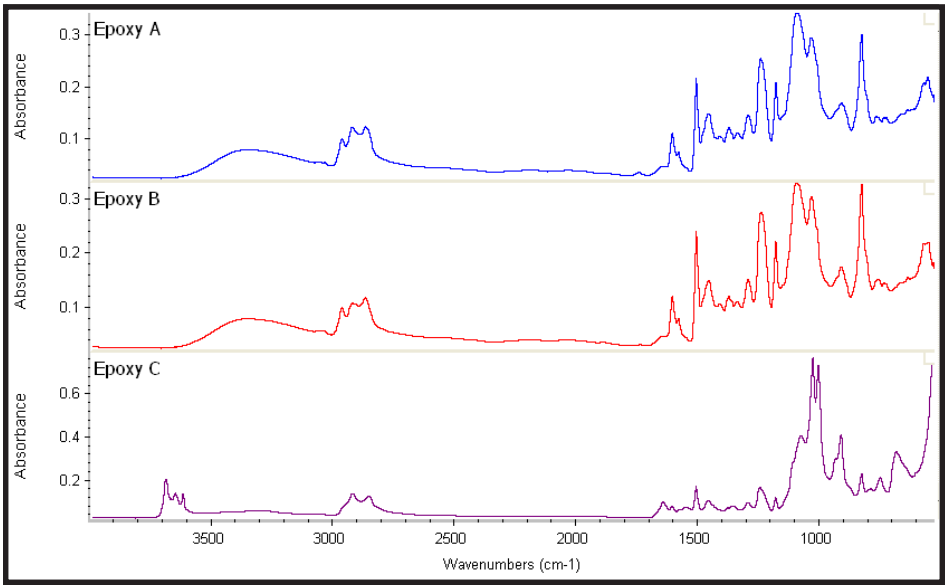

Figure 2: ATR / FTIR Spectra for Cured Epoxy Samples from 3 Different Manufacturers.

Looking closely at the spectral comparisons of samples A and B we can see significant differences especially in the fingerprint region shown in Figure 3. These spectra are scaled to equalize the intensity of the IR absorbance band at 1098 cm-1.

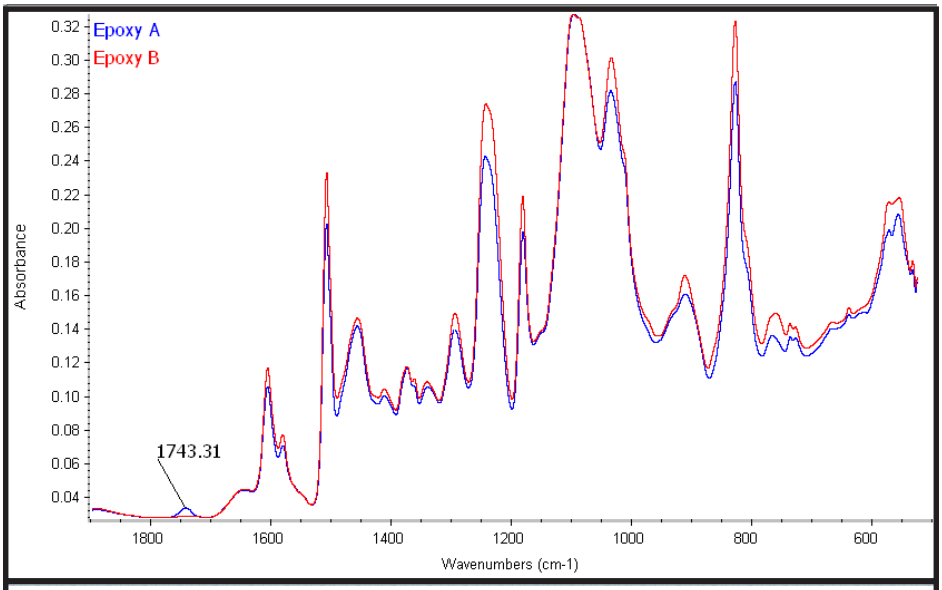

Figure 3: Expanded Fingerprint Region for Epoxy Samples A and B.

It is readily apparent that other IR absorbance bands at 1607, 1508, 1243, 1182, 1034, and 828 cm-1 are present in differing ratios relative to the scaled absorbance at 1098 cm-1. The absorbance band ratio difference indicates similar composition but differing concentrations of the components for samples A and B. Sample A also shows an absorbance band at 1743 cm-1 which is not present in sample B indicating that sample B has a unique ingredient. This unique component and the differing concentrations of other components will most likely affect the performance of the epoxy adhesive relative to characteristics such as hardness, adhesion, solvent resistance and many other features.

Solving Epoxy Adhesive Performance Issues

When the performance of an epoxy adhesive does not meet its desired characteristics, it is often useful to begin with ATR to investigate the source of the problem, especially if it is suspected that formulation is a source of the problem. Within a few minutes a comparison of composition can be made by using the MIRacle ATR accessory.

An example of this determination is shown in the ATR spectra in Figure 4 for cured epoxy adhesives A and B. One of the 2 epoxy samples does not perform according to its specification for hardness. Analysis of the 2 samples using the MIRacle ATR with diamond crystal plate shows that the ATR spectra are similar, however, readily differentiable. Now the question remains "What is the composition difference between samples A and B?"

The result of a spectral subtraction of Sample A and Sample B is shown in Figure 5.

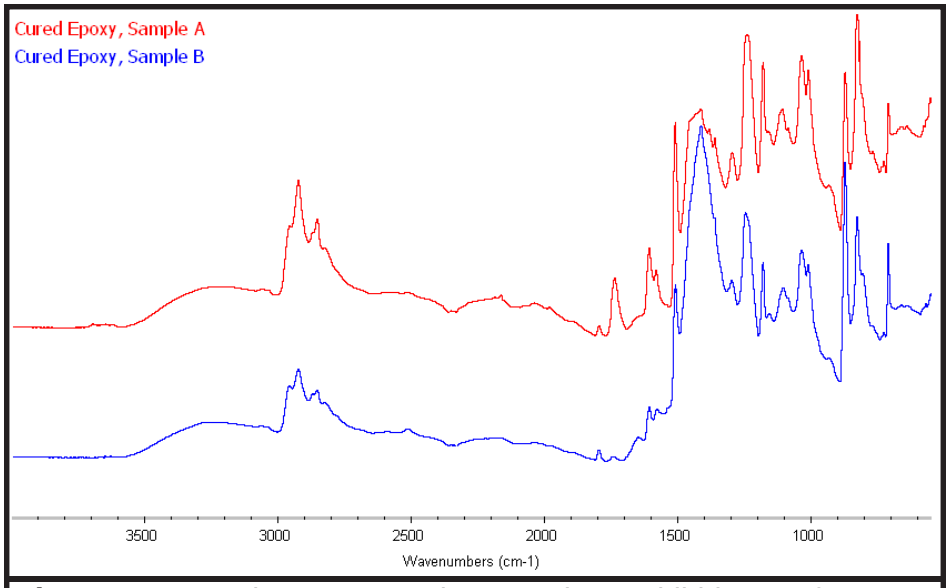

Figure 4. Cured Epoxy Samples A and B, Exhibiting Performance Differences.

Positive bands in the subtraction result represent components more rich in Sample A. Spectral search of the positive bands using the PIKE Technologies ATR Spectral Data Base of Polymers and Polymer additives indicate this to be epoxy resin. Negative bands in the subtraction result represent components at higher concentration in Sample B. This spectrum is multiplied by -1.0 and searched again using the same ATR spectral data base and the residue is identified as calcium carbonate. Our preliminary finding is that the formulation of the epoxy adhesives is different in epoxy resin content and calcium carbonate content.

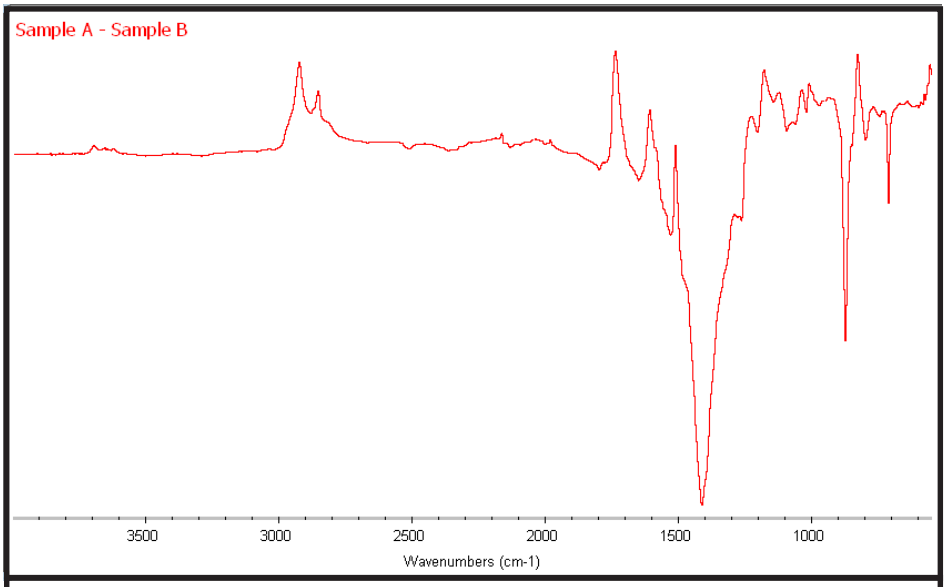

Figure 5. Subtraction Result for Cured Epoxy Samples A Minus B.

Summary

Cured epoxy samples are easily and quickly measured by FTIR using a MIRacle ATR equipped with a diamond crystal and high pressure clamp. Epoxy samples of differing composition, from different suppliers or those demonstrating differences in performance can be readily distinguished using this sampling technology. Cured epoxy samples which do not meet their performance specification may be analyzed by ATR / FTIR to help determine the source of the problem.

References:

1. MIRacle ATR, Product Data Sheet, PIKE Technologies, 2005.
2. ATR Theory and Applications, PIKE Technologies, 2004.
3. United States Patents 5,965,889 & 6,128,075, Philip R. Brierley, PIKE Technologies, 1999, 2000.