

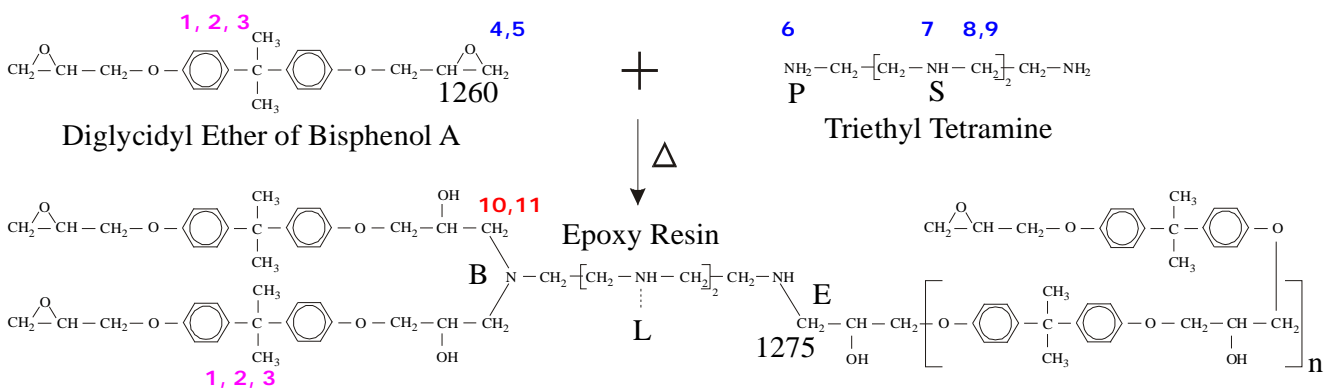
Composite Applications

RTA Application Note # 03

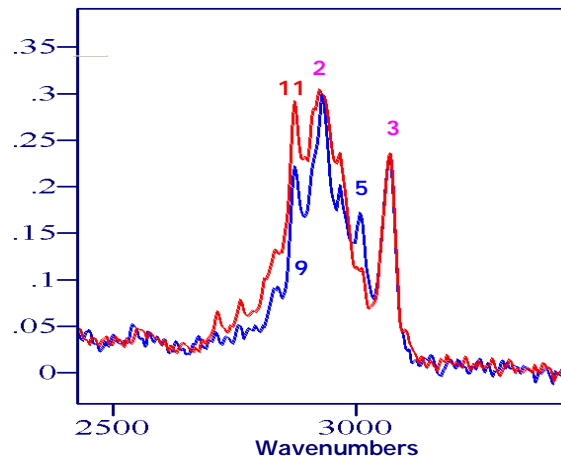
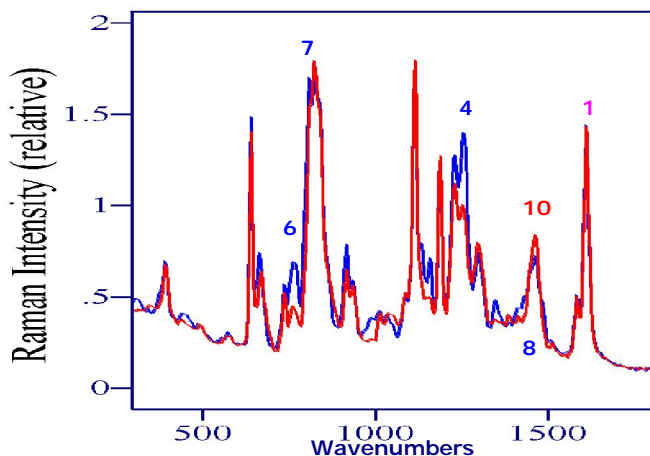
The **Industrial Raman Analyzer** has been designed specifically for operation in demanding production facilities and is ideal for numerous composite manufacturing applications, such as Epoxy Cure Kinetics, Monitoring and Control.

Producing an epoxy-based composite with the desired mechanical properties requires precise control of a heat schedule. Temperature, not only controls cure rates, but also reaction pathways. Low cure temperatures favor chain-extension producing flexible composites, while high temperatures favor cross-linking producing rigid composites. The **Industrial Raman Analyzer** has been used to monitor these molecular changes in real-time, determine activation energies, as well as monitor composite cure in an autoclave.

One of the most common epoxies used in composites is formed by curing diglycidyl ether of bisphenol A (DGEBA) by triethyltetramine (TETA). The basic reaction involves an amine reacting with the epoxy ring. Joining DGEBA and TETA molecules together through the primary amine end groups (P) results in simple chain extension (E), while joining these molecules through the secondary amine mid-chain groups (S) results in cross-linking (L). The former reaction generates a new secondary amine that can also react with DGEBA. This is often referred to as branching (B). The first reaction also produces a hydroxyl group that has long been considered as being ideally located to aid (catalyze) the branching reaction.



We used the **Industrial Raman Analyzer** to monitor many reactions, including the curing of DGEBA and TETA. The high sensitivity (40- second acquisition time), wavenumber stability (0.1 cm^{-1}), and high resolution (4 cm^{-1}), allowed identifying and analyzing numerous bands for this reaction from start to finish. The phenyl ring stretch, phenyl-hydrogen stretch, and methyl stretches (1,2,3) maintain constant intensity. The oxirane ring and its methylene stretch (4,5) decrease as the ring is opened by reaction. The primary and mid-chain secondary amines (6,7) also decrease as they react with this ring. The methylene bridge, wag and stretching modes (10,11) formed by the reaction increase in intensity. They are coincident with the existing TETA methylene bridge, wag and stretching modes (8,9). (Blue is uncured, $t=0$, red is cured, $t = 60$ minutes.)



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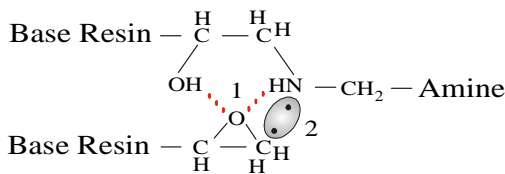
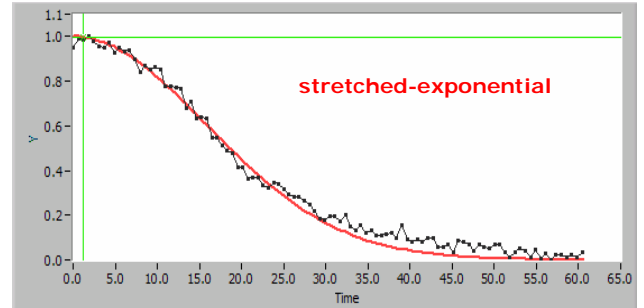
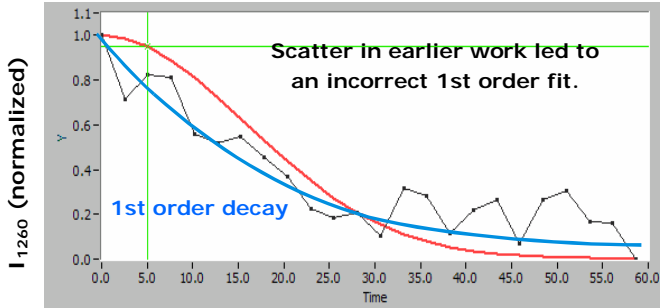
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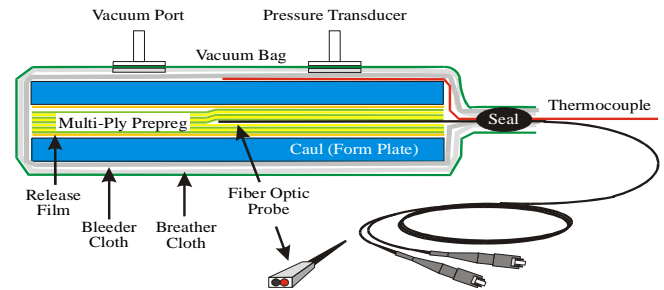
Previous we and other researchers used the 1260 cm⁻¹ epoxy band (I₁₂₆₀) to monitor this reaction and determine kinetics. However, lack of sensitivity for our measurements, and lack of intensity stability for others' measurements led to the incorrect conclusion of a simple exponential decay reaction. The combined sensitivity (40-sec time resolution), intensity and wavenumber stability of the **Industrial Raman Analyzer** allowed determining the correct equation that describes the reaction:

$$I_{1260} = 1 - e^{-kt^2}$$

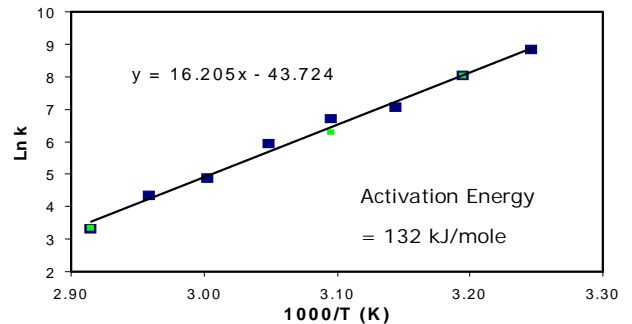
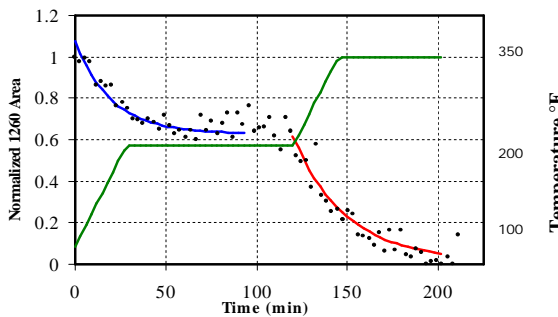
where k is the rate constant and t is time. The use of time squared in the exponential has been referred to as a "stretched-exponential", often found in auto-catalytic reactions. This rate equation supports the proposed formation of a termolecular intermediate in which the hydroxyl group does indeed catalyze the reaction of the newly formed secondary amine.



Termolecular Intermediate



Employing the knowledge of reaction mechanisms and rates, we used the **Industrial Raman Analyzer** to monitor cure of an epoxy-based composite in an industrial autoclave. A two level temperature schedule was followed per manufacturer's recommendations. A simple side-by-side fiber optic probe was inserted through a thermocouple well, into a vacuum bag, and between the plies of a multilayered composite. Analysis of the rate of disappearance of the epoxy band at 1260 cm⁻¹ confirmed primary amine reactions at the lower temperature and secondary amine reactions at the higher temperature.



Once the correct rate equation is found, the reaction can be performed at several temperatures to determine the activation energy of the reaction. We reacted DGEBA with TETA at 30 to 65 °C at 5 degree increments. A plot of the Ln k (rate constants) vs 1000/T (K, absolute temperature) yields a slope of 16.2, which when multiplied by 8.3144 yields the activation energy in kJ/mole. Figure includes lab (■) and field (■) data.

Selected Publications:

"Development of a phase diagram to control composite manufacturing using Raman spectroscopy", *SPIE*, 5272, 19-29 (2004)

"Characterization of polymer composites during autoclave manufacturing by FT-Raman spectroscopy" *SPIE*, 4201, 103-111 (2001)

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