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13. ABSTRACT *(Maximum 200 words)*

We have proposed to investigate Raman scattering of epoxies and polyimides in interfacial regions using fiber optic evanescent spectroscopy. These data will be analyzed with chemometric multivariate statistics to provide an understanding of the curing and bonding process in real composites within 0.1 μm resolution and observe inhomogeneities in the curing process at high optical resolution.

During this funding period, we have obtained IR and Raman spectra of test matrix materials, made assignments of molecular vibrations, performed laboratory measurements of the curing of the bulk matrices at different temperatures, and begun a principal component analysis of the curing process. Construction of a micro-Raman system was also begun.

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Report

Fiber-Optic Raman and Micro-Raman Measurements of Bonding Agents at Interfaces During the Curing Process

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A. Statement of the Problem Studied

The strength of a joint or processed composite depends to a great extent on the physical properties of interfaces and the bulk matrix. These physical properties depend on chemical composition and bonding, characteristics that are readily observable with vibrational spectroscopy. Raman scattering is uniquely applicable to this type of analysis.

We have proposed to investigate Raman scattering of epoxies and polyimides in interfacial regions using fiber optic evanescent spectroscopy. These data will be analyzed with chemometric multivariate statistics to provide an understanding of the curing and bonding process in real composites within 0.1 μm of interfaces. This will be complemented by micro-Raman measurements that will determine the spatial extent of the interface with 1 μm resolution and observe inhomogeneities in the curing process at high optical resolution. This project combines the efforts of two research groups: those of Professor Myrick (experimental measurements) and of Professor Morgan (statistical analysis).

B. Most Important Results

During the First Year of this three-year project, the proposed plan of work called for the following:

Year 1:

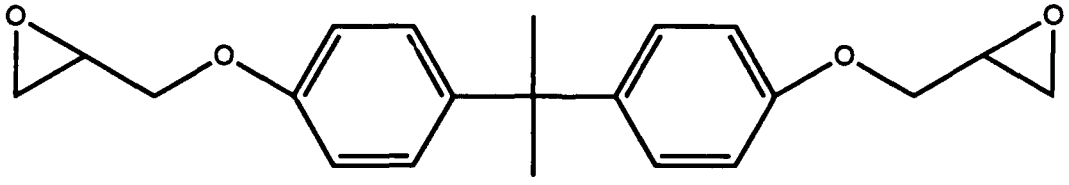
- IR & Raman spectra acquired for raw matrix components
- assignment of vibrations of materials
- Laboratory measurements of curing of bulk matrices at different temperatures
- principal component analysis (statistical)
- Evanescent Raman spectra of raw matrix components
- construction of micro-Raman system

This project was divided into four funding periods, the first being 15 July 1992 to 30 September 1992. This corresponds to the first 2.5 months of the first year of the project. During this period, several of the objectives of the first year have been met.

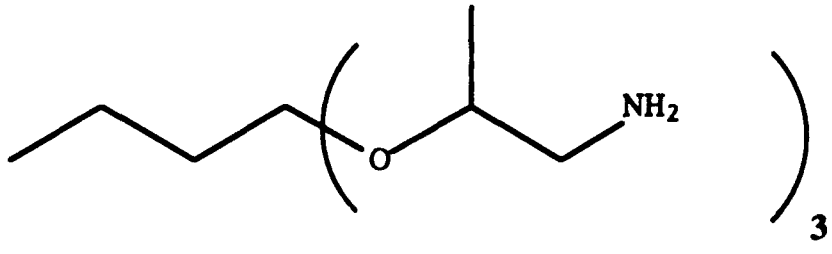
Raman of Raw matrix components

A test polymer system was chosen for this project. This is the DER332/Jeffamine T-403 epoxy cure system, a two-component cure system.

For the epoxy, structures of the two components are shown below in Figure 1.



Diglycidyl ether of bisphenol-A (DGEBA)



Polyoxypropylene
(Jeffamine T-403)

Figure 1: Chemical Structures of DER 332 and Jeffamine T-403

Figure 2 shows Raman spectra acquired for the epoxy resin (DGEBA), which dominates the spectra of the epoxy.

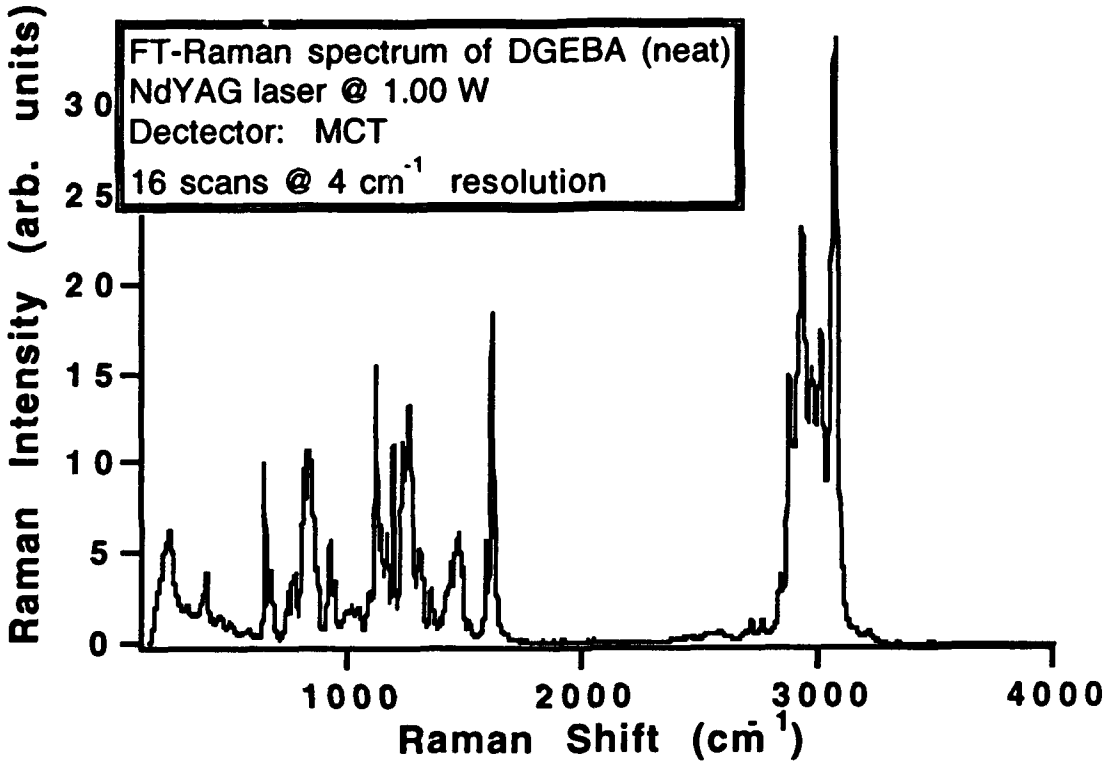
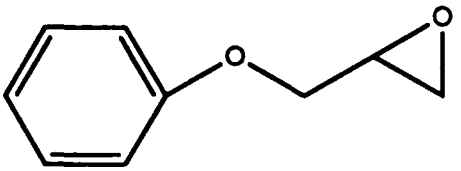


Figure 2: Raman spectrum of DER332 showing signature and C-H stretching region.

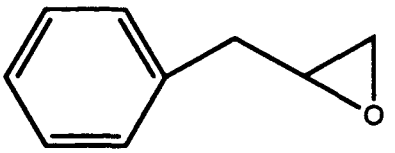
Assignment of Vibrations

Vibrational assignments for the epoxy resin of Figure 1 were obtained by studies of model compounds, ab initio calculations, and comparison with other literature. Table I gives rough assignments for the epoxy components.

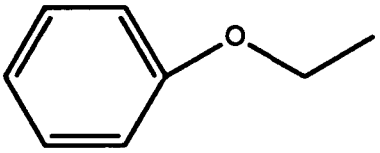
Model compounds studied are shown below in Figure 3.



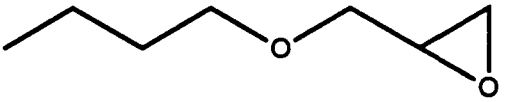
(±)-1,2-Epoxy-3-phenoxypropane



(±)-(2,3-epoxypropyl)benzene



Phenetole



Butyl gylcidyl ether

Figure 3: Model Compounds Used to Generate Vibrational Assignments for DER332

Table 1. Infrared and Raman band assignments for DGEBA. s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, str = stretch, and def = deformation.

IR	Raman	Assignments
1298m	1272w	C-O str. (ether groups)[d]
1248s	----	C-O str. (ether groups) and C-C str.[a,d]
----	1232s	C-O str. and phenolic C_4-O_2 str.[a]
----	1211s	Epoxy group?
1184s	1186s	CH_3/gem-dimethyl def. and C_6-$C_{7/8}$ str.[a,d]
1157vw	1140vw	----
----	1113s	Aromatic C-H str. and in-plane def.[a-d]
1065vw	----	Phenolic C_4-O_2 str.[e]
1036s	----	Substituted aromatic[c,d,e]
1010sh	----	Substituted aromatic[c,d,e]
970w	----	----
916m	924sh	Epoxy group[a,d,e]
862sh	908m	Epoxy group[a,d,e]
806s	819s	Substituted aromatic[c,d,e]
772m	762m	C_3-C_2 skeletal[a]
----	736sh	C_3-C_2 skeletal[a]
----	667m	Aromatic C-H out-of-plane def.[b-e]
----	641s	Aromatic C-H out-of-plane def.[b-e]

[a]This paper. [b]Reference 1. [c]Reference 2. [d]Reference 3. [e]Reference 4.

Laboratory Measurements of Curing

The curing of the epoxy system has been studied using FT-Raman spectroscopy. Figure 4 shows spectra of the epoxy cure system before and after curing.

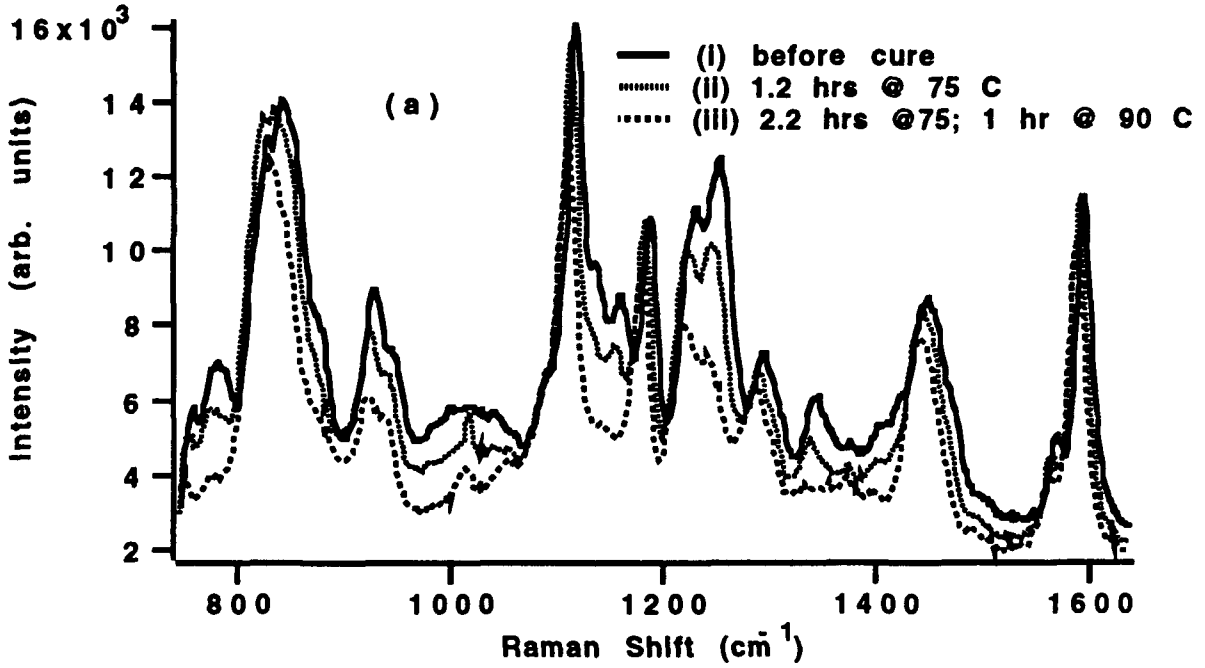


Figure 4: Raman spectra before during and after curing of DER332/Jeffamine T-403.

Principal Component Analysis (statistical)

A basis set for statistical analysis has been generated, but results are not yet available.

Construction of a Micro-Raman System

Materials for the construction of this system have been acquired and designs drawn. Construction is expected to begin in Spring, 1993.

C. List of Publications and Technical Reports

At present, no publications have resulted from this work. Two articles are currently nearing completion with submission expected in January, 1993. Two presentations have been accepted at the Pittsburg Conference in Analytical Chemistry, scheduled for March, 1993.

D. Participating Scientific Personnel, Advanced Degrees earned
The personnel involved in this research are:

Dr. M.L. Myrick, PI
Dr. S.L. Morgan, Co-PI
Dr. John Cooper, post-doctoral associate
Katherine Chike, research assistant
Jeffrey Aust, research assistant
Melinda Hale, research assistant

Because of the brevity of this work, no degrees have yet resulted.

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