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Modulated FT-Raman Fiber-Optic Spectroscopy: A Technique for Remotely Monitoring High-Temperature Reactions in Real-Time

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Summary of Research Report

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Summary of Research

The goal of the research conducted under NASA grant NGT-1-52124 was to investigate methods for monitoring cure reactions in real-time in an autoclave. This is of particular importance to NASA Langley Research Center because polyimides were proposed for use in the High Speed Civil Transport (HSCT) program. Understanding the cure chemistry behind the polyimides would allow for intelligent processing of the composites made from their use. This work has led to two publications in peer-reviewed journals and a patent. The journal articles are listed as Appendix A which is on the instrument design of the research and Appendix B which is on the cure chemistry. Also, a patent has been awarded for the instrumental design developed under this grant which is given as Appendix C.

There has been a significant amount of research directed at developing methods for monitoring cure reactions in real-time within the autoclave. The various research efforts can be categorized as methods providing either direct chemical bonding information or methods that provide indirect chemical bonding information. Methods falling into the latter category are fluorescence, dielectric loss, ultrasonic and similar type methods. Correlation of such measurements with the underlying chemistry is often quite difficult since these techniques do not allow monitoring of the curing chemistry which is ultimately responsible for material properties. Direct methods such as vibrational spectroscopy, however, can often be easily correlated with the underlying chemistry of a reaction. Such methods include Raman spectroscopy, mid-IR absorbance, and near-IR absorbance. With the recent advances in fiber-optics, these spectroscopic techniques can be applied to remote on-line monitoring.

For the research conducted under NGT-1-52124, Raman spectroscopy was chosen because it provides highly specific bonding information via sharp spectral peaks. A distinct advantage of Raman spectroscopy over IR is the ability to use inexpensive and efficient communication grade fiber optics for remote sensing. Due to the low attenuation of these fibers from the visible to the near infrared, spectral information can be transmitted over very long distances. Since Raman is a scattering technique, it is not prone to the baseline shift problems encountered with absorbance spectroscopies and sampling is greatly simplified. When combined with fiber optic sampling, Raman spectroscopy provides a way of remotely obtaining direct thermoset chemical bonding information in real-time within the autoclave. As an example from earlier research conducted here by Lori Byers, Figure 1 displays the real-time fiber-optic Raman spectra acquired during the autoclave curing of a bisphenol cyanate ester thermoset. The temperature program for this cure cycle is currently used in commercial autoclaves. As shown in Figure 2, the in-situ Raman data indicates that the commercial program exceeds

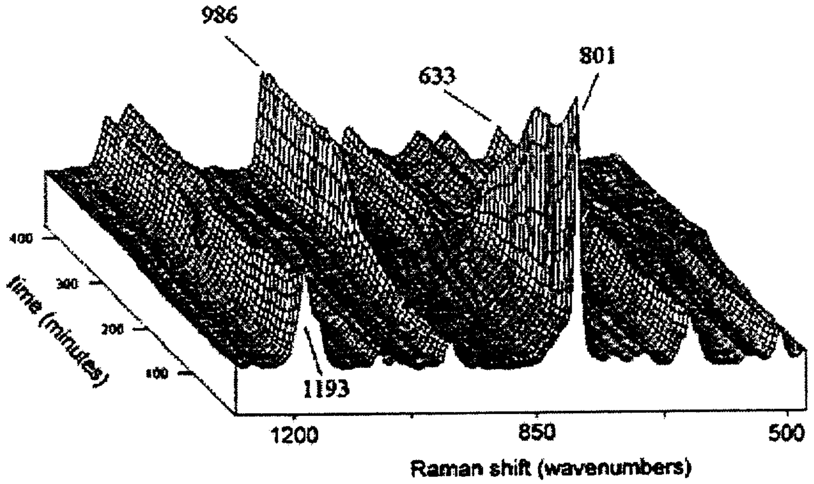

Figure 1: Real-Time in-situ Raman spectra of a thermoset cure.

the 100% cure time by two hours. The Raman spectra for this cure cycle were acquired using a near-IR laser at 805 nm.

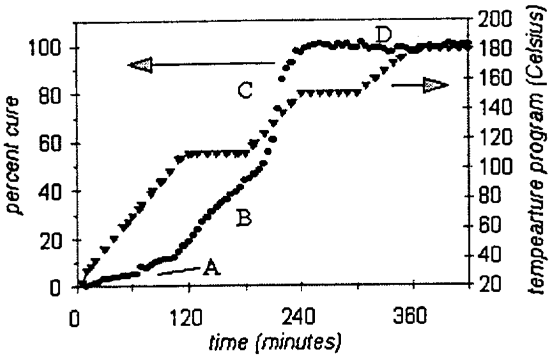

Figure 2: Raman predicted %cure and autoclave thermal program. The last leg of the thermal program takes place after 100% cure is obtained

Although this is practical for a few low molecular weight epoxies and triazines, the vast majority of advanced thermosets (including the polyimides proposed for use in the HSCT) give rise to an intense fluorescent background when excited at such short wavelengths (Figure 3). An alternative approach is to use a long wavelength laser (1.064 μm) and a Fourier Transform (FT) Raman spectrometer which has been the main focus of the research conducted under NGT-1-52124 . Unfortunately, FT-Raman spectrometers are large, expensive (typical cost exceeds $100,000) and due to the use of an interferometer, are not stable in industrial environments. Some of the research conducted under NGT-1-52124 has led to the development of a low cost viable alternative to FT-Raman spectroscopy with 1.064 μm excitation. To date, no such commercial instrument exists. However, recent advances in near-IR sensor arrays and near-IR lasers now make this approach feasible

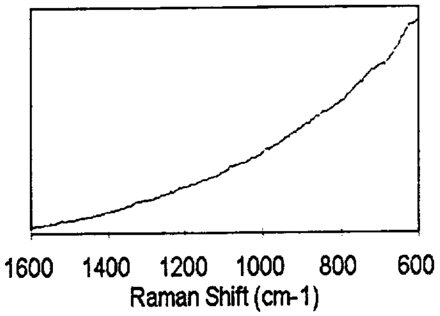

Figure 3: Raman spectrum of a 4-PPEB polyimide thermoset acquired using 852 nm excitation. Fluorescence background overwhelms Raman signals

and highly cost effective. As an example, in Figure 4 (top spectrum) is shown the Raman spectrum of the of a thermoset taken with a the prototype instrument developed under NGT-1-52124 compared to spectra taken with a FT-Raman spectrometer at different resolutions. This spectrum was acquired using a 1.064 μm Nd:YAG laser for excitation and an f/3 off-axis Fastie-Ebert spectrograph with a 256-element InGaAs array for detection. A remote fiber-optic probe was used to acquire the spectrum. As shown, the Raman spectrum is free from fluorescent background.

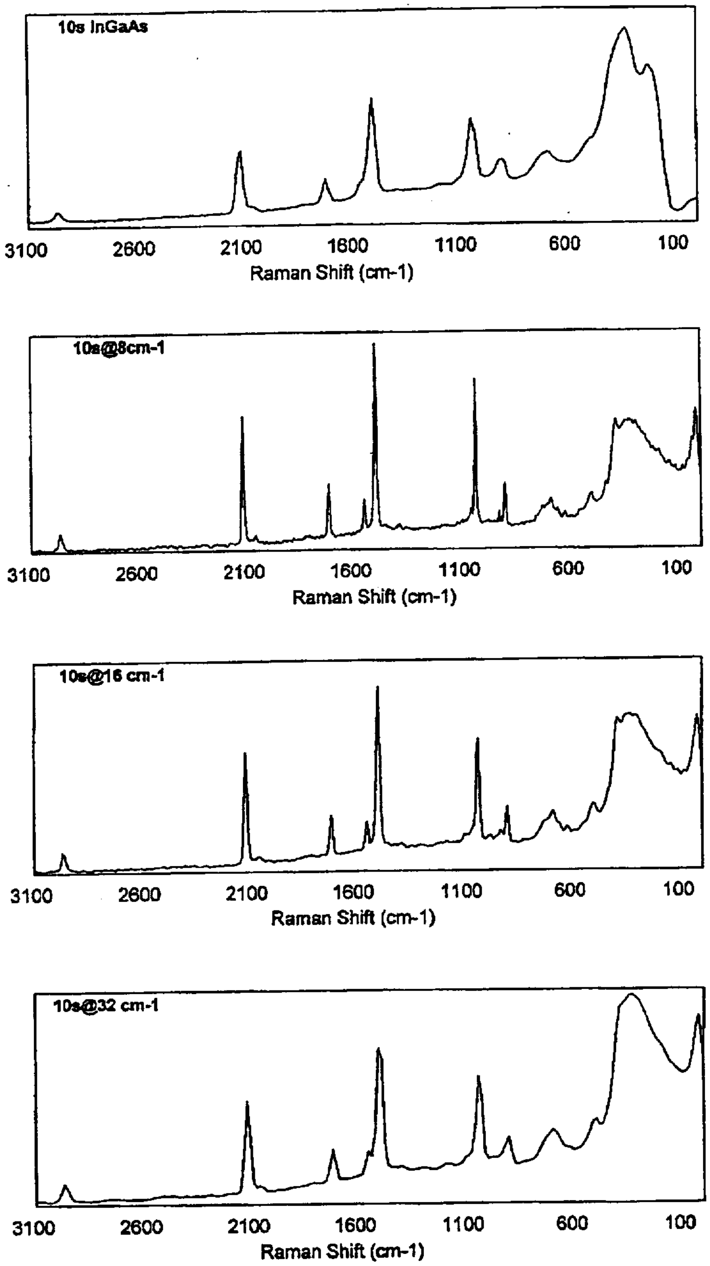

Figure 4: Dispersive (top) and FT-Raman (bottom three) spectra of a thermoset using 1064nm excitation.

Appendix A