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EVALUATION OF EPOXY COMPOSITES USING PHOTOACOUSTIC FOURIER TRANSFORM INFRARED SPECTROSCOPY

JAMES M. SLOAN POLYMER RESEARCH DIVISION

July 1986

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AREA & WORK UNIT NUMBERS
D/A Project: ITI61101A91
12. REPORT DATE
July 1986
13. NUMBER OF PAGES
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Unclassified
154. DECLASSIFICATION/DOWNGRADING
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SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

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ABSTRACT

Fourier transform infrared spectroscopy (FT-IR) using a photoacoustic sampling cell has been used to obtain high quality infrared spectra of various fiber-reinforced epoxy composites and the corresponding resin matrixes.

Photoacoustic spectroscopy (PAS) offers the advantages of having little or no sample preparation for high quality spectra to be obtained and no alignment of the infrared incident beam is necessary. This makes PAS an ideal sampling method for fin-field testing of composite laminates. The spectra revealed information on the degree of cure of the resin system by monitoring the 915 cm⁻¹ absorption band and the type of reinforcement material used (glass or Kevlar)

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INTRODUCTION

Fiber-reinforced epoxy resin composite systems are currently in use in military structure applications where their increased materials strength-to-weight ratio advantage can be utilized. Applications include bridging structures, weapon components, and aircraft components. While engineering applications of composite materials have advanced very rapidly in recent years, nondestructive testing methods for these materials have not progressed as rapidly. An effort has been made at MTL to develop a nondestructive method for monitoring the degree of cure in fiber-reinforced epoxy composite laminates.

In recent years, a different type of spectroscopic technique known as photoacoustic spectroscopy (PAS) has been found very useful for the study of spectra of certain types of samples.¹ PAS employs the photoacoustic effect in which the absorption of modulated electromagnetic radiation is converted into thermal energy by nonradiative processes. The thermal energy is then transferred to the surrounding gas and produces a pressure wave or acoustic wave in the cell. This acoustic wave is ' then detected by a microphone.

The strength of the PAS signal (I_{PAS}) is the product of the number of photons incident on the sample and the energy per photon and a function of the thermal diffusivity. The thermal diffusivity depends on the particular modulated frequency of the interferometer incident on the sample. The PAS signal would, therefore, be larger for higher frequencies than for lower frequencies if the number of photons incident in the sample remained constant. Thus, early spectroscopic work performed using the PAS technique was primarily directed toward the UV - visible region of the electromagnetic spectrum.

Buse and Bullemer² were the first investigators to employ this technique with a commercial Fourier transform infrared spectrometer. The authors compared normal infrared spectra of methanol vapor to that of PAS. Rockley³ used the technique to obtain a highly quality spectrum of polystyrene. Low⁴ followed this by adapting the technique for use with a dispersive infrared spectrometer. It is clear, that the high throughput and multiplex advantages of FT-IR spectrometers offer the potential to make FT-IR PAS a routine, analytical technique for qualitative analysis.

The advantages of this technique over the more widely used KBr pellet technique for the study of composite are twofold.^{5,6} First, grinding of composite laminate into a powder of small particles and then proceeding to pressurize the KBr/powder mixture would alter the structure of the coupling agent and break and create bonds, thus forming new species not at all characteristic of the original composite laminate. Secondly, KBr (or any other alkali salt) is extremely hydrophilic. This would drastically alter the amount of water present in the composite. This effect would be manifested as a removal of water from the composite (present naturally in the sample) into the salt. The major advantages of PAS over other sampling techni-7 ques are the absence of sample preparation and the maintenance of sample integrity.

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In this paper we will report the use of this technique to the study of fiberreinforced epoxy resin composite laminates used in a variety of military structural applications.

EXPERIMENTAL

All infrared spectra were obtained on a Digilab Model 10M Fourier transform infrared spectrometer. Each spectrum was recorded in double precision at a resolution of 8 cm⁻¹ for a total of 4096 scans. A reference helium-neon laser was used to calibrate the interferometer to allow a frequency accuracy of ± 5 cm⁻¹. Data manipulations were done on a Nova 2 minicomputer from Data General.

A Digilab photoacoustic accessory was employed for all measurements. The moving mirror in the Michelson interferometer was translated with a velocity to 0.16 cm/s, which yielded modulation frequencies between 130 and 1300 Hz which gave a spectral range of 400 cm⁻¹ to 4000 cm⁻¹. Drierite (Xenia, OH) was used in the sample compartment of the PAS accessory to remove residual water vapor in the cell. Figure 1 shows a schematic drawing of the sampling accessory.

Samples were either ground in a Spex freezer mill (Spex Industries, Edison, NJ) to obtain powders or cut up into chunks and placed in the cell. A comparison of spectra taken with chunks and after grinding revealed that no differences in the quality of the spectra could be detected. Carbon black (Cabot Corp., Billerica, MA) was used as a reference material.



Ipas ⁼ Number of photons x energy per photon x f(thermal diffusivity of sample).



RESULTS AND DISCUSSION

State of Cure

Figures 2 and 3 show a DGEBA/anhydride resin system cured and post cured and analyzed using the PAS accessory. This system does not contain any glass fibers. The spectral differences are indicative of the state of cure of the resin system.



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Figure 2. PAS-IR spectrum of cured DGEBA/anhydride resin system.



Figure 3. PAS-IR spectrum of post-cured DGEBA/anhydride resin system.

Figure 2 represents a normal cure for the resin system as recommended by the manufacturer. The spectrum is well resolved with many of the features of the cure clearly seen. Absorption bands at 1511 cm⁻¹ and 1600 cm⁻¹ remain invariant with reaction and can be used as internal standards. The remaining bands are characteristic of the curing reaction. Absorption bands can be seen at 3008 cm⁻¹ [assigned to the v_s (CH₂) of the epoxide ring] and at 910 cm⁻¹ (epoxide group). They are residual epoxide bands, indicating that complete cure has not taken place. It is interesting that no absorptions are visible at 1858 cm⁻¹ and 1780 cm⁻¹ [v_s (C=0) and v_s (C=0) of the anhydride group, respectively]. This indicates that all the anhydride has reacted. Absorptions characteristic of the curing reaction can be seen by the formation of the ester group and nearby structures at 2963 cm⁻¹ [v_s (CH₂)] adjacent to the ester group, at 1750 cm⁻¹ [v(c=0) ester] and at 1250 cm⁻¹ [v(c=0) of the ester].⁸

8. ANTOON, M., Ph. D. Thesis, Case Western Reserve University, 1980, Appendix I.

Figure 3 shows the DGEBA/anhydride system after post cure. In this spectrum all the same absorption bands are present as in the previous spectrum with the exception of the 915 cm⁻¹ and 3008 cm⁻¹ bands of the epoxide group. These bands are not seen due to the complete disappearance of the epoxide functionalities, indicating a complete cure cycle has occurred.

Glass Fiber-Reinforced Epoxy Laminate

Spectra were obtained of various types of glass-epoxy laminates in an attempt to elucidate the structures at the glass-coupling agent-epoxy interface. Spectral subtraction was used to eliminate the strong spectral features of the glass. Figure 4 shows the PAS-IR spectrum of the E-glass mat with a coupling agent deposited on its surface. The coupling is known to be Y-amino-propyltriethoxysilane (Y-APS). Absent from the spectrum are infrared maxima at 1595 cm⁻¹ (NH₂ wag) and 1474 cm⁻¹ (CH₂ wag) of the Y-APS, as well as an absorption band at 830 cm⁻¹. These IR bands are²all well known IR absorption bands of Y-APS.



Figure 4. PAS-IR spectrum of E-glass mat with coupling agent deposited along surface.

It becomes clear that no IR absorbances due to the Y-APS can be detected. It can be assumed that the concentration of Y-APS on the glass mat is beyond the detection limits of the photoacoustic technique. It is approximated that the Y-APS is present in concentration levels, from 0.1% to 1.5% by weight. It is interesting to note that other IR sampling methods have been reported that are able to detect the Y-APS at these concentration levels.⁹,10

Figure 5 shows a DGEBA/anhydride resin system cured with glass. The spectrum of the glass has been subtracted so only the spectrum of the resin system appears. It appears the laminate is completely cured, as no 910 cm⁻¹ absorption band can be detected. In Figure 3, no absorptions are visible at 1858 cm⁻¹ and 1780 cm⁻¹ [v_s (c=0) and v_{AS} (c=0) of the anhydride, respectively]. This indicates all the anhydride curing agent has been reaction during the cure cycle. Formation of cross-linking C-O groups can be detected by the IR absorption bands at 1250 cm⁻¹. Figure 5 essentially shows the same spectral features as Figure 3.

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Figure 5. PAS-IR spectrum of a DGEBA/anhydride resin system with the spectrum of the glass subtracted.

Kevlar-Reinforced Laminates

Kevlar-reinforced composite laminates offer a different challenge to the PAS-IR technique. Kevlar is an extremely strong absorber of infrared radiation. In fact, it has a tendency to dominate the IR spectrum so much that the infrared spectrum of the resin is hardly seen. Figure 6 shows a spectrum of an amine-cured Epon 828 resin system reinforced with Kevlar. The strong absorption bands at 3325 cm⁻¹ (asymmetric OH stretch) and 3420 cm⁻¹ (symmetric OH stretch) can be seen at the high frequency end of the spectrum. More Kevlar absorptions appear at 1540 cm⁻¹ and 1640 cm⁻¹ (amide I and II bands), 1300 cm⁻¹, 1400 cm⁻¹, and 1110 cm⁻¹. These appear at strong, well defined IR absorptions. Infrared intensities of the resin system can be seen although they are not as pronounced as the intensities of the Kevlar. Absorptions in the 3100 cm⁻¹ - 2800 cm⁻¹ are characteristic of the aromatic CH stretches and aliphatic CH of the epoxy resin. Infrared maxima at 1510 cm⁻¹ and 1605 cm⁻¹ due to the aromatic ring stretch can clearly be seen. Absorptions in the 1150 cm⁻¹ - 1250 cm⁻¹ can be attributed to the C-0 crosslinking group. No infrared absorptions appear at 910 cm⁻¹ indicating a complete cure has occurred.

Dicy-Cured Epoxy Laminate

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Figure 7 shows a spectrum of SP 250 resin system accelerated with Monuron, a chlorinated accelerator. The glass has not been subtracted as evidenced by the infrared absorption at 1100 cm⁻¹ and a broad absorption at 3500 cm⁻¹. Here again absorptions at 1510 cm⁻¹ and 1605 cm⁻¹ are present. These are due to the aromatic ring stretches of the resin. Evidence for an incomplete cure is present by the small IR band at 910 cm⁻¹. This represents residual epoxide groups. The strong doublet at approximately 2240 cm⁻¹ and 2260 cm⁻¹ is due to unused Dicy. There appears to be a considerable amount of Dicy present in the laminate.



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Figure 7. PAS-IR spectrum of SP 250 composite laminate.

CONCLUSIONS

Photoacoustic infrared spectroscopy has been used to evaluate various types of reinforced epoxy laminates. Information on the degree of cure and the type of reinforcing material has been derived. It has also been concluded that no information could be obtained on the nature of the glass-coupling agent-epoxy interface. The concentration level of the coupling agent (Y-APS) is too small to be detected by this technique.

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The photoacoustic infrared spectroscopic technique does, however, offer the advantage of being an easy and reproducible method for obtaining high quality infrared spectra of the epoxy laminates. This case of use makes it an ideal sampling method for possible "in-field" testing of composite laminates. No. of Copies To 1 Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301 Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1145 1 ATTN: SLCIS-IM-TL Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145 2 ATTN: DTIC-FDAC 1 Metals and Ceramics Information Center, Battelle Columbus Laboratories, 505 King Avenue, Columbus, OH 43201 Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211 1 ATTN: Information Processing Office Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333 1 ATTN: AMCLD Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005 1 ATTN: AMXSY-MP, H. Cohen Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703 1 ATTN: AMDSD-L AMDSD-E 1 Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35898 1 ATTN: AMSMI-RKP, J. Wright, Bldg. /574 AMSMI-TB Redstone Scientific Information Center 4 AMSMI-RLM 1 1 Technical Library Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801 2 ATTN: Technical Library 1 AMDAR-SCM, J. D. Corrie AMDAR-QAC-E ł t AMDAR-LCA, Mr. Harry E. Pebly, Jr., PLASTEC, Director Commander, U.S. Army Natick Research and Development Center, Natick, MA 01760 1 ATTN: Technical Library Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703 1 ATTN: Technical Document Center Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090 1 ATTN: AMSTA-ZSK AMSTA-UL, Technical Library 2 Commander, White Sands Missile Range, NM 88002 1 ATTN: STEWS-WS-VT President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307 I ATTN: Library Director, U.S. Army Ballistic Research Laboratory, Aberdeen Poving Ground, MD 21005 1 ATTN: AMDAR-TSB-S (STINFO) Commander, Dugway Proving Ground, Dugway, UT 84022 1 ATTN: Technical Library, Technical Information Division

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