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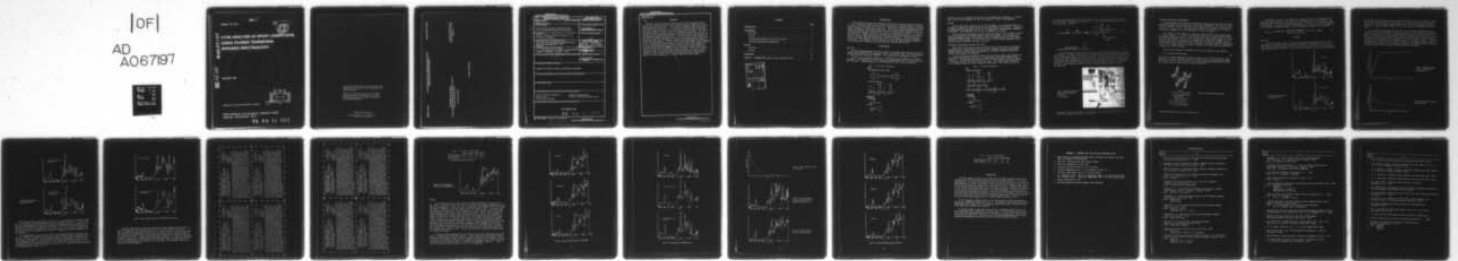
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NOV 78 J F SPROUSE, B M HALPIN, R E SACHER
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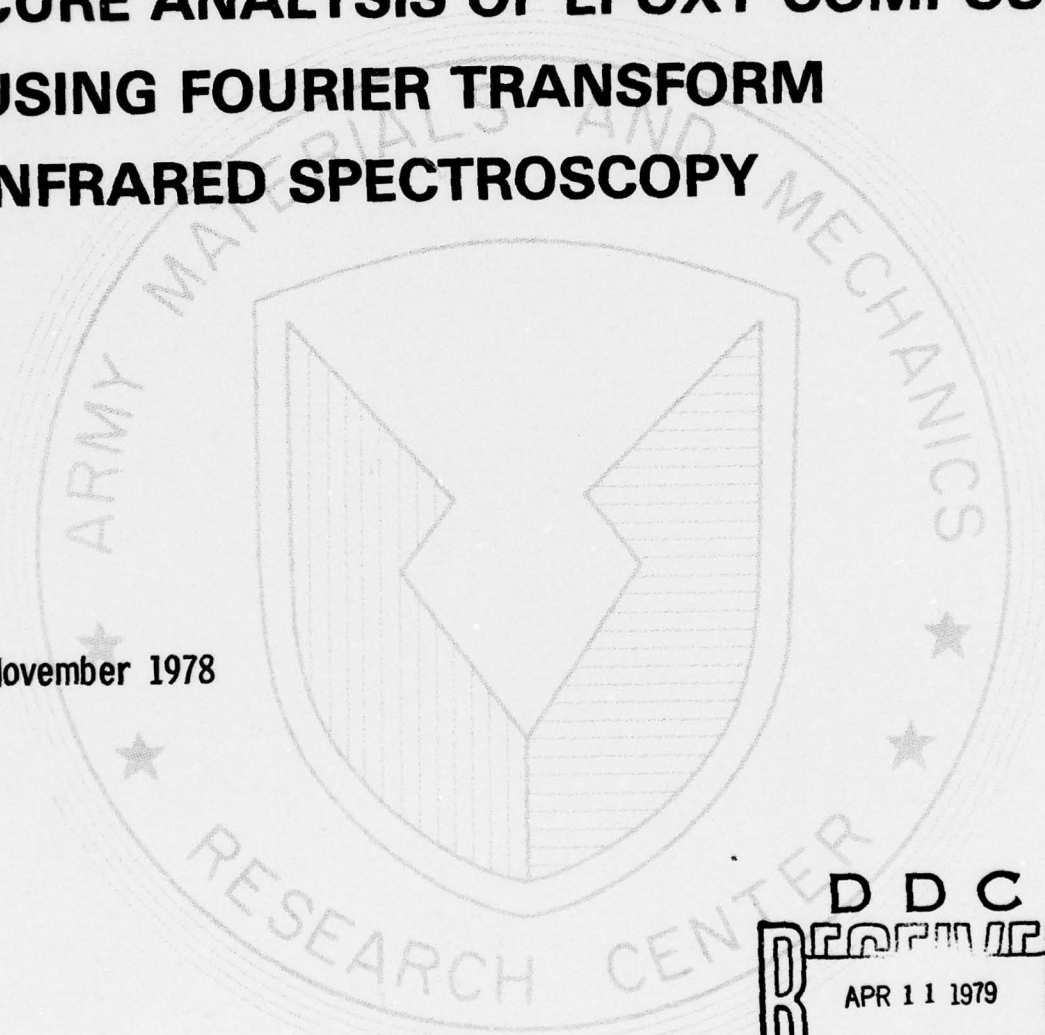
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CURE ANALYSIS OF EPOXY COMPOSITES USING FOURIER TRANSFORM INFRARED SPECTROSCOPY



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CURE ANALYSIS OF EPOXY COMPOSITES USING FOURIER
TRANSFORM INFRARED SPECTROSCOPY

Sprouse, Halpin, and Sacher

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ABSTRACT

Fourier transform infrared spectroscopy (FT-IR) has been used to measure the extent of cure in fiber-reinforced epoxy composites and the corresponding resin matrixes. Two sampling techniques have been used to study the curing processes: (1) thin films of neat resin held between salt plates and (2) internal reflectance spectroscopy (IRS). Thin films have been studied by curing them in a temperature-controlled cell that allowed the same temperature program to be followed that was used in the corresponding composite fabrication. Infrared spectra were recorded at short time intervals throughout the cure cycle and the results were used to measure extent of cure based on epoxide ring absorbance at approximately 915 wave numbers. Internal reflectance measurements were performed on the corresponding composite materials and results were compared with the thin film measurements. The two techniques had a high degree of correlation and clearly demonstrated the thin film studies were characteristic of the cure of multi-ply composite panels. The thin film measurements offer an excellent means for optimizing cure cycles in the laboratory and FT-IR/IRS offers a nondestructive means of performing extent of cure measurements in a plant fabrication environment.

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INTRODUCTION

Fiber-reinforced epoxy resin composite systems are currently being considered for use in military structural applications where their increased material strength-to-weight ratio advantage can be utilized. Applications include bridging structures, weapon components, and aircraft components. While the engineering applications of composite materials have advanced very rapidly in recent years, nondestructive testing methods for following the materials have not progressed as rapidly. An effort has been made at AMMRC to develop a nondestructive testing method for following the state of cure in fiber-reinforced epoxy composite materials. The technique uses Fourier transform infrared spectroscopy (FT-IR) with internal reflection sampling techniques. Two commercial resin formulations have been studied under different curing conditions, Reliable Manufacturing's RAC 7250 and 3M's SP 250.

EXPERIMENTAL

RAC 7250

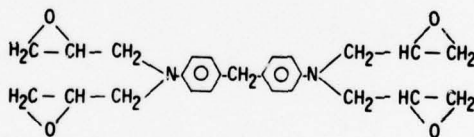
Reliable Manufacturing's RAC 7250 system is a tetraglycidyl methylene dianiline (TGMDA) based system with dicyandiamide (DICY) curing agent and a 3,4-dichlorophenyl-1,1-dimethylurea accelerator (DIURON). The formulation is summarized in Table 1.

The RAC 7250 system was obtained as a prepreg with three different fiberglass materials. The composition of the prepreg was approximately 30% by weight resin and 70% glass. During production of the prepreg the resin cure was partially

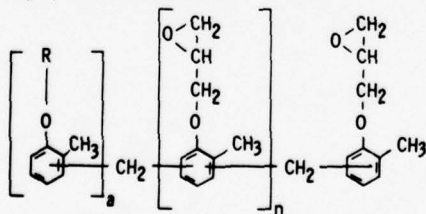
Table 1. RAC 7250 MAIN COMPONENTS

Resins

1. Tetraglycidyl(methylene Dianiline (TGMDA)

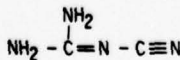


2. Epoxy Cresol Novolac (ECN)

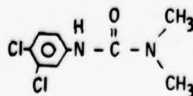


Curing Agents

1. Dicyandiamide



2. DIURON



advanced to aid in subsequent processing of the prepreg into laminates. A typical 250 F (127 C) cure procedure for RAC 7250 prepreg is given in the Appendix.

SP 250

The SP 250 system, manufactured by the 3M Company, is a diglycidyl ether of bisphenol A (DGEBA) and epoxy cresol Novolac (ECN) based resin system. It also has a dicyandiamide curing agent but uses a 4-chlorophenyl-1,1-dimethylurea (MONURON) accelerator. The formulation for SP 250 is summarized in Table 2.

The SP 250 glass-reinforced prepreg system also consists of 30 weight percent resin formulation and 70 weight percent reinforcing fibers. The production of composite laminates from SP 250 prepreg would be accomplished in the same manner as from RAC 7250 prepreg. SP 250 is also a 250 F (127 C) cured composite and an identical cure to the RAC 7250 cycle is used.

Infrared Cure Studies of Resin Thin Films

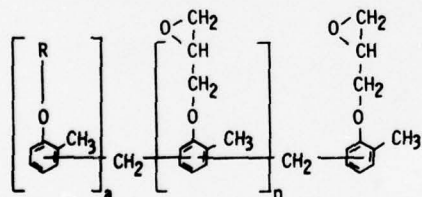
Thin films of the RAC 7250 and SP 250 neat resins were cured in the sample compartment of a Digilab Model FTS-10M Fourier transform infrared spectrometer. Infrared spectra of the resins were measured at selected intervals during the thermal cure program (see Appendix).

The cure data were measured by placing a thin film of neat resin between two salt plates and mounting the plates in a temperature-controlled sample holder (Figure 1). An infrared spectrum from 3800 to 450 wave numbers was then measured at 1-minute intervals while the resin was cured. The spectra were measured at 4 wave number resolution using triangular apodization. The extent of cure was

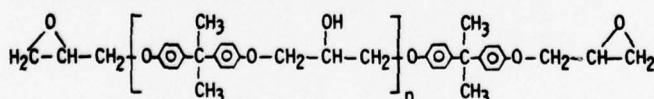
Table 2. SP 250 MAIN COMPONENTS

Resins

1. Epoxy Cresol Novolac (ECN)

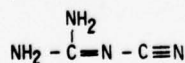


2. Diglycidyl Ether of Bisphenol A (DGEBA)

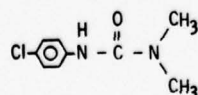


Curing Agents

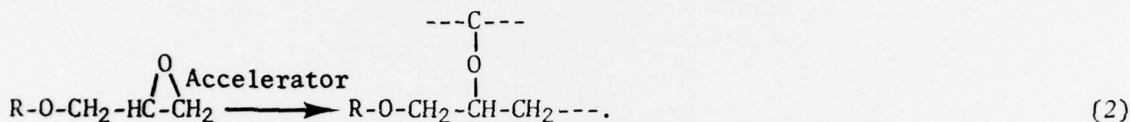
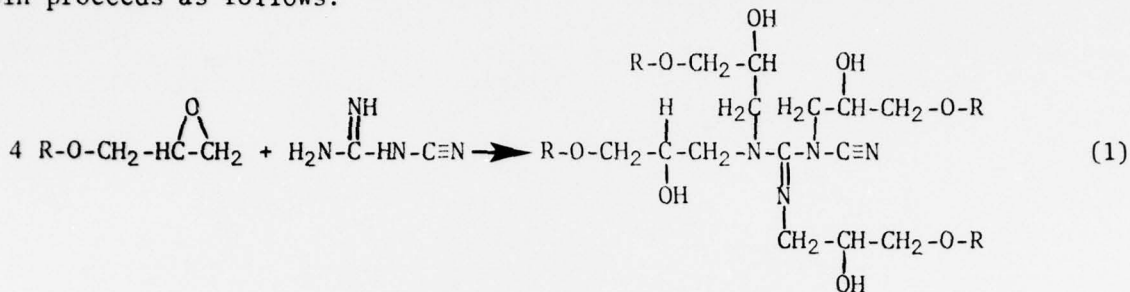
1. Dicyandiamide



2. MONURON



monitored by measuring the infrared absorbance for selected functional groups in the epoxy resin. According to Saunders et al.¹ the dicyandiamide cure of an epoxy resin proceeds as follows:



The state of cure is monitored by measuring the epoxy ring absorbance at ~ 915 wave numbers. The exact location of the epoxide ring absorbance must be determined for the particular resin system being analyzed. As the cure reaction proceeds, the intensity of the absorbance at ~ 915 wave numbers decreases in accordance with the ring opening and indicates the completeness of cure for the epoxide. The data are normalized to the 915 wave number intensity for the uncured resin, therefore producing a ratio indicating unreacted epoxide groups relative to the starting concentration.

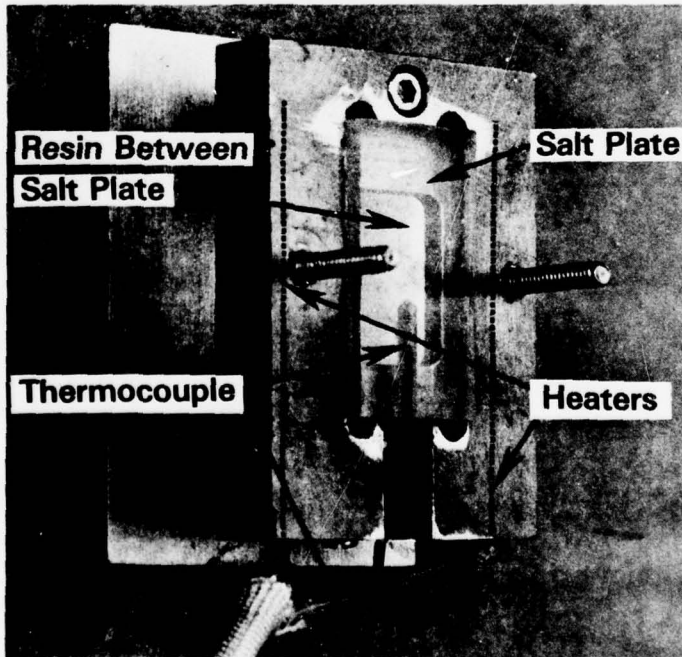


Figure 1. Temperature-controlled sample holder for transmission measurement.

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1. SAUNDERS, T. F., LEVY, M. F., and SERINO, J. F. *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resin.* *Journal of Polymer Science, Part A-1*, v. 5, 1967, p. 1609-1617.

Internal Reflectance Measurements

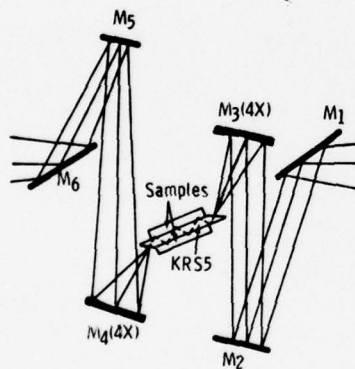
Infrared spectra were measured on composite samples by using a Harrick Model 4X-TBC-VA internal reflectance spectroscopy (IRS) attachment. The IRS unit used a 4X beam condenser with a single-pass parallelepiped KRS5 internal reflection crystal $50 \times 3 \times 2$ mm in size. The angle of incidence for radiation was 45 degrees. A schematic diagram² of the IRS attachment is shown in Figure 2.

Two samples of the composite or neat resin were placed in the sample holder as shown in Figure 2. To obtain a reflectance spectrum on a particular material two samples approximately 50×3 mm on the surfaces were placed in optical contact with the KRS5 crystal. Thickness was unimportant as long as the samples fit conveniently into the C-clamp holding the samples in contact with the KRS5 crystal. A calibrated torque wrench (10 to 100 inch ounces) was used to apply a reproducible force at the surface crystal interface. Typically, 30 inch ounces was applied to a single bolt on the C-clamp.

Spectra were recorded in absorbance units (A) according to the equation:

$$A = \log_{10} [SCA \cdot PFA / SCB \cdot PFB], \quad (3)$$

where SCA is a mixed number scaling factor equal to 1.0, PFA is the single beam spectrum for sample plus KRS5 reflection element, SCB is a mixed number scaling factor equal to 1.0, and PFB equals the single beam reference spectrum for KRS5. All spectra were measured under a nitrogen atmosphere.



$$d_p = \frac{\lambda / n_{KRS5}}{2\pi [\sin^2\theta - (n_{SAM}/n_{KRS5})^2]^{1/2}}$$

d_p = depth of penetration into sample
($n_{KRS5} > n_{SAM}$)

λ = wavelength of radiation in μm

n_{KRS5} = refractive index of KRS5

n_{SAM} = refractive index of sample

θ = angle of incidence of radiation

Figure 2. Internal reflectance spectroscopy.

2. HARRICK SCIENTIFIC CORP., Croton Dam Rd., Ossining, New York.

In addition to analysis of composites, internal reflection spectroscopy was used for prepreg analysis. When measuring the extent of cure on a composite, the absorbance for the unreacted epoxide ring can be ratioed to its intensity measured in the prepreg. For all reflectance measurements, the epoxy ratios were normalized to the aromatic absorbance band at 1510 wave numbers according to the equation

$$A_{915 \text{ cm}^{-1}} (\text{normalized}) = \frac{A_{1510 \text{ cm}^{-1}} (\text{sample})}{A_{1510 \text{ cm}^{-1}} (\text{prepreg})} \cdot A_{915 \text{ cm}^{-1}} (\text{sample}). \quad (4)$$

RESULTS

RAC 7250

A thin film of RAC 7250 was cured in the sample compartment of the FTS-10M spectrometer. Figure 3a shows an infrared spectrum of the RAC 7250 neat resin. Figure 3b shows an infrared spectrum of the resin after two hours into the thermal cure program shown in Figure 4. As may be seen in Figure 3b, epoxy ring absorbance

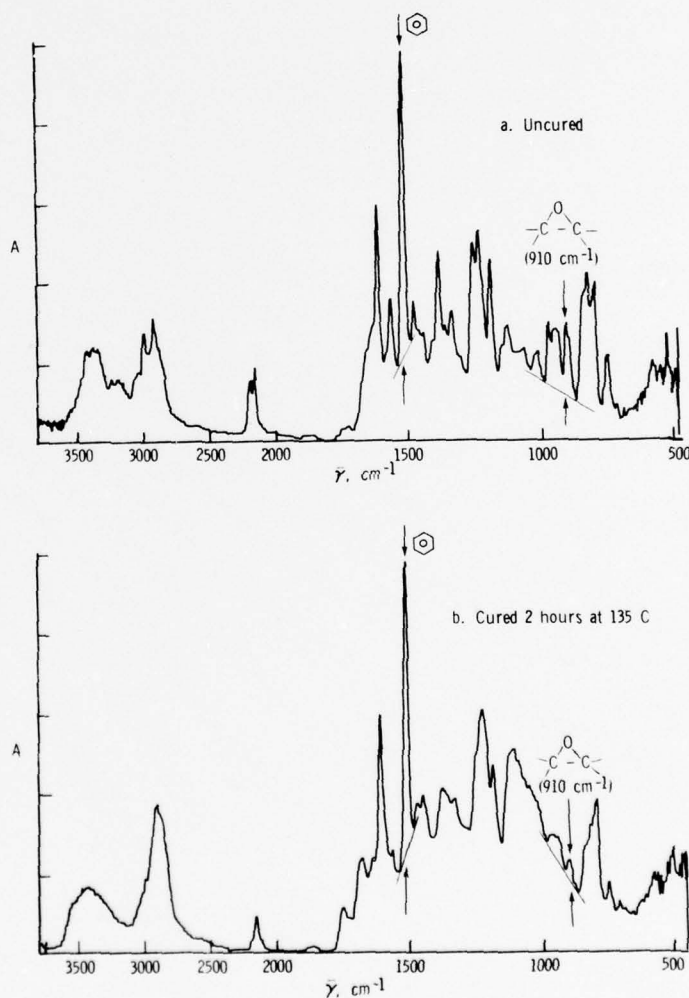


Figure 3. Infrared spectra of RAC 7250 thin film.

at 910 cm^{-1} for RAC 7250 was still present after the two hours of heating. When the intensity of the epoxide ring absorbance in Figure 3b was ratioed to that in Figure 3a, it was found that approximately 24% of the epoxide groups were still unreacted. Figure 5 shows a graph of the epoxy ratios as a function of time at 135 C.

In an attempt to further cure the RAC 7250, the sample temperature was increased to 177 C and held there an additional hour. As may be seen from Figures 5 and 6a essentially no further cure was completed during the additional hour of heating. Only after the sample temperature was increased to 220 C were the remainder of the epoxide groups reacted. Figure 6b shows an infrared spectrum after reaching 220 C and holding this temperature for an additional 0.5 hour. It should be noted that although the epoxy ring absorbance is no longer measured, thermal oxidation of the sample has considerably increased. This may be seen by the large increase in the 1740 wave number aliphatic carbonyl absorbance.

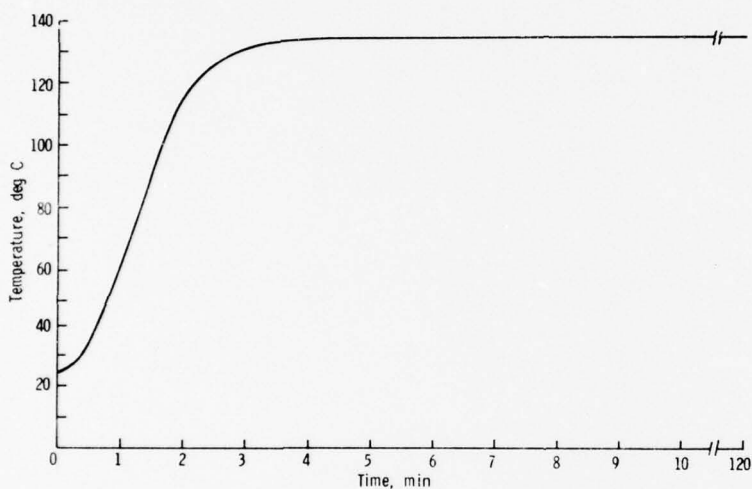


Figure 4. Temperature program for cure of RAC 7250 and SP 250 thin films.

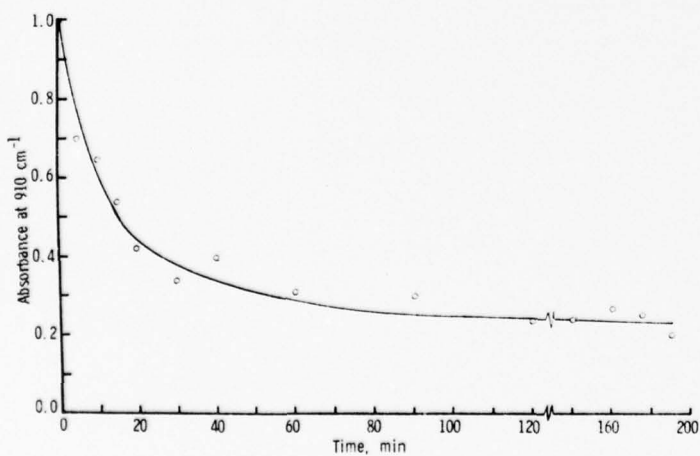


Figure 5. Epoxy absorbance during cure of RAC 7250.

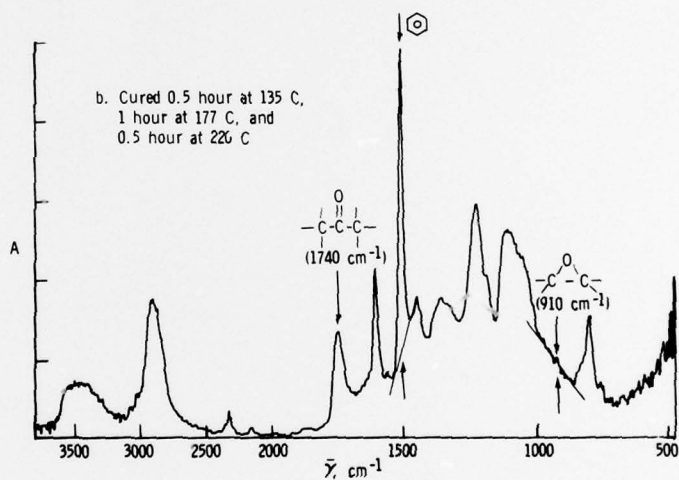
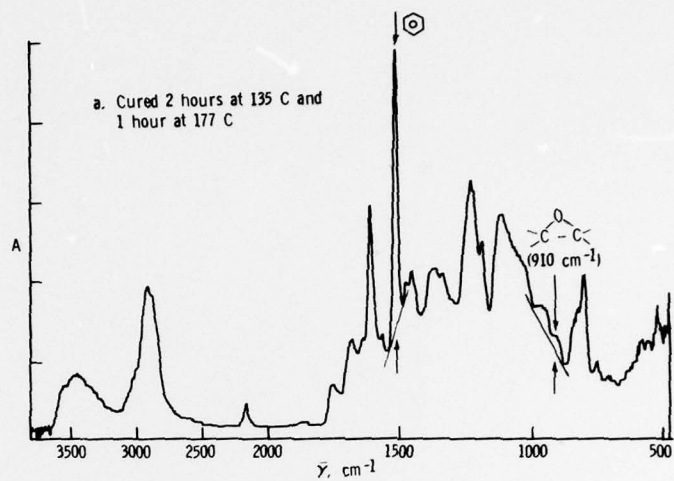


Figure 6. Infrared spectra of RAC 7250 thin film.

RAC 7250 neat resin panels that were $12 \times 12 \times 1/8$ inches were cured two hours at 127 C and their infrared reflectance spectra measured (Figure 7a). These panels also show approximately 20% unreacted epoxide corresponding to the incomplete cure measured in the thin films previously described. Figure 7b shows the spectrum of the same panel after its temperature was raised 220 C. Note that the epoxide ring absorbance at 910 wave numbers has essentially disappeared into the background of the spectrum.

Cure measurements were also made on RAC 7250 laminated glass reinforced composites. Samples of modified unidirectional and crossply composite laminates were subjected to three thermal cure conditions, denoted as undercure, standard cure, and overcure treatments. The three conditions were simple modifications of step 6 in the Appendix. The undercured samples were subjected to one hour cure at 127 C. Standard cure samples were subjected to two hours at 127 C and the overcured samples were subjected to 16 hours at 127 C.

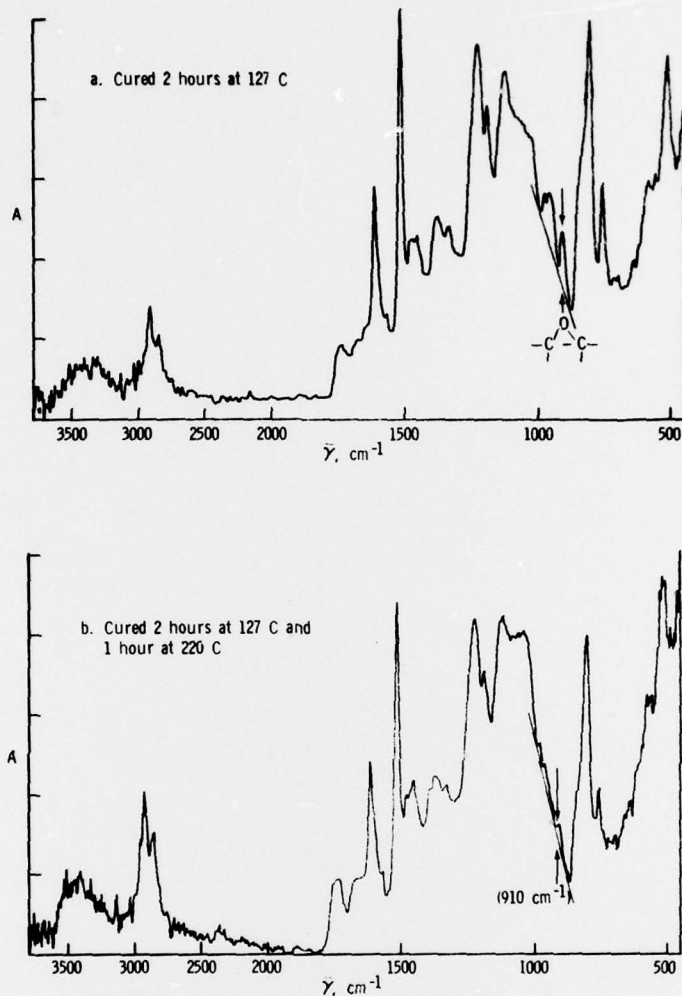


Figure 7. Internal reflectance spectrum of RAC 7250 neat resin plate.

Internal reflectance spectra were measured on four samples cured at each of the cure conditions and the average extent of cure calculated in each case. Table 3 summarizes the results of this analysis where the ratio of unreacted epoxy was relative to that measured in the RAC 7250 prepreg system. Figure 8 shows an IRS spectrum for the RAC 7250 prepreg and Figure 9 shows an IRS spectrum from the surface for the under-, standard, and overcured composites. In order to compensate for small differences in path length during internal reflection measurements, the epoxy ring absorbance for all spectra was normalized to the aromatic ring absorbance at 1510 wave numbers.

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Infrared spectroscopy

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Epoxy resins
Infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) has been used to measure the extent of cure in fiber-reinforced epoxy composites and the corresponding resin matrices. Two sampling techniques have been used to study the curing processes: (1) thin films of neat resin held between salt plates and (2) internal reflectance spectroscopy (IRS). Thin films have been studied by curing them in a temperature-controlled cell that allowed the same temperature program to be followed that was used in the corresponding composite fabrication. Infrared spectra were recorded at short time intervals throughout the cure cycle and the results were used to measure extent of cure based on epoxide ring absorbance at approximately 915 wave numbers. Internal reflectance measurements were performed on the corresponding composite materials and results were compared with the thin film measurements. The two techniques had a high degree of correlation and clearly demonstrated the thin film studies were characteristic of the cure of multi-ply composite panels. The thin film measurements offer an excellent means for optimizing cure cycles in the laboratory and FT-IR/IRS offers a nondestructive means of performing extent of cure measurements in a plant fabrication environment.

Army Materials and Mechanics Research Center

Watertown, Massachusetts 02172
CURE ANALYSIS OF EPOXY COMPOSITES USING FOURIER
TRANSFORM INFRARED SPECTROSCOPY - James F. Sprouse,
Bernard M. Halpin, Jr., and Robert E. Sacher

AD

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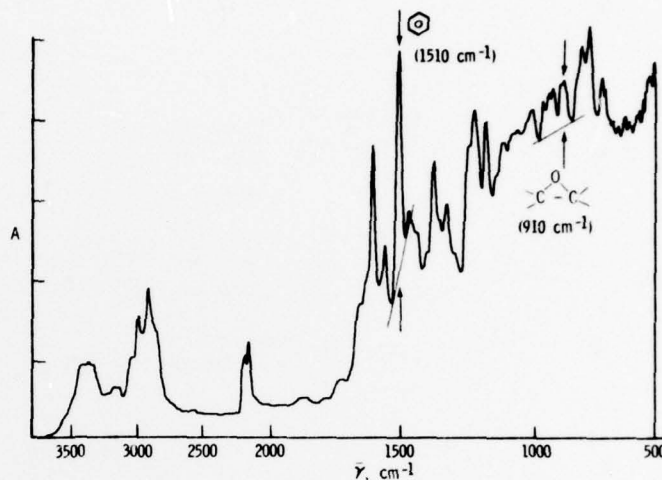
Fourier transform infrared spectroscopy (FT-IR) has been used to measure the extent of cure in fiber-reinforced epoxy composites and the corresponding resin matrices. Two sampling techniques have been used to study the curing processes: (1) thin films of neat resin held between salt plates and (2) internal reflectance spectroscopy (IRS). Thin films have been studied by curing them in a temperature-controlled cell that allowed the same temperature program to be followed that was used in the corresponding composite fabrication. Infrared spectra were recorded at short time intervals throughout the cure cycle and the results were used to measure extent of cure based on epoxide ring absorbance at approximately 915 wave numbers. Internal reflectance measurements were performed on the corresponding composite materials and results were compared with the thin film measurements. The two techniques had a high degree of correlation and clearly demonstrated the thin film studies were characteristic of the cure of multi-ply composite panels. The thin film measurements offer an excellent means for optimizing cure cycles in the laboratory and FT-IR/IRS offers a nondestructive means of performing extent of cure measurements in a plant fabrication environment.

Table 3. CURE OF RAC 7250 COMPOSITE

	Prepreg	Undercure	Standard	Overcure
Average Peak Height (SD) ^a	20.0 (2.8)	11.4 (1.9)	7.2 (1.9)	3.9 (0.2)
Ratio of Unreacted Epoxy	1.00	0.57	0.36	0.19

^aSD = Standard Deviation based on three data points.

Figure 8. Internal reflectance spectrum of RAC 7250 prepreg.



SP 250

A cure study for the SP 250 system was completed similarly to that of the RAC 7250. A thin film of the neat resin was cured in the sample compartment of the FTS-10M spectrometer. Figure 10a shows a spectrum of the uncured SP 250 and Figure 10b shows a spectrum of the same sample after two hours at 135 C. The epoxy ring absorbance at $\sim 915 \text{ cm}^{-1}$ for SP 250 disappears in the thin film after the two-hour cure treatment, indicating a fully cured resin system. (Note: Epoxy ring absorbance disappearance is based on the minimum detection limit of the instrument.) Figure 10c shows the infrared spectrum of the same sample after one hour of additional curing at 177 C. The small band that still remains at ~ 915 wave numbers does not result from the epoxide ring absorbance and is not eliminated from the sample by additional thermal treatment. Figure 11 shows a graph of the epoxy ring absorbance ratio relative to the ring absorbance of the unreacted SP 250 resin. The same temperature program was used for the SP 250 cure study shown in Figure 4 for the RAC 7250. Figure 12 shows an IRS spectrum of an SP 250 resin panel that was cured for two hours at 127 C. There is no evidence of unreacted epoxide from the infrared spectrum.

A series of glass-reinforced SP 250 composites were also fabricated using the under-, standard, and overcured criteria. The SP 250 panels were modified unidirectional and crossply 14-ply laminates prepared from the SP 250 prepreg. Figure 13 shows an IRS spectrum of the SP 250 prepreg and Figure 14 shows the spectra measured on the surface of the under-, standard, and overcured composites. Table 4 shows the ratio of epoxy reacted for the SP 250 composites.

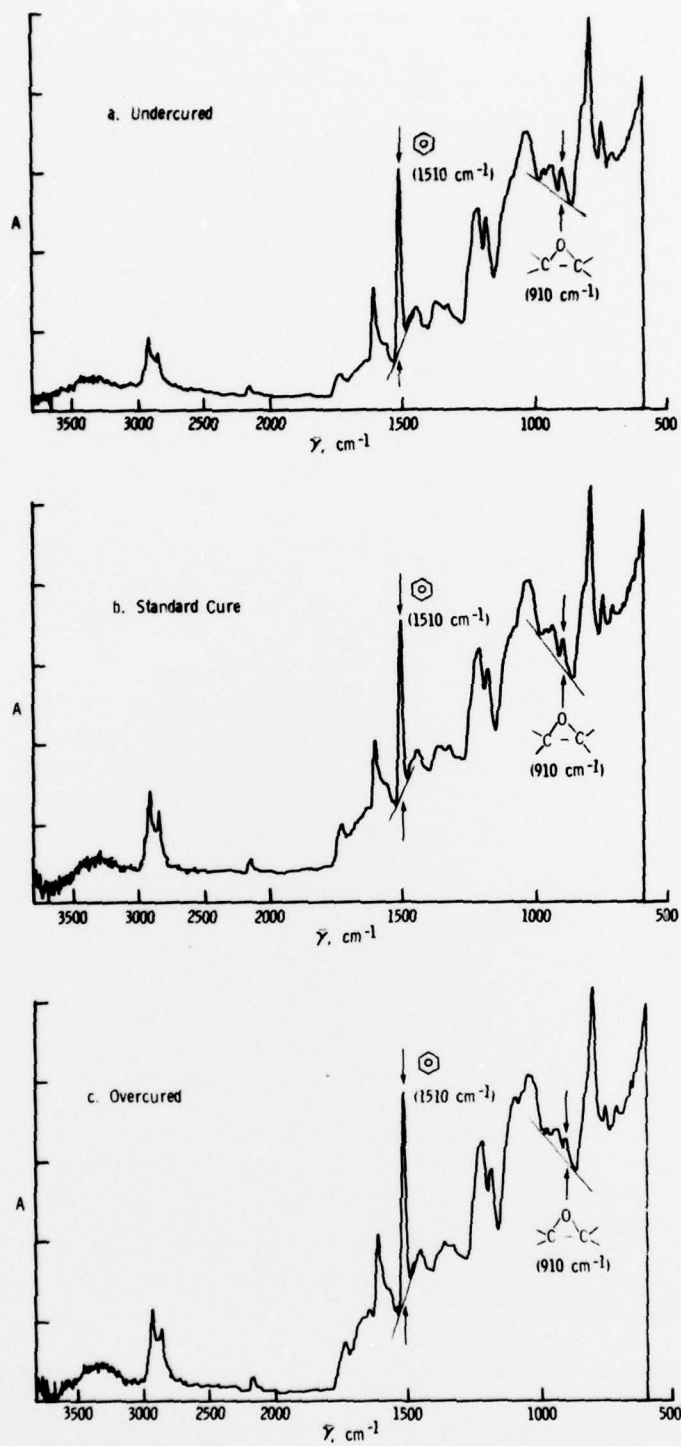


Figure 9. Internal reflectance spectra for RAC 7250.

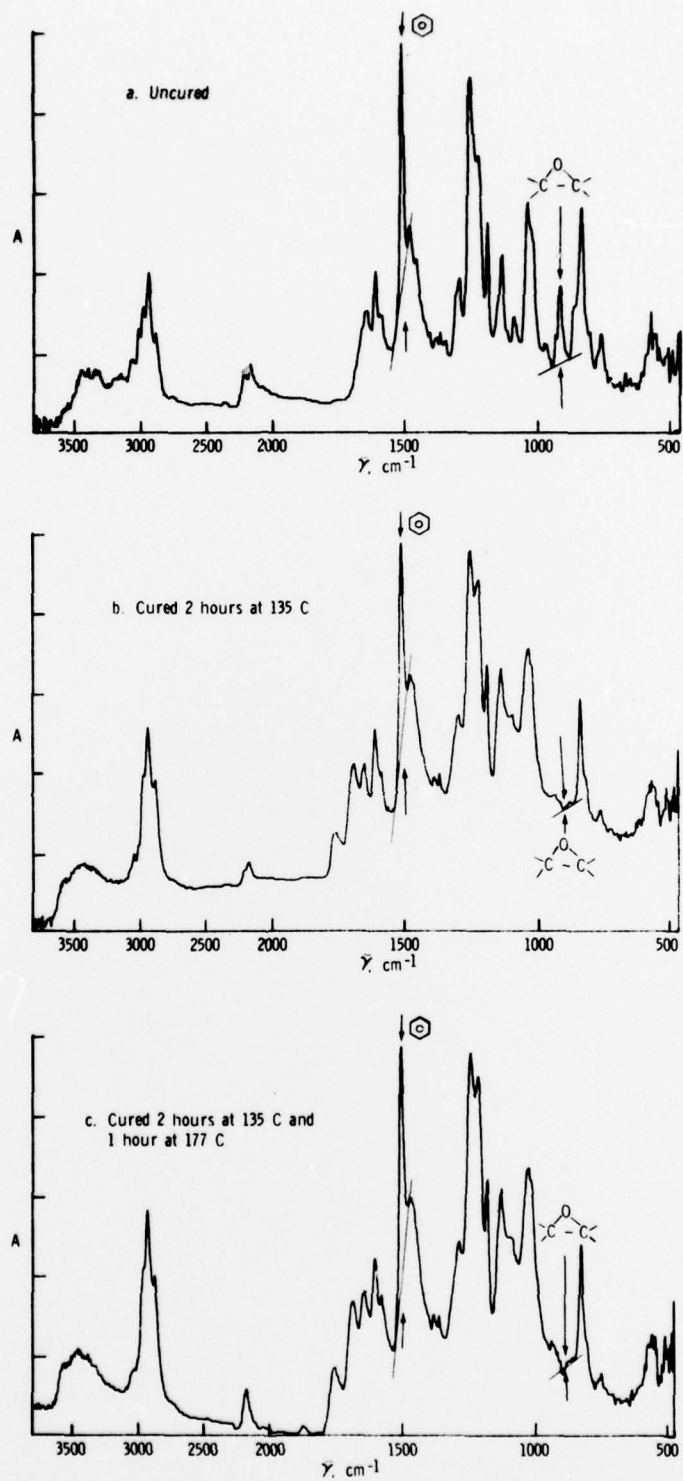


Figure 10. Infrared spectra of SP 250 thin film.

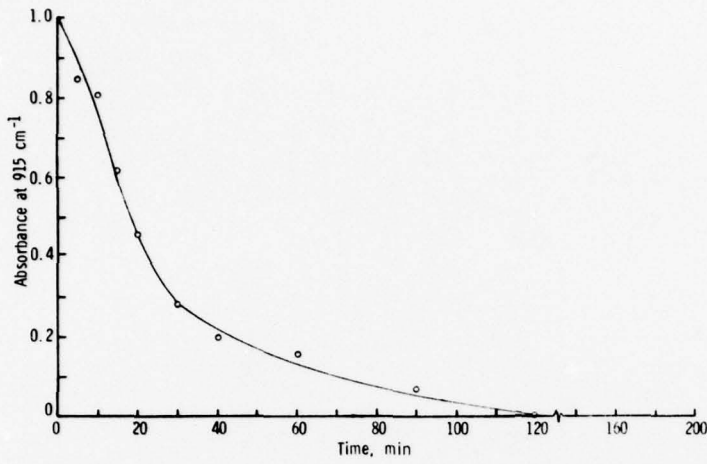


Figure 11. Epoxy absorbance during cure of SP 250.

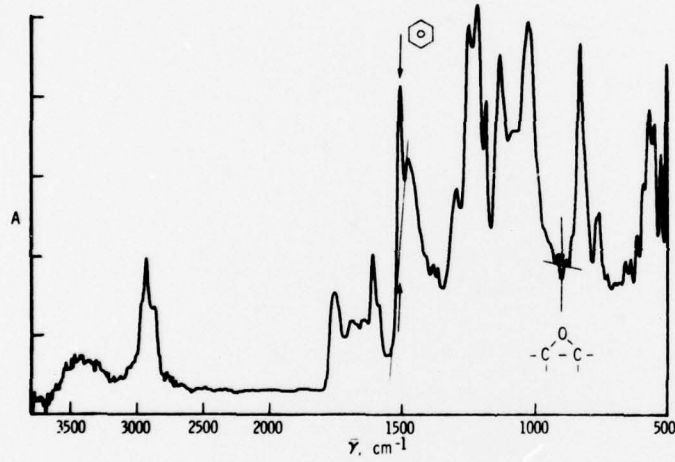


Figure 12. Internal reflectance spectrum of SP 250 neat resin plate cured 2 hours at 127 C.

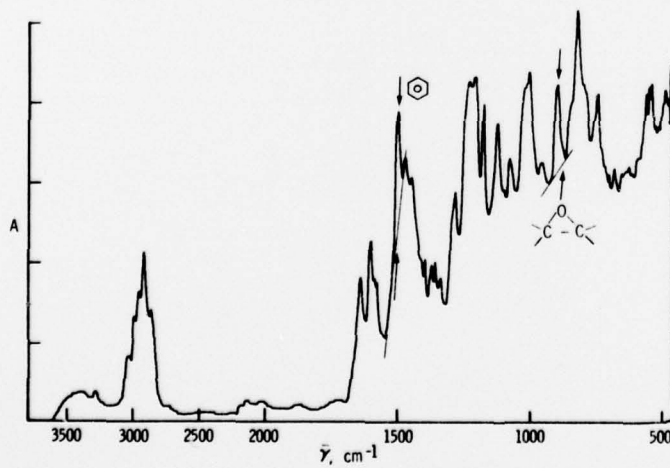


Figure 13. Internal reflectance spectrum of SP 250 prepreg.

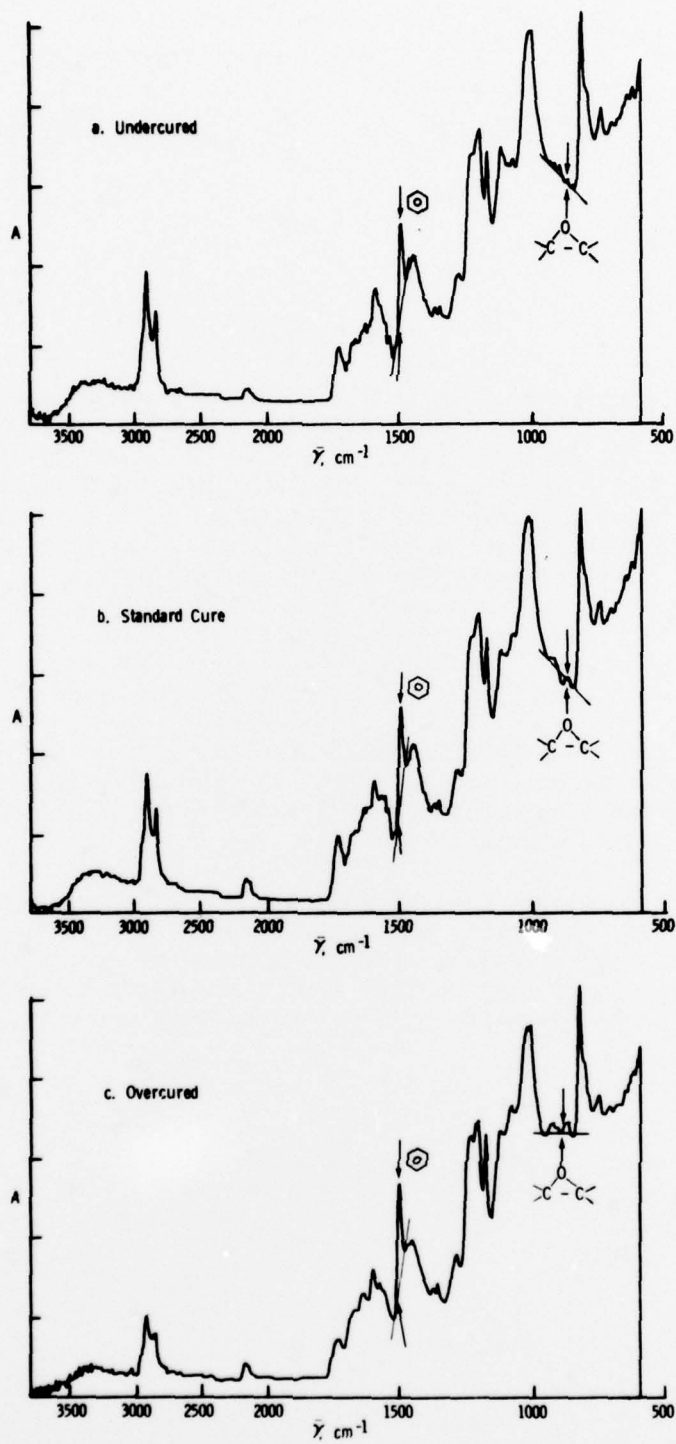


Figure 14. Internal reflectance spectrum of SP 250.

Table 4. CURE OF SP 250 COMPOSITE

	Prepreg	Undercure	Standard	Overcure
Average Peak Height (SD)	20.3 (2.7)	2.5 (2.1)	0.0	0.0
Ratio of Unreacted Epoxy	1.00	0.12	0.0	0.0

CONCLUSIONS

RAC 7250 composites that were studied did not undergo complete epoxide ring opening based on FT-IR/IRS measurements during a two-hour cure at 127 C. Only approximately 70 to 80% of the epoxide groups are reacted relative to the starting concentration in the RAC 7250 prepreg. The remainder of the epoxide rings can be reacted by subjecting the sample to a temperature of 220 C. Exposing the sample to this higher cure temperature results in excessive thermal oxidation of the resin at the cost of reacting the remainder of the epoxide groups. A good correlation exists between evaluating the extent of cure for RAC 7250 composite materials by FT-IR/IRS and by measuring transmission spectra of the thin films of the neat resin. While the composites showed 36 percent remaining epoxide after 2 hours at 127 C, the thin films showed approximately 25 percent after 2 hours at 135 C.

SP 250 composites undergo complete cure based upon FT-IR/IRS measurements during the standard two-hour cure at 127 C. No unreacted epoxy functional groups were measured in either the SP 250 composite panels or in the SP 250 resin thin films after the standard cure treatment.

FT-IR/IRS offers an excellent technique for evaluating extent of cure for fiber-reinforced epoxy composites and neat resins. FT-IR also provides an excellent method for evaluating thermal cure treatments for epoxy resin formulations in the form of thin films. The results are in excellent agreement with internal reflection measurements completed on fiber-reinforced composite panels.

APPENDIX. STANDARD CURE CYCLE FOR RAC 7250 AND SP 250

1. Apply vacuum to laminated preregs after inclosing in a plastic bag, then place the sample in an autoclave.
2. Apply 20 ± 5 psig pressure and release vacuum.
3. Raise the temperature to 160 ± 10 F.
4. Increase pressure (at 160 F) to 90 ± 10 psig.
5. Increase temperature at 6 ± 1 F per minute to 260 ± 5 F.
6. Hold this temperature (260 ± 5 F) for two hours.
 - (a) Undercure cycle: Hold this temperature (260 ± 5 F) for only one hour.
 - (b) Overcure cycle: Hold this temperature (260 ± 5 F) for sixteen hours.
7. Reduce temperature to 150 F.
8. Release pressure and remove samples from autoclave.

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