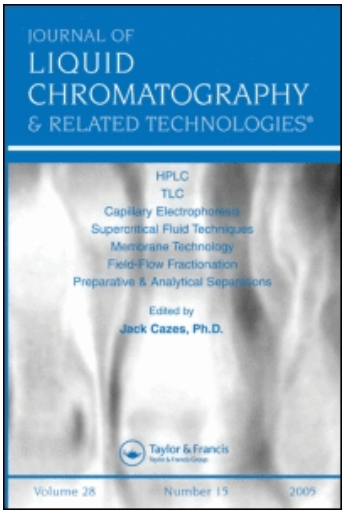


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# Compositional Analysis of Epoxy Resin Formulations

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# COMPOSITIONAL ANALYSIS OF EPOXY RESIN FORMULATIONS

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## ABSTRACT

Liquid chromatographic (LC) methods are developed for the quality control of epoxy resin formulations. Primary components in two different commercial resin formulations are separated by LC and identified by Fourier transform infrared spectroscopy. Standard test methods for fingerprinting and specific component analysis are established. Examples are given of applications of the test methods to determine compositional variations in prepregs and to establish acceptance criteria for prepreg quality control.

## INTRODUCTION

Epoxy resin formulations are complex mixtures of resins, curing agents, accelerators, diluents, rubber modifiers, etc. The processability and physio-mechanical properties of epoxy-based composite systems are directly related to the chemical formulation of the resin prepreg material. Furthermore, formulated resins are reactive and compositional changes in prepreg materials may occur during transport and storage. A major problem in the manufacture of composite materials is the quality control and reproducibility of resin formulations. Because present quality control techniques are oftentimes inadequate and do not directly address the problem of resin formulation composition, composite material specifications must be quite rigid and item rejections are high in critical application areas.

This paper concerns the development of liquid chromatographic methods for the quality control of epoxy resin formulations. Liquid chromatography (LC) is a powerful technique for the separation and analysis of soluble components in complex mixtures. Instrumentation is commercially available at relatively low cost and requires a minimum of technical training for operation. Recent improvements in instrumentation and the development of microporous column substrate materials have resulted in reduced analysis times and improved detectability and resolution of components. Modern LC is highly reliable and particularly well-suited for quality control applications to "fingerprint" and analyze compositional differences or changes in resin formulations and prepregs.



Two different commercially formulated resin systems are examined in developing LC test methods. Initially, no information was available concerning composition except that both systems were of the "catalyzed" 250 resin type. Therefore preparative LC techniques and Fourier transform infrared spectroscopy were used to isolate and identify principal components in the resin formulations. LC test methods were then developed for "fingerprinting" formulation compositions and for the quantitative analysis of specific components. Test methods are described and examples are given of their applications to determine compositional variations in prepregs and to establish acceptance criteria for prepreg quality control.

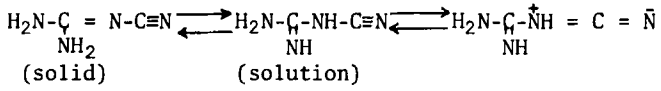
## EXPERIMENTAL

A Waters Associates ALC/GPC 244 instrument with M6000A solvent delivery system, U6K injector, 660 solvent programmer, R-400 differential refractometer and 440 dual wavelength UV absorbance detector was used for LC analysis. All tests were performed using Waters Associates μ-styragel (30 cm x 7.8 mm ID),

μ-porasil (30 cm x 3.9 mm ID) and μ-bondapak $C_{18}$ (30 cm x 3.9 mm ID) columns. Distilled in glass 2,2,4-trimethylpentane (C8) was used as received from Burdick & Jackson Labs (Muskegon, MI). Tetrahydrofuran (THF), chloroform ($CHCl_3$) and water were distilled just prior to solution preparation and LC analysis. All solvents were filtered through 0.45μ Millipore filters. Solutions of component standards, formulated resins, prepregs and prepreg extracts were prepared by weighing the samples in volumetric flasks and diluting to the appropriate volume with solvent. After mixing the solutions were centrifuged and/or filtered through 0.2μ filters. Actual sample mass, injection volume, and LC operating parameters are indicated on each chromatogram. An injected sample mass of 5μg and solution volume of 10μℓ is designated, for example, as 5μg/10μℓ.



Formulated resin batches, designated FR-A and FR-B, were supplied in gallon metal containers and were kept refrigerated except for sampling. The FR-A formulation was received as a heterogeneous mixture with about 20% by weight methylene chloride. After vigorous mixing, aliquots were taken for LC studies and the methylene chloride was removed by evaporation under partial vacuum. The FR-B formulation was received as a pale yellow, sticky semi-solid. Upon centrifugation of $CHCl_3$ solutions of FR-A and FR-B, a white precipitate was recovered and identified as the epoxy curing agent (1)




dicyanodiamide (DICY)

Next the solutions were analyzed and components were separated preparatively by normal phase chromatography (Figure 1). Repeated 15 or 25μℓ injections were made and selected components in the effluent were collected. After concentration, solutions

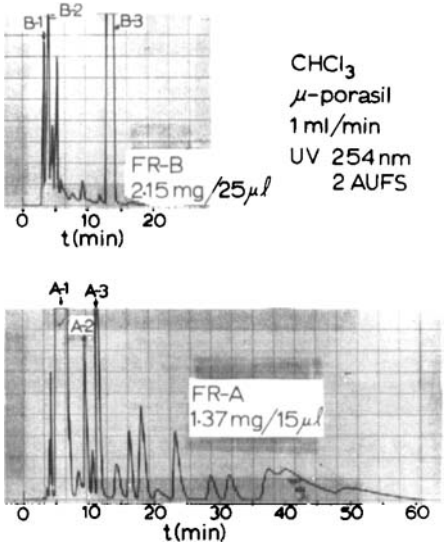
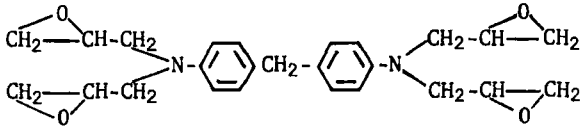


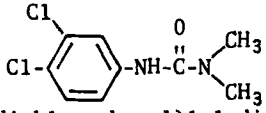

FIGURE 1

of the collected components were cast onto salt plates and the remaining $CHCl_3$ was removed by evaporation. A Digilab Model FTS-10M Fourier transform infrared spectrometer was then used to measure the spectra of components on the salt plates (2). Analysis revealed that for FR-A peak A-1 is the resin



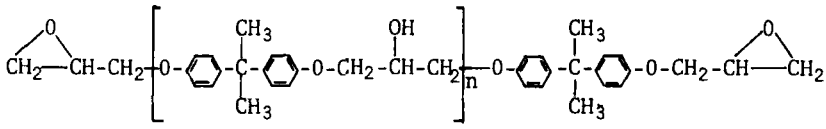
tetraglycidylmethylenedianiline (TGMDA),

peak A-2 may be a dimer of TGMDA and peak A-3 is the accelerator

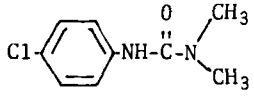


3-(3,4-dichlorophenyl)1,1-dimethylurea (diuron)

and that for FR-B peak B-1 is p-tert-butylphenyl-2,3-epoxy-propyl ether or one of its isomers, peak B-2 is the resin



and peak B-3 is the accelerator



3-(p-chlorophenyl)-1,1-dimethylurea (monuron).

Samples of the identified components were obtained commercially to verify infrared spectra and to aid in the development of LC test methods.



## METHODS DEVELOPMENT

In developing quality control methods, various LC techniques are utilized not only to fingerprint chemical composition but also to monitor and quantitatively analyze specific sample components. Different LC separation modes are used for analyzing the resin formulations; and since the mechanism for separation is different in each mode, unique and different information may be obtained concerning the compositions of such complex samples.

### Gel Permeation Chromatography (GPC)

GPC separates components on the basis of their "size" or molar volume in solution which, in the absence of adsorption and intermolecular association effects, is an unambiguous molecular parameter. The size of a molecule is inversely related to its elution time; that is, smaller molecules generally take longer to elute from the column(s) since they are better able to penetrate into the porous packing. A GPC fingerprint of the THF soluble portion of FR-A (Figure 2) requires about 24

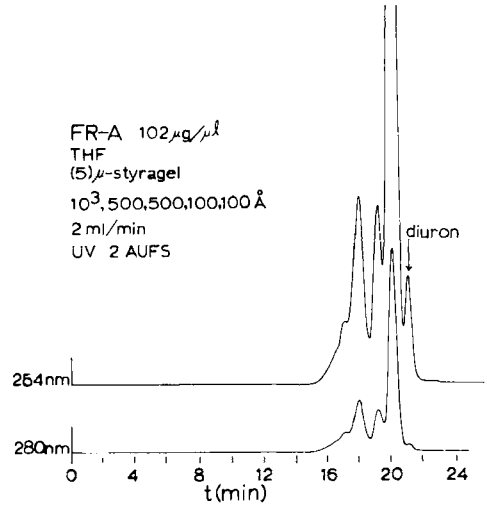



FIGURE 2

minutes and at least five components are evident as indicated by the number of peaks in the chromatograms monitored at 254 and 280 nm. Components are first detected near t = 16 minutes which corresponds to the time for a 5000 g/mol polystyrene standard to elute. The final component eluted is diuron and it is noted that peak UV absorbances are greater at 254 nm than at 280 nm.

The GPC fingerprint of FR-B (Figure 3) is different from that of FR-A. The peak UV absorbances are greater at 280 nm than at 254 nm except for monuron. The enhanced UV absorption at 280 nm is consistent with the behavior of DGEBA and is illustrated by the GPC fingerprint of EPON 828. It is also noted that detectable components in FR-B first appear at t = 13.5 minutes which is equivalent to the elution time of a 20,000 g/mol polystyrene standard. The first component of EPON 828 starts to elute at t = 17 minutes which suggests that FR-B may contain an unidentified, high molecular weight

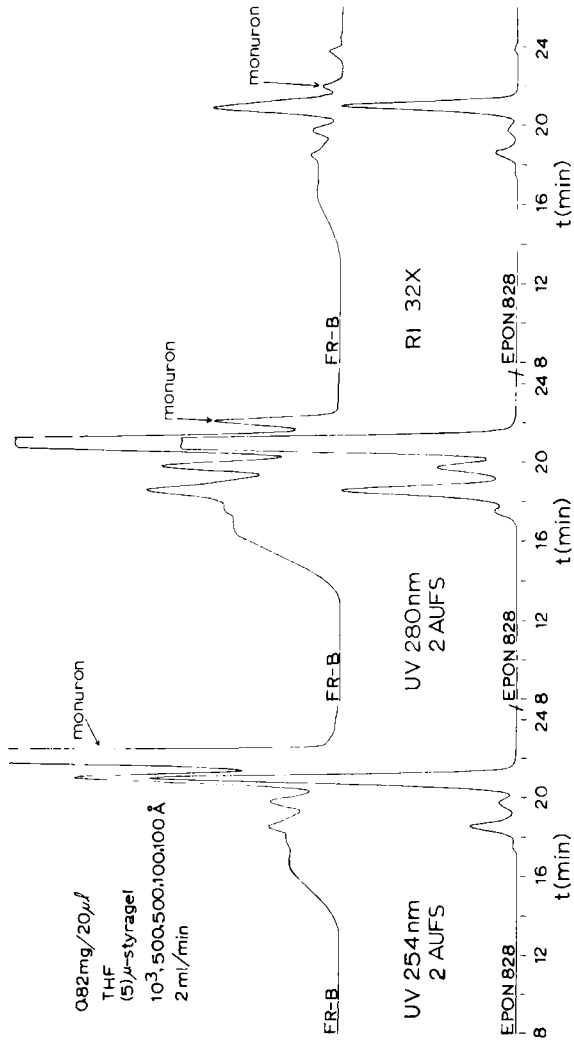



FIGURE 3

component (e.g., a rubber modifier) or perhaps that higher molecular weight species are present in FR-B due to staging. Figure 3 also illustrates how a refractive index (RI) monitor may be utilized to detect components that do not have chromophores absorbing strongly in the UV.

## Normal Phase Chromatography

Adsorption or normal phase chromatography generally relies on a highly polar, silica packing which reversibly adsorbs the solutes and facilitates separation usually on the basis of polarity. Components of higher polarity and with more interactive (polar, hydrogen bonding, ionic) functional groups tend to be adsorbed and therefore are retained for a longer time on the column packing. Normal phase fingerprints have already been illustrated (Figure 1) for the $CHCl_3$ soluble portions of FR-A and FR-B. In Figure 4 the compositional profiles of FR-A and FR-A-S2 are compared. Sample FR-A-S2 designates FR-A extracted from S2 glass fiber prepreg. The relative heights of certain peaks are quite different. Considerably less diuron is evident eluting at 8.4 minutes in the FR-A-S2 extract. The component eluting at 9.4 minutes is perhaps an isomer of the diuron indicated in FR-A.

Figures 5 and 6 illustrate the use of solvent programming or elution gradient techniques to fingerprint formulation compositions. In each case THF solutions of FR-A and FR-B are injected and a 30 minute gradient from 0 to 100% THF is run. A slightly concave gradient 7 is programmed for the $CHCl_3 \longrightarrow$THF fingerprint. Injecting FR-A with THF as the solvent causes the TGMDA peak to split with the first component unretained and eluted with the THF. Succeeding peaks elute sharper and earlier than when run isocratically with $CHCl_3$ and components are eluted by the THF gradient that previously were not apparent. A linear

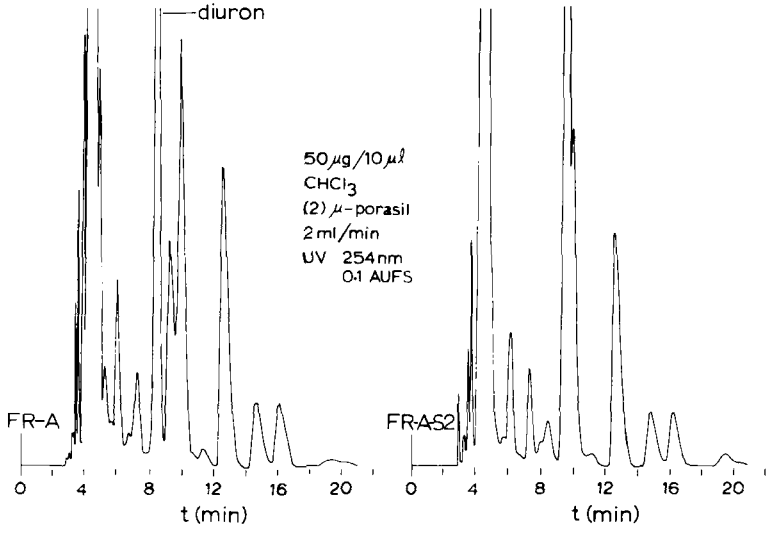



FIGURE 4

gradient 6 is programmed for the 60% C8/40% THF to 100% THF gradient. Because C8 is less polar and functionally different than $CHCl_3$, retention times are generally larger and the sequence in which components elute may be different.

Normal phase LC may also be used to quantitatively analyze the resin and accelerator in the formulated resins and prepregs. To optimize analysis by the method of peak heights, the following conditions are required - (1) full separation of components, (2) narrow peak widths, and (3) large displacement of peak maxima from baseline. These conditions are achieved using one μ-proasil column with $CHCl_3$ as the eluent at a flow rate of 2ml/min, while minimizing sample size and increasing UV detector sensitivity (0.05 - 0.2 AUFS). Component standards were purified when necessary. TGMDA was obtained from Ciba Geigy Corporation as the main component in their MY720 resin. Shell's EPON 828 was the source of the DGEBA resin. Diuron and

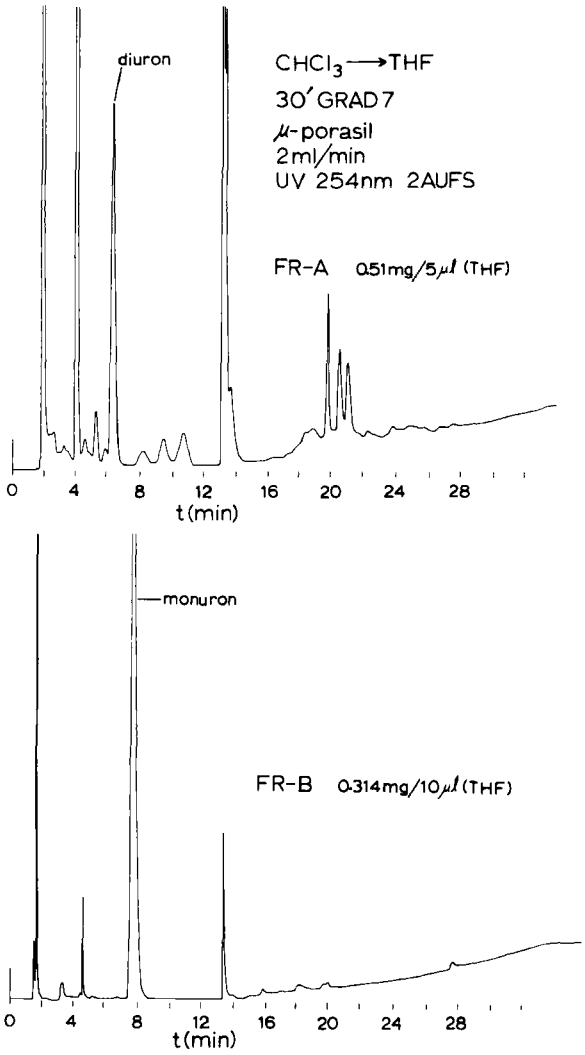



FIGURE 5

monuron were obtained from DuPont Biochemicals Department and Pfaltz & Bauer Inc., respectively. Since the monomer-oligomer retention times and peak height ratios in MY720 and in EPON 828 correlate with component peak data in FR-A and FR-B, MY720 and

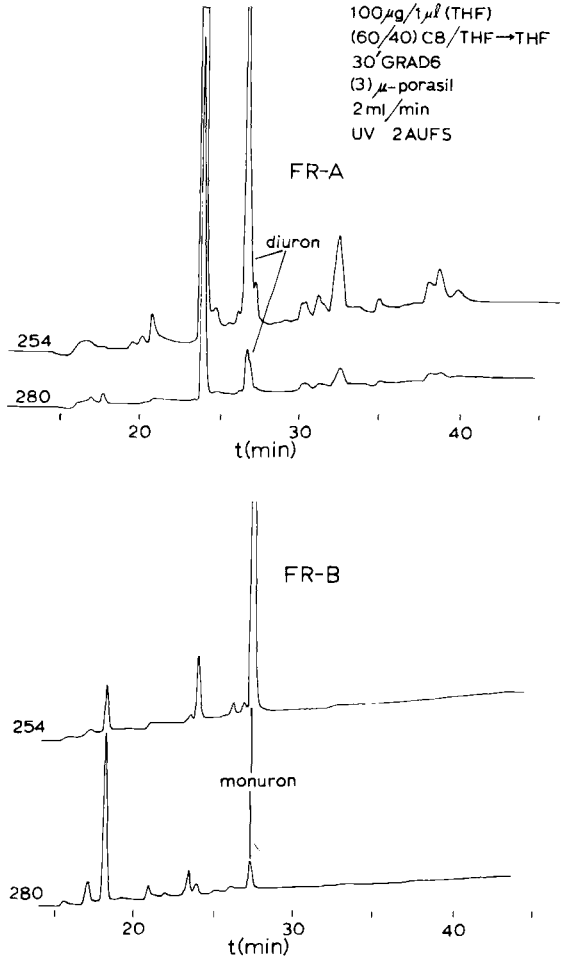



FIGURE 6

EPON 828 are assumed to be the principal resin sources and therefore are used directly for calibration. Calibration data are obtained by successive injection of different volumes of the standard solutions. In all the calibration plots (e.g., Figure 7), the intercepts are greater than zero possibly due to impurities present in the standards. Also, it is noted that weighing and solution preparation errors are not included

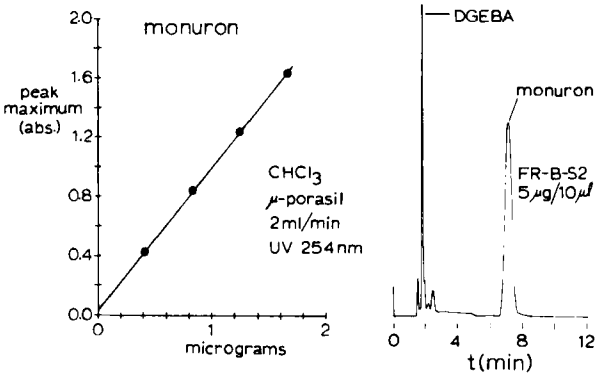



FIGURE 7



in the variance of the calibration constants (slope) K, Component capacity factor k', peak height ratio $A_{254}/A_{280}$ and calibration constants at two different UV wavelengths λ are given in TABLE 1. The k' and $A_{254}/A_{280}$ values are specific for each component and may be evaluated in each analysis to assure component purity. Examples are given in the APPLICATIONS section.

TABLE 1

Normal Phase Chromatography - Calibration Constants

| Component | k' | $A_{254}/A_{280}$ | λ(nm) | K($\mu g^{-1}$) | Intercept |
|---|---|---|---|---|---|
| MY720 | 0.80 | 3.21 | 254 | 0.540±0.009 | 0.043±0.026 |
| | | | 280 | .168±0.003 | .017±0.010 |
| EPON 828 | 0.20 | 0.328 | 254 | .154±0.001 | .006±0.002 |
| | | | 280 | .470±0.007 | .024±0.009 |
| diuron | 2.90 | 17.1 | 254 | .872±0.019 | .016±0.027 |
| | | | 280 | .051±0.001 | .002±0.002 |
| monuron | 3.75 | 16.2 | 254 | .966±0.009 | .031±0.010 |
| | | | 280 | .060±0.001 | .003±0.001 |

## Reverse Phase Chromatography

Converse to normal phase LC, reverse phase methods described herein rely on a low-polarity, bonded-phase $C_{18}$ packing with a highly polar mobile phase for separation. Separation is based on the relative solubility and distribution of solutes between the mobile and stationary phases with components of highest polarity tending to elute earliest. Figure 8 illustrates how reverse phase LC separations may be optimized using an $H_2O$/THF gradient. THF solutions are injected and the percent $H_2O$ in the eluent upon injection and initiation of the gradient is indicated at t = 0.



Optimum resolution of components and time for analysis is achieved with the (40/60) $H_2O$/THF$\longrightarrow$THF gradient. Quite distinctive fingerprints are shown for FR-A and FR-B in Figure 9. The THF gradient is initiated after the chromatograph is run isocratically (40% $H_2O$/60% THF) for a period of time to improve resolution. In contrast to the normal phase separations, monuron and diuron elute before the resins. Comparisons of peak heights monitored at 254 and 280 nm help identify components. It is noted that FR-B has a number of low polarity components eluting with the THF gradient.

Identified formulation components may also be quantitatively analyzed using reverse phase techniques. Reverse phase LC is especially appropriate for DICY analysis. DICY elutes as an unretained component when injected as a (50/50) $H_2O$/THF solution onto μ-bondapak $C_{18}$ with $H_2O$ as the eluent (Figure 10). DICY's peculiar solubility and elution behavior may be a consequence of its ionic structure and its tendency to associate (1). A linear calibration is obtained using an RI detector when sample mass is plotted versus integrated peak area. The calibration constant (slope) is K = 175.1 ± 1.5 μV-sec/μg. The sample mass

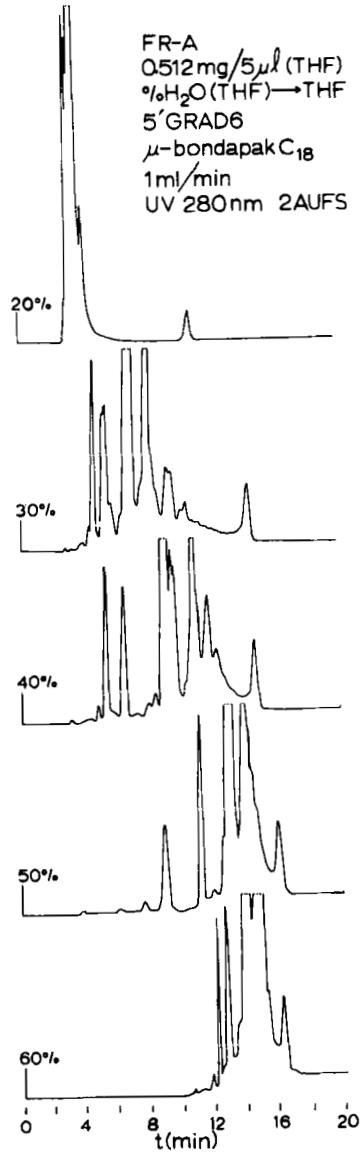



FIGURE 8

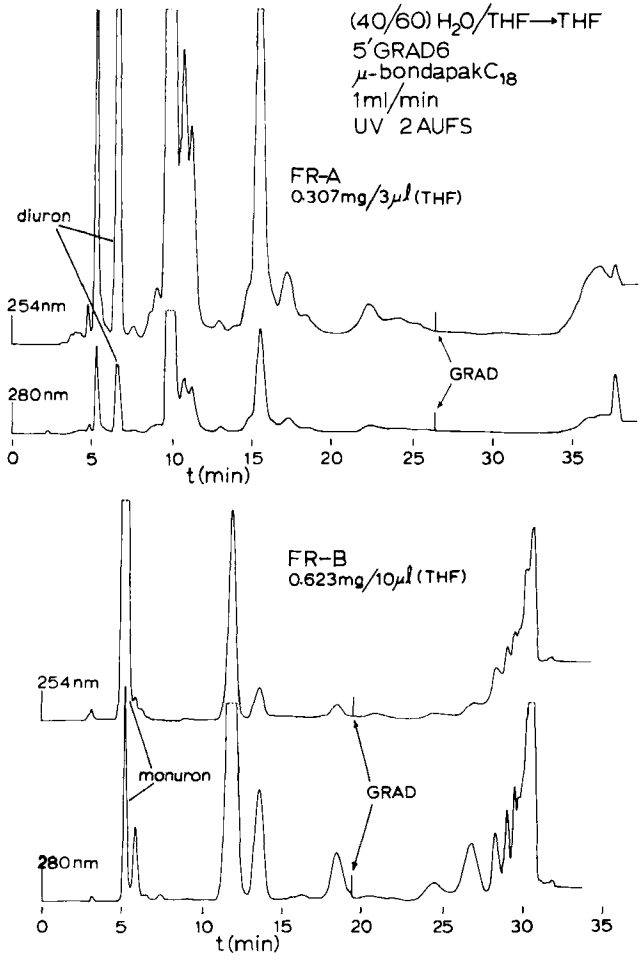



FIGURE 9

0.32 mg indicated for the FR-A-S2 prepreg in Figure 10 is the mass of the unextracted prepreg. Glass fiber content is determined separately by pyrolysis and is included as a weight fraction $f_{glass}$ in the equation

$$\% \text{ DICY} = \frac{(\text{DICY peak area})}{K \times (\text{prepreg mass}) \times (1 - f_{glass})} \times 100\%$$

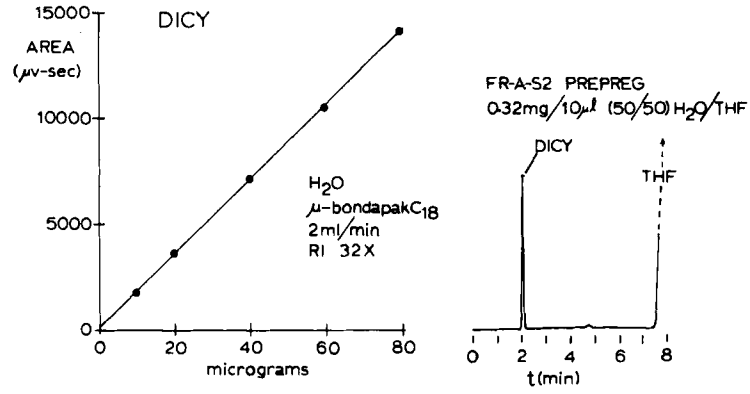



FIGURE 10



According to this method, the prepregs FR-A-S2 and FR-B-S2 consist of 29.13% and 38.02% formulated resin of which 3.5% and 7.4%, respectively, is DICY.

## APPLICATIONS

The normal phase LC method was used to quantitatively analyze resin and accelerator compositions in the formulated resins and prepreg extracts. Calibration curves were run just prior to analysis. Good agreement of k' and $A_{254}/A_{280}$ values of sample components with their respective standard values guaranteed that the proper peaks were being evaluated and that no unresolved impurities were present in the peaks. The 254nm UV detector was used to monitor all components except EPON 828 which was monitored at 280 nm. Analysis revealed that the E-glass fiber prepreg FR-A-E contains considerably more MY720 resin than either the FR-A formulation or the S2-glass prepreg. Also, FR-B-E has about 30% more monuron accelerator than FR-B. Such differences could significantly affect prepreg processability and ultimate composite properties.

TABLE 2

Formulated Resin and Prepreg Extract Analysis

| sample | component MY720 | weight -% diuron |
|---|---|---|
| FR-A | 69.1±1.1 | 2.07±0.05 |
| FR-A-S2 | 68.5 | 1.99 |
| FR-A-E | 83.7 | 2.15 |
| | EPON 828 | monuron |
| FR-B | 29.6±0.5 | 3.14±0.04 |
| FR-B-S2 | 32.8 | 3.05 |
| FR-B-E | 30.2 | 4.08 |



Prepregs from batches which produced acceptable and unacceptable composites were fingerprinted and analyzed by reverse phase LC. Equivalent prepreg solutions were prepared using 0.830 g samples in 25-ml volumetric flasks with THF as the solvent. After several hours of vigorous mixing, the solutions were centrifuged, filtered, and analyzed. Fingerprints obtained for a standard-good prepreg and an unacceptable prepreg are compared in Figure 11. Several differences are evident. First, the relative amounts of TGMDA and diuron are much less in the unacceptable prepreg (TABLE 3). Unacceptable prepregs are found to have over 60% less TGMDA and 33% less diuron than the standard-good prepreg. However, prepregs may have almost 40% less TGMDA than the standard and still be acceptable. It is also noted in comparing fingerprints that the relative areas of peaks in the unacceptable prepreg are markedly smaller at higher retention times (e.g., 10.6, 11.3, and 11.7 minutes) and larger at lower retention times (5.2, 5.7, and 6.4 minutes) than in the standard-good prepreg. The fingerprints are highly reproducible and the method is proven to be reliable for the quality control of FR-A-S2 prepregs.

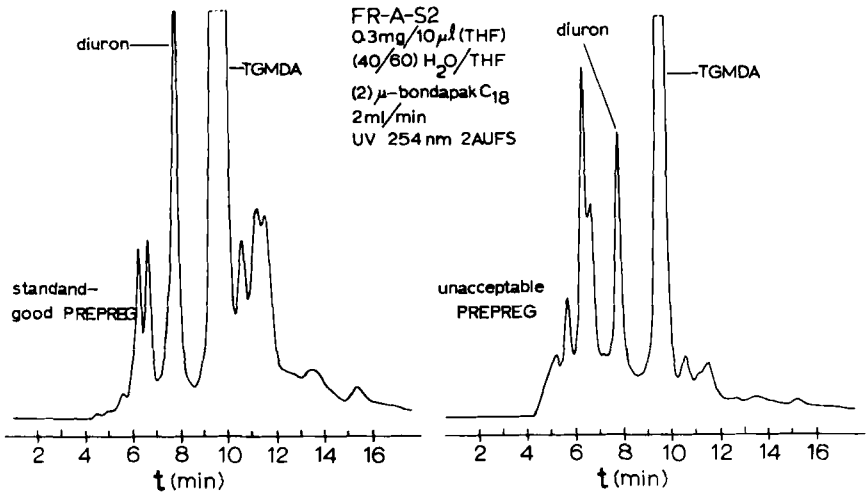



FIGURE 11

TABLE 3

LC Analysis of FR-A-S2 Prepregs

| sample | weight fraction with respect to component in standard prepreg: TGMDA | diuron |
|---|---|---|
| Standard-Good Prepreg | 1 | 1 |
| Acceptable Prepreg (stored 4 months at room temperature) | 0.75 | 1.0 |
| Acceptable Prepreg (stored 2 months in freezer) | 0.61 | 1.0 |
| Unacceptable Prepreg ("boardy" after 3 months storage in freezer) | 0.36 | 0.67 |
| Unacceptable Prepreg ("boardy" after 9 months storage in freezer) | 0.32 | 0.67 |

## ACKNOWLEDGEMENTS

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