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EVALUATION OF NEW TECHNIQUES FOR THE QUALITY CONTROL OF EPOXY R--ETC(U)
JAN 78 G L HAGNAUER, J F SPROUSE, R E SACHER

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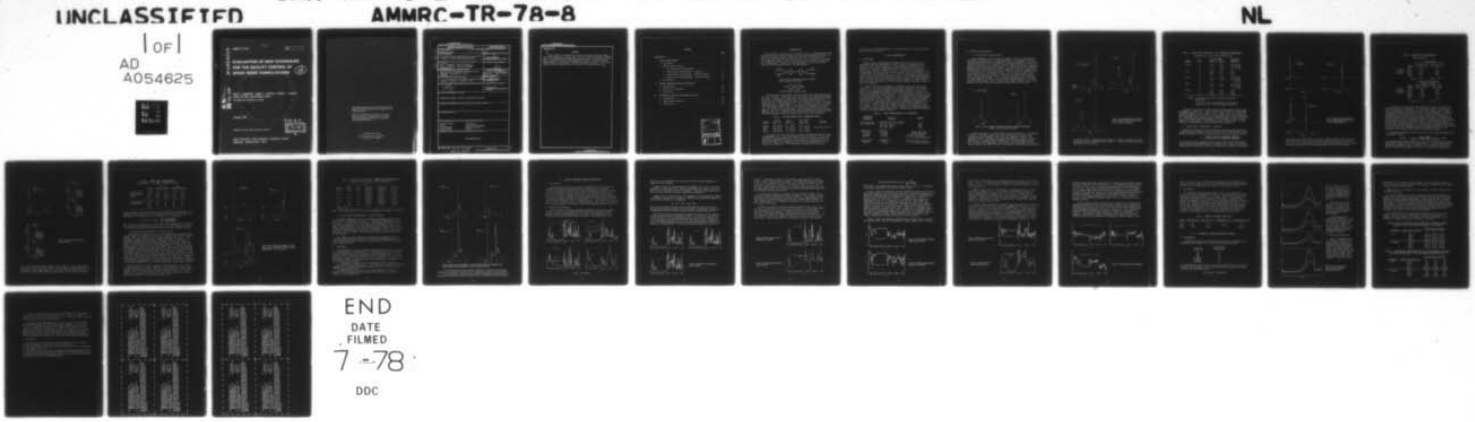

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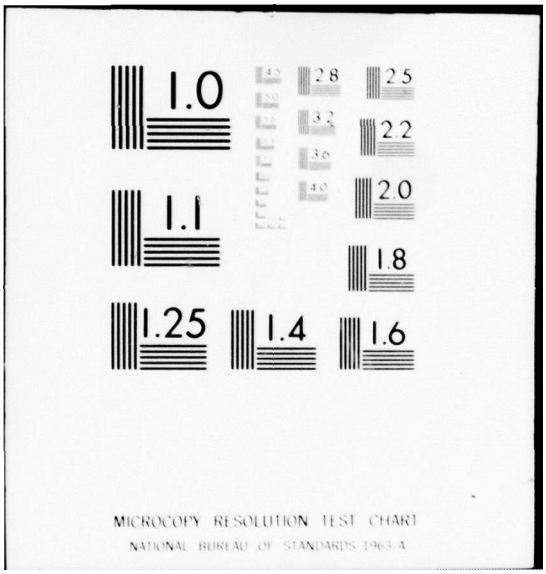
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EVALUATION OF NEW TECHNIQUES FOR THE QUALITY CONTROL OF EPOXY RESIN FORMULATIONS

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GARY L. HAGNAUER, JAMES F. SPROUSE, ROBERT E. SACHER, ISAAC SETTON, and MICHAEL WOOD

POLYMER AND CHEMISTRY DIVISION

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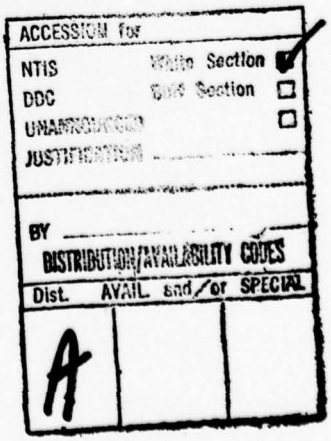
ABSTRACT

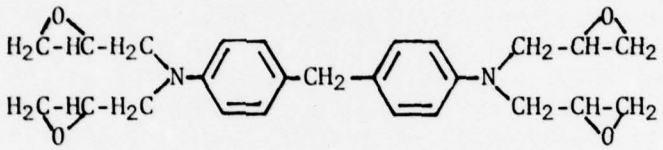
Three different techniques are utilized to assess chemical composition and/or degree of B-staging for four resin samples containing an MY720 resin, a diaminodiphenylsulfone (DDS) hardener and a BF_3 complex catalyst. These techniques are liquid chromatography, Fourier transform infrared spectroscopy, and differential scanning calorimetry analysis. These techniques and their applicability are discussed in separate sections.

CONTENTS

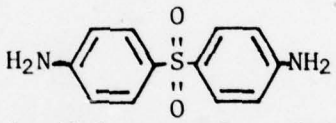


INTRODUCTION

Resin samples each consisting of an MY720 resin, a diaminodiphenylsulfone (DDS) hardener and a BF_3:MEA (boron trifluoride monoethylamine) catalyst, but varying in composition and/or degree of B-staging, were formulated and distributed by Lockheed Missiles and Space Co., Inc., Sunnyvale, CA, as part of a round-robin effort to assess test methods for defining and controlling resin formulations. Lockheed also provided samples of the actual MY720 resin and the DDS hardener used in the formulations.



tetraglycidyl methylene dianiline (TGMDA)
(main component of MY720)



diaminodiphenylsulfone (DDS)

In formulating, fixed amounts of MY720 and DDS were heated and mixed at 135 C for 2 minutes. This mixture was then cooled to 85 C whereupon BF_3:MEA was added. B-staging was accomplished by allowing the formulation to remain at 80 C for an extended period of time. The actual proportions of the components used in the formulations are given in Table 1 in parts per hundred resin (pph) and in weight percent (%). No precautions were taken to refrigerate the samples during transit. Upon receipt, the samples were stored at -15 C and removed only for sampling. It was considered likely that some degree of reaction or staging occurred during the mixing process and catalyst addition, and it was conceivable that further compositional changes may have resulted, depending on handling during transit and in the laboratory.

Table 1. INITIAL COMPOSITIONS OF FORMULATED RESINS

SAMPLE	MY720 pph	MY720 (%)	DDS pph	DDS (%)	BF_3 Complex pph	BF_3 Complex (%)	STAGING
254-1A	100	(70.4)	40	(28.1)	2.14	(1.51)	-
254-1	100	(70.4)	40	(28.1)	2.14	(1.51)	60 minutes at 80 C
254-2	100	(68.0)	45	(30.6)	2.14	(1.45)	-
254-3	100	(70.9)	40	(28.4)	1.07	(0.76)	-

The objective of this work was to evaluate the applicability of liquid chromatography (LC), Fourier transform infrared spectroscopy (FTS-IR), and differential scanning calorimetry (DSC) as quality control techniques for monitoring composition variations in the epoxy resin formulations and to measure the extent of B-staging that the resin has undergone prior to its final use or application. The experiments performed and results and

discussions are presented separately for each technique. Conclusions appear at the end of each section.

I. LIQUID CHROMATOGRAPHY

A. Experimental

Various liquid chromatographic techniques were utilized not only to fingerprint chemical composition but also to monitor and quantitatively analyze specific sample components. These techniques included (1) gel permeation or exclusion chromatography (GPC) which separates components on the basis of their molar volume or "size" in solution; (2) normal-phase chromatography where a relatively nonpolar eluent is used in conjunction with a highly polar packing material, e.g., silica, to facilitate molecular separation usually on the basis of polarity; and (3) reverse-phase chromatography which requires the use of a polar solvent with a rather low polarity packing, such as an alkylated silica or bonded-phase C_{18} column. To reduce analysis time and improve resolution, isocratic solvent mixtures and solvent gradients were also employed.

A Waters ALC/GPC-244 instrument, with M6000A solvent delivery system, U6K injector, 660 solvent programmer and 440 dual wavelength UV absorbance detector, was used for the liquid chromatographic analyses. Distilled in glass 2,2,4-trimethylpentane (C8) was obtained from Burdick & Jackson Labs. Tetrahydrofuran (THF), chloroform ($CHCl_3$), and water were distilled just prior to solution preparation and LC analysis. All solvents were filtered through 0.45-μ Millipore filters. Solutions of the formulated resins were prepared by weighing about 200 mg of sample in a 25-ml volumetric flask and adding THF (8 μg/μl). More dilute solutions were then prepared by pipeting 5 ml of the 8-μg/μl solutions into 100-ml volumetric flasks and diluting with THF (0.4 μg/μl). The MY720 and DDS standard solutions were prepared in a similar manner. Actual sample mass, injection volume, and LC operating parameters are indicated on each chromatogram. Standard test conditions developed for this work are described in Table 2.

Table 2. LIQUID CHROMATOGRAPHY TEST CONDITIONS

SEPARATION MECHANISM	COLUMN(S)	SOLVENT
Size separation (gel permeation)	μ-Styragel (30 cm × 7.8 mm ID)	
	10^3, 500, 500, 100, 100 Å	THF
	500, 100, 100 Å	THF
	10^3, 500, 500 Å	$CHCl_3$
Normal phase	μ-Porasil	
isocratic	3 columns	(50/50) $CHCl_3$/THF
isocratic	1 column	(50/50) $CHCl_3$/THF
gradient	3 columns	(60/40) C8/THF→THF, 30 min convex gradient 7
Reverse phase	μ-Bondapak C_{18}	
gradient	2 columns	(70/30)→(20/80) H_2O/THF, 20 min linear gradient 6

B. Results and Discussion

1. Gel Permeation Chromatography

A major advantage of GPC for quality control is that, in the absence of adsorption and intermolecular association effects, the separation provides an unambiguous measure of a distinguishable molecular parameter, molar volume. Complete resolution of MY720 and DDS is achieved when chloroform is used as the eluent with μ-Styragel columns (Figure 1). MY720 has two major components, probably the monomer and dimer of TGMDA. The smaller peak due to the higher MW component(s) of MY720 is observed to broaden and shift to a slightly lower elution volume in the formulated samples. DDS has one major component which is observed to elute after MY720 in accord with its smaller molar volume. Quite different UV peak absorbance ratios are observed for MY720 A_{280}/A_{254} = 0.354, and for DDS A_{280}/A_{254} = 1.36. Based on the peak heights of DDS and the major component of MY720, calculated weight percentages are 65.3% MY720 and 23.3% DDS in sample 254-1A. These values compare favorably with results obtained by normal phase chromatography discussed in a later section.

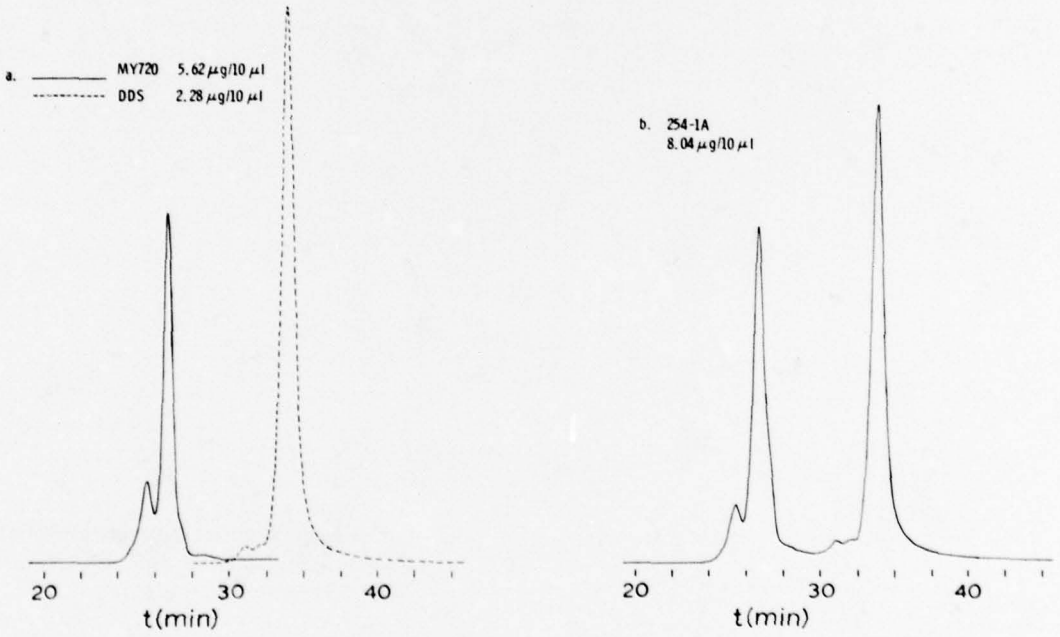


Figure 1. GPC chromatograms with $CHCl_3$ as the eluent: μ-Styragel 10^3, 500, 500 Å; $CHCl_3$, 1 ml/min; UV, 280 nm, 0.2 AUFS.

Solvent selection is a critical factor in the GPC analysis. For example, when THF is the eluent (Figure 2), MY720 and DDS are not resolved; DDS overlaps and elutes slightly before the major component of MY720. The behavior of DDS is anomalous and suggests that DDS may be highly solvated in THF solution. Although complete resolution of the MY720 components from DDS is desirable for unambiguous interpretation and quantitative analysis, GPC with THF as the eluent still may be utilized as a fingerprinting technique

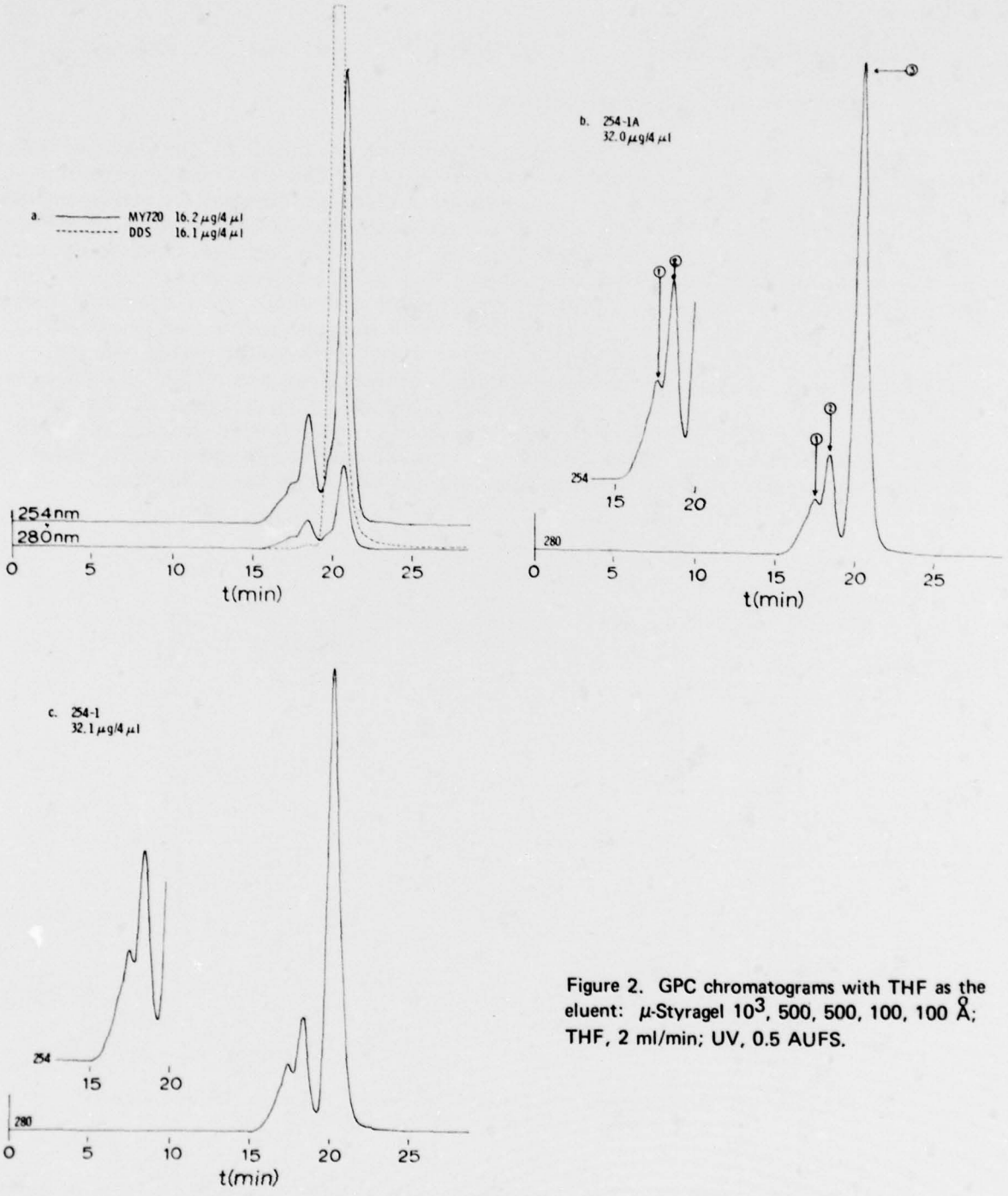


Figure 2. GPC chromatograms with THF as the eluent: μ-Styragel 10^3, 500, 500, 100, 100 Å; THF, 2 ml/min; UV, 0.5 AUFS.

in quality control. Labelling elution peaks 1, 2, and 3 in order of increasing elution volume, comparisons may be made of relative peak heights and peak absorbance ratios (Table 3).

Table 3. PEAK HEIGHTS AND RATIOS – GEL PERMEATION CHROMATOGRAPHY

μ-Styragel THF 2 ml/min (UV 254 and 280 nm)

SAMPLE	PEAK	PEAK MAXIMUM 254 nm	PEAK MAXIMUM 280 nm	PEAK RATIO A280/A254
254-1A	1	1.67	0.92	0.55 (0.54)
	2	3.34	1.66	0.50 (0.50)
	3	--	8.26	-- (0.86)
254-1	1	1.84	1.13	0.61
	2	3.51	1.9	0.54
	3	9.51	7.8	0.82
254-2	1	1.6	0.91	0.57 (0.56)
	2	3.26	1.68	0.52 (0.52)
	3	--	--	-- (0.93)
254-3	1	1.5	0.77	0.51 (0.52)
	2	3.29	1.52	0.46 (0.48)
	3	--	--	-- (0.90)
MY720	1	1.4	0.4	0.29
	2	3.64	0.92	0.25
	3	15.24	2.8	0.18

NOTE: Peak maxima which were off-scale are denoted by hyphens.

Peak ratio values in parentheses were obtained using a 500, 100, 100 Å μ-Styragel column set.

Changes in the relative height of peak 3 reflect reactant changes due to staging and excess DDS. A mixture of reaction products as well as MY720 components probably elute as peaks 1 and 2. Peaks 1 and 2 are largest for the staged sample 254-1 and smallest for the sample 254-3 with low catalyst. Peak absorbance ratio A_{280}/A_{254} values provide a measure of peak composition, e.g., the relatively greater abundance of the DDS moiety in peak 3 as compared to the other peaks. The absorbance ratios of peaks 1 and 2 are also sensitive to B-staging and increase as DDS reacts with MY720.

2. Normal Phase Chromatography - Isocratic

MY720 and DDS are fully resolved and may be quantitatively analyzed by normal phase chromatography run isocratically with a 50/50 THF/$CHCl_3$ solvent mixture (Figure 3). For the 3-column μ-Porasil system the capacity factor

$$k' = \frac{\text{elution time of an adsorbed component}}{\text{elution time of an unadsorbed component}} - 1$$

is 0.19 for the main component of MY720 (peak 1) and 1.56 for DDS (peak 2). The broad peak eluting approximately 33 minutes after sample injection most likely represents products formed during formulation, staging, and handling.

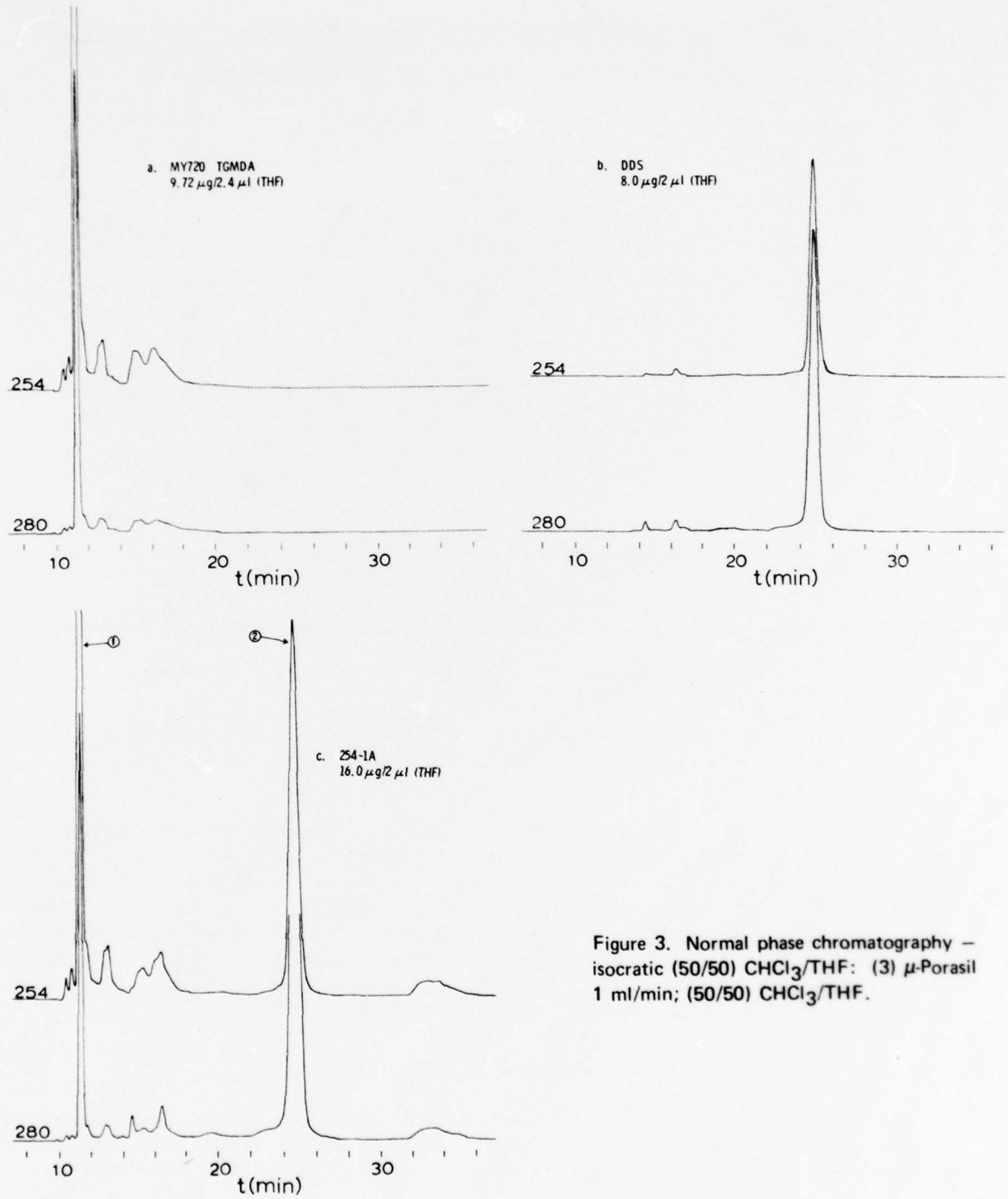


Figure 3. Normal phase chromatography – isocratic (50/50) $CHCl_3$/THF: (3) μ-Porasil 1 ml/min; (50/50) $CHCl_3$/THF.

The sample peak heights (Table 4) relate to expected compositional variations in MY720 and DDS. It is also noted that the absorbance ratios for peaks 1 and 2 are in good agreement with the respective standard values, which suggests that reaction products in the formulated samples are eluting elsewhere.

Table 4. NORMAL PHASE CHROMATOGRAPHY

50/50 THF/$CHCl_3$

		PEAK HEIGHTS	
	SAMPLE	Peak 1, 280 nm MY720	Peak 2, 254 nm DDS
3 columns,	254-1A	7.15	6.32
μ-Porasil	254-1	6.90	5.88
1 ml/min	254-2	6.91	6.65
	254-3	8.0	6.95
		k'_{MY720} = 0.19	k'_{DDS} = 1.56

		AVERAGE PEAK ABSORBANCE RATIOS A_{280}/A_{254}	
	SAMPLE	Peak 1, MY720	Peak 2, DDS
1 column,	254-1A	0.262	1.49
μ-Porasil	254-1	.259	1.48
2 ml/min	254-2	.259	1.52
	254-3	.261	1.50
	MY720	.260	-
	DDS	-	1.46
		k'_{MY720} = 0.10	k'_{DDS} = 1.24

To optimize the technique for the quantitative analysis of MY720 and DDS by the method of peak heights, the following conditions were required: (1) full separation of components, (2) narrow peak widths, and (3) large displacement of peak maxima from baseline. These requirements were achieved by adjusting the $CHCl_3$/THF solvent ratio and increasing flow rate, while minimizing solution concentration and increasing detector sensitivity. To minimize impurity effects, calibration curves were based on the same MY720 and DDS material used to prepare the samples. Calibration data were obtained by successive injections of different volumes of the standard solutions. In all the calibration plots (Figure 4), the intercepts are greater than zero, possibly due to other components besides MY720 and DDS present in the standards. It is also noted that weighing and solution preparation errors are not included in the variance of the calibration constants (slope).

The weight percentages of MY720 and of DDS in the formulated samples were calculated as follows

$$\text{weight \%} = \frac{\text{(peak height)}}{\text{(slope)} \times \text{(sample mass injected)}} \times 100\%$$

for component peak heights determined at the same UV wavelength and detector sensitivity settings as used for standardization. From the least-squares analysis of calibration data, the error in the calibration constants are about ±2% for MY720 and about ±4% for DDS. These errors are reflected in

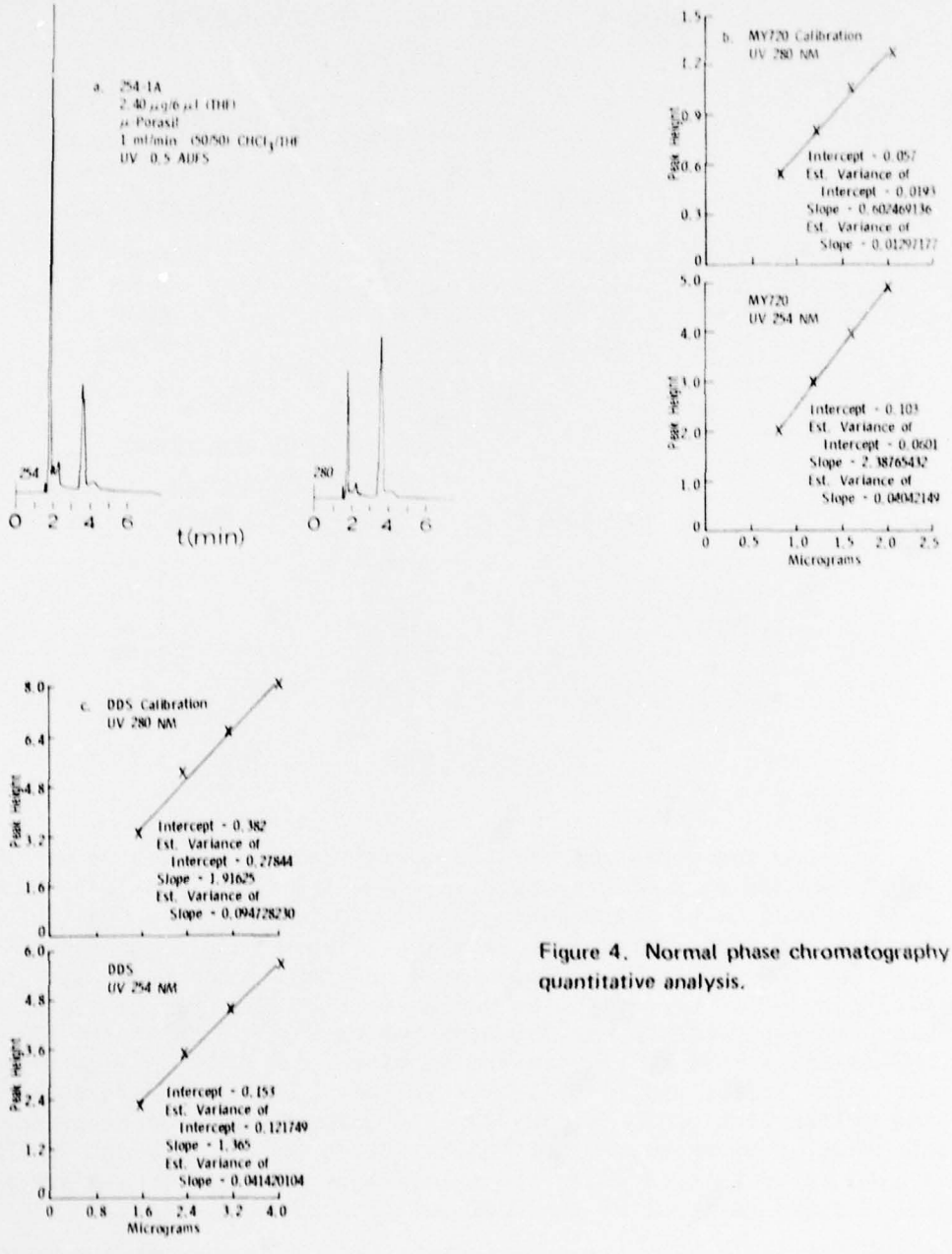


Figure 4. Normal phase chromatography – quantitative analysis.

the calculated weight percent values shown in Table 5. The standard sample 254-1A has 6% to 8% less MY720 and 2% to 4% less DDS by weight than used in formulation. The staged sample 254-1 has 10% to 12% less MY720 and 6% to 7% less DDS by weight. These compositional changes are the result of chemical

Table 5. NORMAL PHASE CHROMATOGRAPHY
50/50 THF/CHC_3 — 1 Column, μ-Porasil 2 ml/min

		MY720		DDS	
	SAMPLE	254 nm	280 nm	254 nm	280 nm
Weight Percent in Formulated Sample	254-1A	62.0	64.2	24.2	25.8
	254-1	58.8	60.5	22.2	23.5
	254-2	58.9	60.4	26.2	28.1
	254-3	66.3	68.4	25.6	27.3
Percent Reaction of Components	254-1A	12	9	14	8
	254-1	16	14	21	16
	254-2	13	11	14	8
	254-3	6	4	10	4

reactions and/or staging taking place during formulation and handling. Less change occurred in the case of 254-3 which had a lower initial catalyst concentration. The percent reaction of components was calculated as

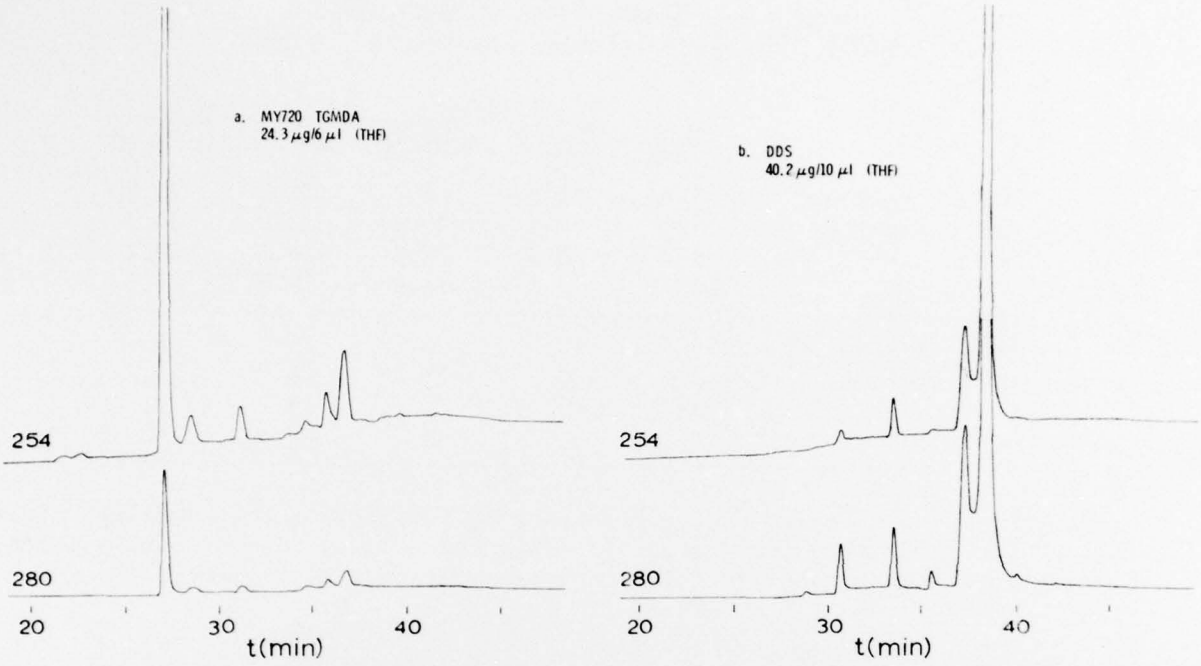
$$\% \text{ reaction} = 100\% \left(1 - \frac{(\text{wt\% calculated})}{(\text{wt\% formulated})}\right).$$

This data is of interest since it shows that within experimental error about the same amount of MY720 has reacted as DDS. This result suggests that the 1:1 reaction of MY720 with DDS functional groups was the dominant reaction.

3. Normal Phase Chromatography - Solvent Gradient

A much improved separation was achieved using gradient elution chromatography (Figure 5). Capacity factors k', peak heights, and absorbance ratios A_{280}/A_{254} are given for at least five sample components in Table 6. Peak 1 represents the major MY720 component (TGMDA) while peak 2 represents a secondary component, possibly an isomer, of DDS. The relative heights of peaks 1 and 2 correlate with expected compositional variations in the 254 samples. Peak 3 is not evident in the chromatograms of either MY720 or DDS and therefore may be due to a reaction product. Since the 280-nm absorbance of DDS tends to swamp and attenuate peak 3, the peak is poorly resolved and its A_{280}/A_{254} value may be overly large. Peak 3 does not correlate well with anticipated changes in peak heights for either reactants or products. Peaks 4 and 5 are not present in the chromatograms of MY720 and DDS. The peaks are fairly well resolved and their heights correlate with the relative amounts of reaction products that might have been created during formulation, staging, and handling. Furthermore, the absorbance peak ratio values (0.70 to 0.81) are in the range expected for the 1:1 reaction product(s) between DDS and MY720.

Better resolution of reaction products can be achieved if the initial solvent composition is richer in THF, e.g., (50/50) C8/THF, using the same gradient profile and run time. Gradient elution C8/THF normal phase chromatography seems to be an excellent method for quality control. The method allows one to quantitatively analyze the depletion of reactants as well as monitor the amounts of various products being formed.



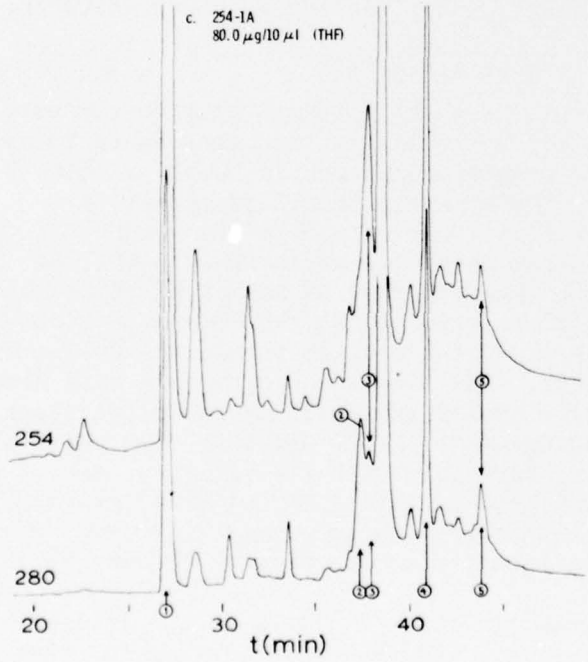


Figure 5. Normal phase chromatography – C8/THF solvent gradient: (3) μ-Porasil; 1 ml/min 30'GRAD7; (60/40) C8/THF → THF; UV, 2 AUFS.

Table 6. PEAK HEIGHTS AND RATIOS — NORMAL PHASE CHROMATOGRAPHY
μ-Porasil C8/THF Gradient (UV 254 and 280 nm)

	PEAK				
	1	2	3	4	5
SAMPLE	(280)	(280)	(280/254)	(280/254)	(280/254)
254-1A	6.1	2.3	1.83/4.0 (0.46)	5.32/7.43 (0.72)	1.33/1.7 (0.78)
254-1	5.46	2.23	1.79/4.12 (0.43)	6.12/8.7 (0.71)	1.77/2.18 (0.81)
254-2	5.67	2.91	1.96/4.42 (0.44)	5.38/7.57 (0.71)	1.3/1.65 (0.79)
254-3	6.47	2.45	2.0/5.0 (0.40)	4.55/6.51 (0.70)	0.73/1.24 (0.75)
k'	1.92	2.93	2.97	3.27	3.58

$k'_{DDS} = 3.01$

NOTE: Peak height (280/254) ratios are in parentheses for peaks 3, 4, and 5.

4. Reverse Phase Chromatography - Solvent Gradient

Excellent separations were also obtained using gradient elution with reverse phase chromatography (Figure 6). For the main components of MY720 and DDS, k' = 2.77 and 1.47, respectively. Additional peaks appear in the 254 sample chromatograms that are evident neither in MY720 nor in DDS. Most likely, these peaks represent reaction products formed during formulation, staging, and/or handling. The components appearing 25 minutes after injection are poorly resolved; however, the peak at 24 minutes is well resolved and variations in size correlate with anticipated trends in product amounts for the four samples.

More recent work has shown that modifications in gradient conditions result in improved product separation. Reverse phase chromatography is a viable technique for quality control and quantitative analysis of the epoxy resin staging reaction.

C. Conclusions

The feasibility of using LC techniques for the quality control of epoxy resin formulations has been demonstrated. Improvements in the LC separation of resin components are still possible. Electronic integrators and other detectors (e.g., differential refractometer and infrared) should improve the quantitative analysis and detectability of resin components. In applying LC as a quality control technique for epoxy resin formulations (prepregs), future efforts should include:

(1) developing a standard set of LC operating and test procedures;

(2) evaluating the reproducibility of LC results as obtained in different laboratories on standard formulations (without BF_3 catalyst?) using such standard operating conditions;

(3) determining the reliability of LC, particularly with respect to detecting and distinguishing between impurities, additives, or chemical changes in resin formulations;

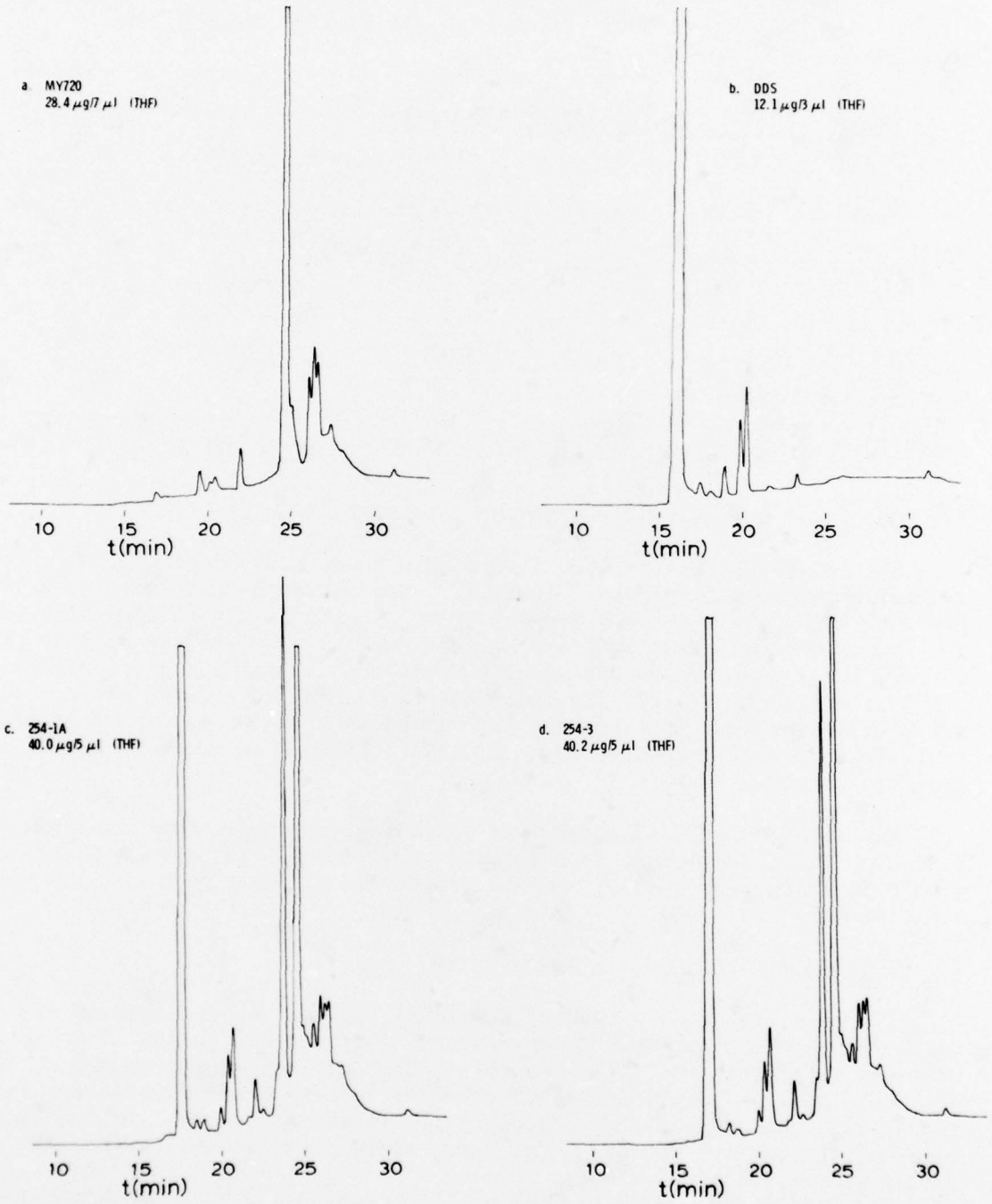


Figure 6. Reverse phase chromatography – H_2O/THF solvent gradient: (2) μ-Bondapak C_{18}; 70/30 → 20/80 (H_2O/THF; 20'GRAD6 1 ml/min; UV, 280 nm, 0.5 AUFS.

(4) developing quantitative analysis methods to accurately measure the amounts and variations of specific resin components utilizing *pure* standards;

(5) establishing an overall resin supplier-prepregger-user philosophy regarding the capabilities and limitations of LC as a quality control technique.

II. FOURIER TRANSFORM INFRARED SPECTROSCOPY

A. Experimental

A Digilab Model FTS-10M stored-ratio spectrometer was used for Fourier transform infrared spectroscopy (FTS-IR) to analyze the resin samples. Spectra were measured on thin films of resin spread onto a salt plate. Thin films were prepared by warming a salt plate on a heated microscope stage held at 50 C, placing a small drop of resin onto the plate, then spreading it into a thin film. No effort was made to produce identical film thicknesses from sample to sample although the film thickness was always adjusted to keep the absorbance between 0.5 and 1.0 absorbance units. All spectra were measured at 4 cm^{-1} resolution using 32 signal averages. The spectra were retained in the computer memory as absorbance spectra for computing difference spectra.

B. Results and Discussion

Figure 7a shows an infrared absorbance spectrum for the control sample 254-1A: Figure 7b, a spectrum for MY720; Figure 7c, a spectrum of DDS prepared in a KBr pellet; and Figure 7d shows the BF_3:MEA after most of the solvent had been evaporated from the sample. Superimposing the three

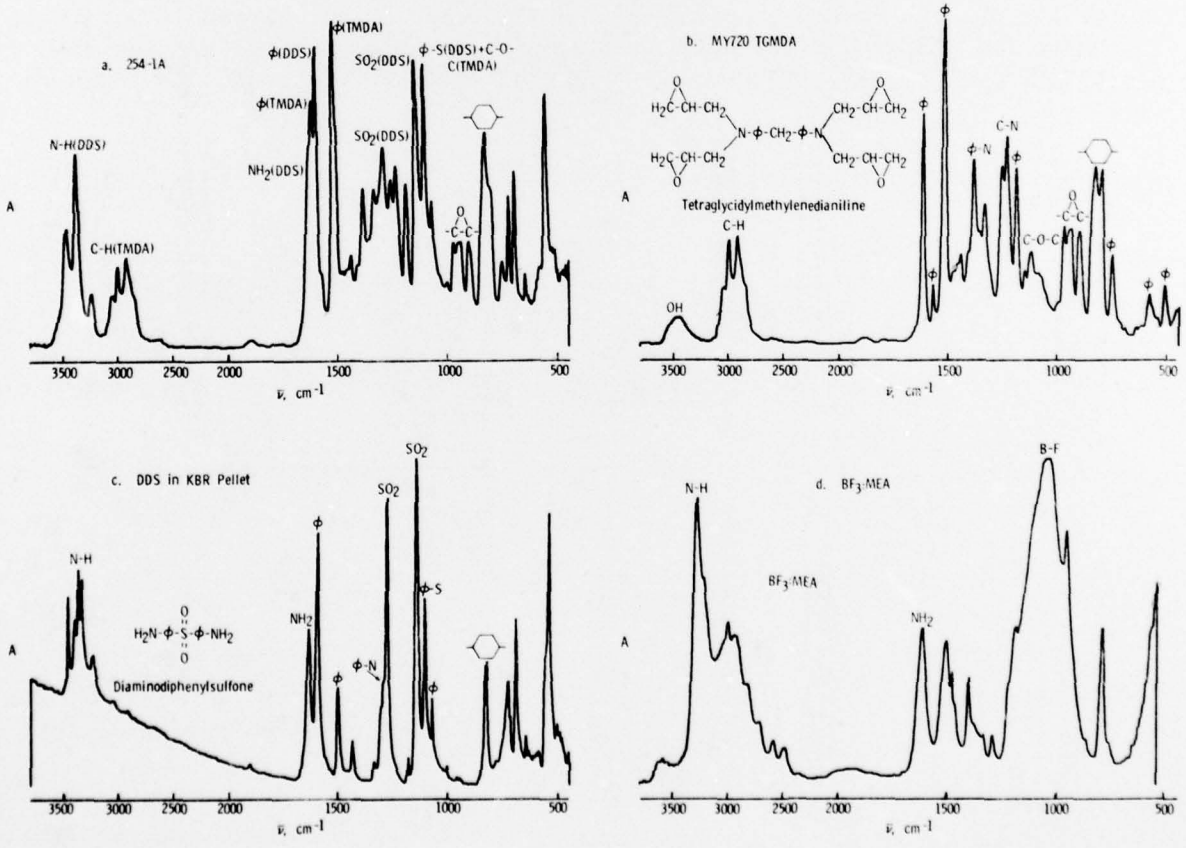


Figure 7. Infrared spectra.

spectra for the components onto each other allows the band assignments in sample 254-1A to be made.

Figure 8 shows the infrared spectra for samples 254-1, 254-2, and 254-3. Comparison of the conventional infrared fingerprints in Figures 7a and 8 do not show any differences between the samples. Therefore, difference spectra must be used to measure any small compositional variations.

Sample 254-1 was separated into its components by using difference spectra. A difference spectrum ΔA is computed by subtracting one absorbance spectrum from another according to the equation

$$\Delta A = SCA \times PFA - SCB \times PFB.$$

SCA is a mixed number scaling factor for plotting file PFA, which is the absorbance spectrum from which plotting file PFB is subtracted. PFB is also an absorbance spectrum and SCB is a mixed number scaling factor for PFB.

The initial step for separating the components in 254-1 was to subtract the MY720 spectrum from the spectrum for 254-1. Scaling factor SCA was set to one; PFA was set to the absorbance spectrum file for 254-1, PFB was set to the absorbance spectrum file for MY720, and SCB was varied in magnitude until the computed difference spectrum showed no absorbance for the 950, 940, and 905 cm^{-1} epoxide bands. The resulting difference spectrum is shown in

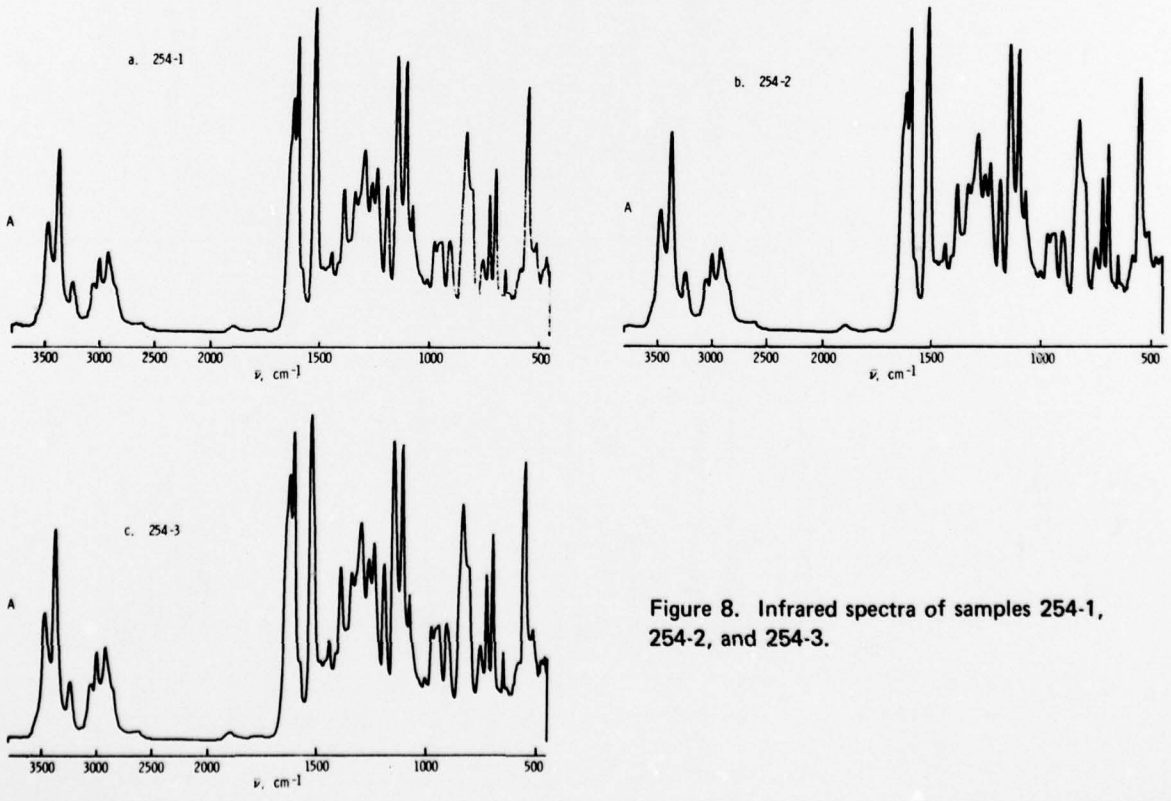


Figure 8. Infrared spectra of samples 254-1, 254-2, and 254-3.

Figure 9. Comparison of Figure 7c with Figure 9 shows the latter predominantly results from the DDS curing agent. The major differences in Figures 9 and 7c are the primary amine N-H bands which are for the crystalline form in Figure 7c and for the structure in solution in Figure 9. Also, the 1110 cm^{-1} phenyl-sulfur band appears more intense in the difference spectrum. The enhanced intensity results from an ether band which absorbs at nearly the same frequency and forms during cure.

In an attempt to detect the BF_3:MEA, the DDS spectrum in Figure 7c was subtracted from the difference spectrum in Figure 9. The resulting spectrum in Figure 10 shows the DDS bands from 1050 to 1150 cm^{-1} superimposed on the broad inorganic boron-fluorine absorption band. The BF_3:MEA is present in such a small amount it is difficult to distinguish its bands from the baseline under the DDS bands.

In order to measure the difference between samples 254-1A, 254-1, 254-2, and 254-3 the spectrum for each was subtracted from the control sample 254-1A. The scaling factor for each of the samples was based on the individual 1510 cm^{-1} phenyl band absorbance. Each scaling factor was determined by measuring the minimum and maximum absorbance between 2000 and 1450 cm^{-1}. The two inflection points were computed automatically using the data system of the FTS-10M. Each scaling factor was calculated according to the equation

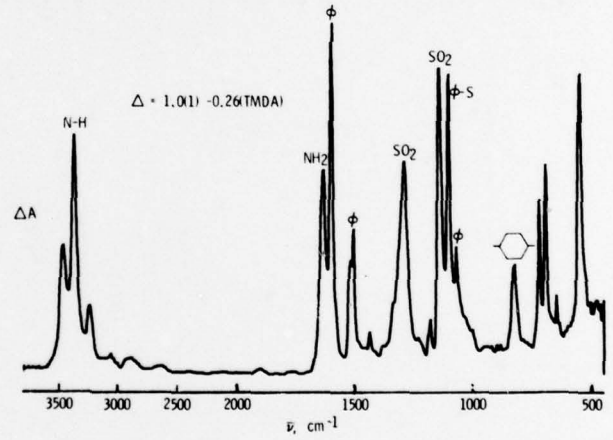


Figure 9. Difference spectrum between sample 254-1 and TGMDA.

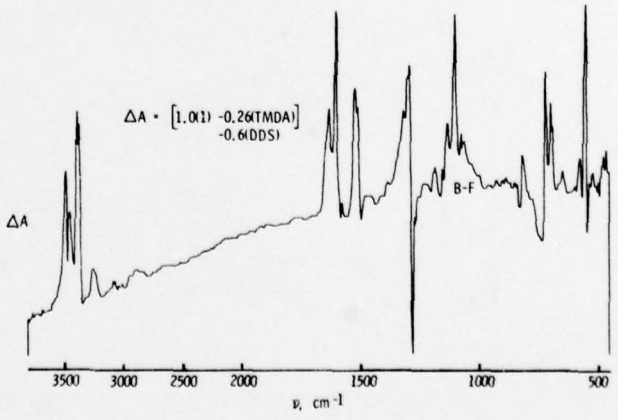


Figure 10. Difference spectrum between Figure 9 and DDS.

$$\text{SCALING FACTOR (SCA or SCB)} = \frac{100}{\text{YMAX - YMIN}},$$

where YMAX is the maximum absorbance between 2000 and 1450 cm^{-1}, and YMIN is the minimum absorbance in the same wave number region.

Figure 11 shows the difference spectrum computed between 254-1A and 254-1. Bands going negative from the baseline indicate a greater concentration of a particular functional group in samples 254-1 than in 254-1A. Examination of Figure 11 shows OH formation has occurred in sample 254-1. There is 17.7 percent more OH in 254-1 than in 254-1A. A baseline shift occurred at approximately 1700 cm^{-1} as indicated by the 1500 cm^{-1} region where the difference between the two spectra was approximately zero. Only a small change had occurred in the amine bands, therefore the DDS concentrations in samples 254-1A and 254-1 were nearly equal. There was 10.5 percent more epoxide absorbance in sample 254-1A than in sample 254-1, therefore showing more curing had occurred in sample 254-1. Based on the OH formation and the small loss of absorbance from the epoxide ring, it is apparent that the sample had undergone thermal staging and there was no difference in the initial compositions of resin, curing agent, and accelerator.

Figure 12 shows the difference spectrum between samples 254-1A and 254-2. The spectrum shows a greater concentration of DDS in sample 254-2. Based on

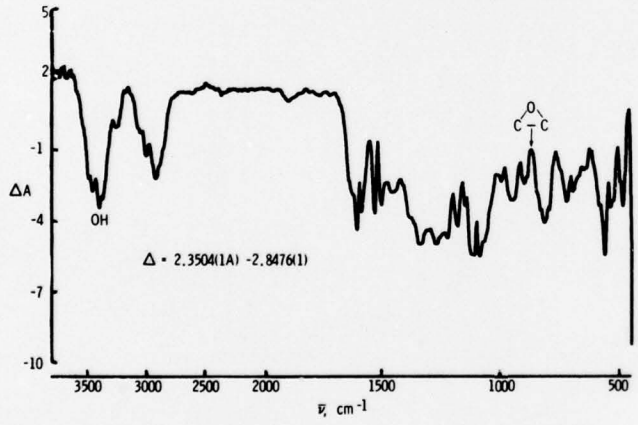


Figure 11. Difference spectrum between samples 254-1A and 254-1.

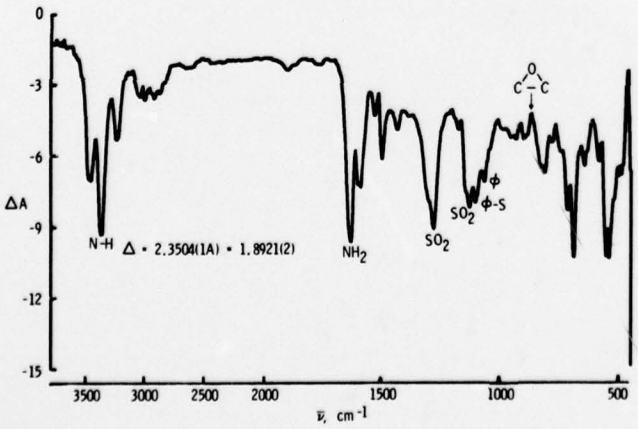


Figure 12. Difference spectrum between samples 254-1A and 254-2.

the 3370 cm^{-1} N-H band there is 9.4 percent more DDS in sample 254-2 than in 254-1A. There is 3.5 percent more absorbance for the epoxide bands in 254-1A than in 254-2. This small difference indicates curing has taken place during the mixing process.

Figure 13 shows the DDS concentration is 7.5 percent greater in sample 254-3 than in sample 254-1A. It also shows that BF_3:MEA is present in greater concentration in sample 254-1A than in 254-3. There is not an absorbance band for the BF_3:MEA that is easily isolated in Figures 7a or 8c, therefore, a numerical percentage difference cannot be calculated. A small amount of curing has also occurred in sample 254-3 as may be seen from the decrease in epoxide band absorbance.

In order to make valid band assignments during the epoxide cure reactions, and to interpret the difference spectra for samples 254-1A, 254-1, 254-2, and 254-3, a cure curve was measured for sample 254-1A. A thin film of the resin was placed on a salt plate and cured in a forced air oven using the thermal conditions given in Figure 14. The infrared spectrum is that of sample 254-1A after having undergone the thermal treatment. After raising the temperature from 30 C to 135 C at a rate of 16 C per minute, an infrared spectrum was measured. The difference spectrum in Figure 15a was computed using as a reference the uncured resin spectrum in Figure 7a. The

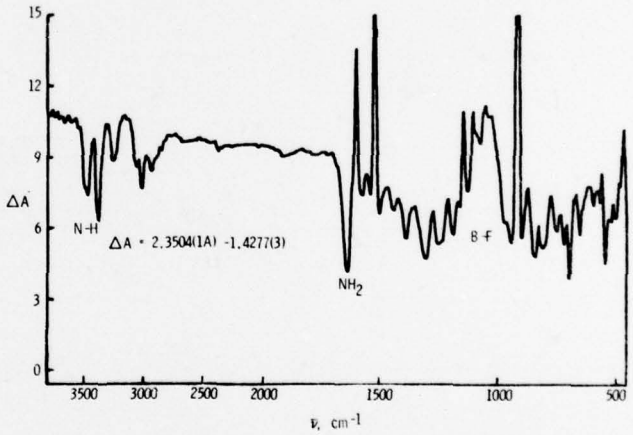


Figure 13. *Difference spectrum between samples 254-1A and 254-3.*

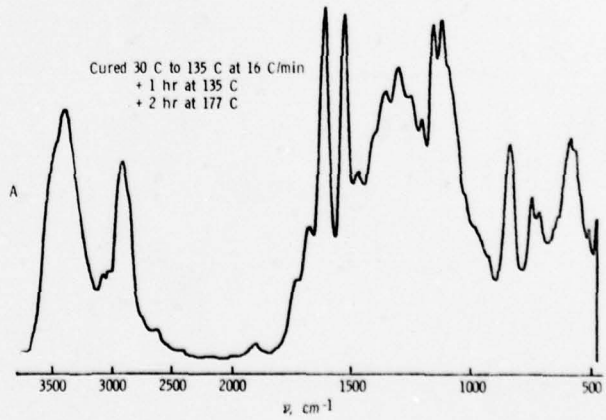


Figure 14. Infrared spectrum of sample 254-1A after curing.

difference spectrum showed a decrease in the primary amine functional groups for DDS at 3465, 3370, 3240, and 1630 cm^{-1}. This showed the curing reaction had been initiated. Also, the epoxide band absorbance started decreasing in intensity. Figure 15b, measured after one hour at 135 C, showed further loss of primary amine bands in the DDS and the formation of OH absorbance measured at the 3450 cm^{-1} region. Also, the epoxide band intensity decreased an additional amount and the aliphatic ether band became more intense at 1120 cm^{-1} indicating the presence of crosslinking. A small increase in intensity of the carbonyl absorbance band at 1720 cm^{-1} showed the onset of thermal oxidation.

Finally, after two hours of cure at 135 C (Figure 15c) considerable OH formation occurred with only small additional reaction of the primary amine. Absorbance was strong at the 1720 cm^{-1} region showing thermal oxidation had occurred during the forced air oven cure. The 1120 cm^{-1} C-O-C band showed strong absorbance suggesting an increase in amount of crosslinking had occurred. The epoxide band had decreased in intensity considerably. The changes in the amine, OH, ether, and epoxide band intensities measured during cure were used to interpret the differences between samples 254-1A,

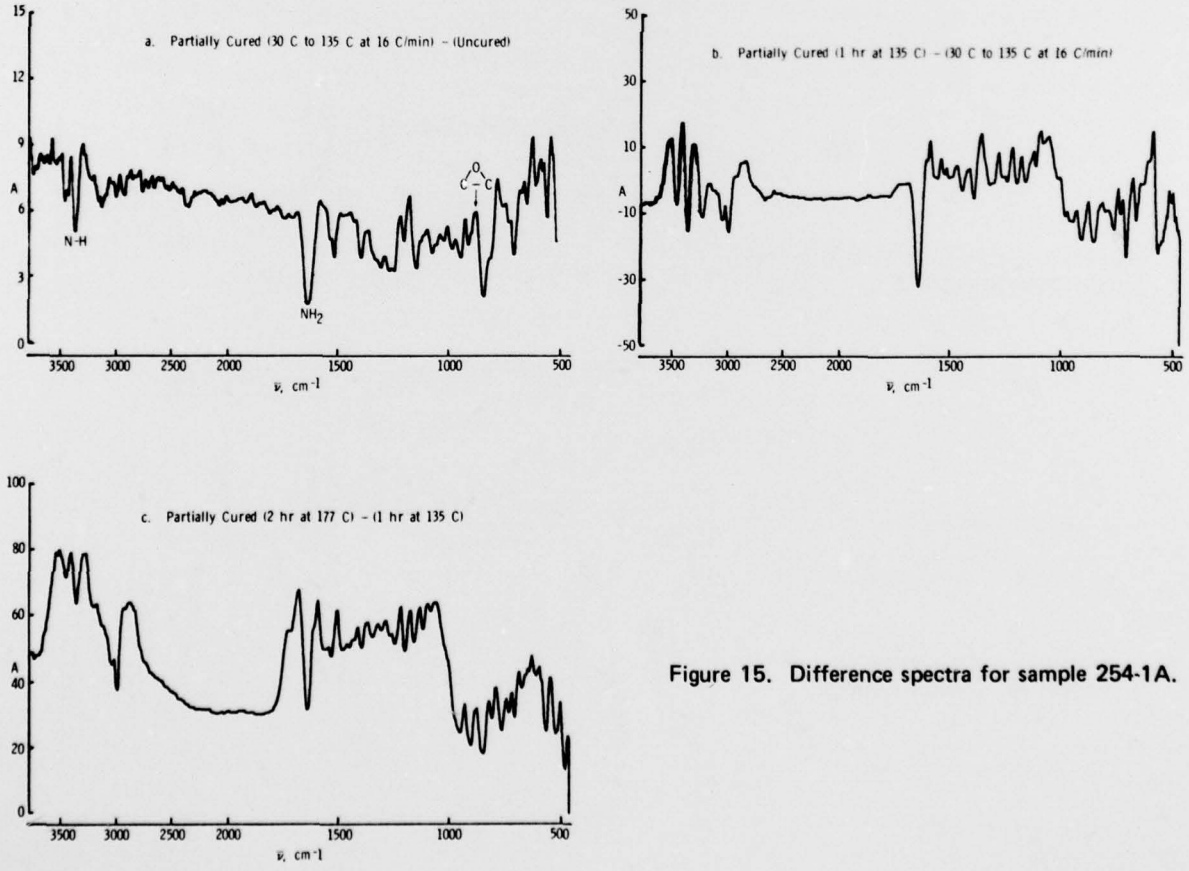


Figure 15. Difference spectra for sample 254-1A.

254-1, 254-2, and 254-3. The functional groups that were involved in the chemical reactions during cure were easily followed and the band assignments could be used for identifying band changes in the difference spectra.

C. Conclusions

The differences between samples 254-1A, 254-1, 254-2, and 254-3 as measured by FTS-IR are summarized in Table 7. FTS-IR offers a fast method for characterizing epoxy resins since infrared spectra can be measured by spreading a thin film of the resin onto a salt plate. A conventional infrared fingerprint is not useful for detecting small differences between samples, but difference spectra are required to gain useful results. FTS-IR can be used to detect resin/curing agent compositional variations quite easily, and a quantitative measure is practical when a reference standard is used for the comparisons. BF_3:MEA can be detected but a quantitative measure is not practical since an individual absorbance band cannot be isolated in the fingerprint which is attributable only to BF_3:MEA.

Table 7. PERCENT DIFFERENCE FROM 254-1A

SAMPLE	OH^-(3460 cm^{-1})	DDS(3370 cm^{-1})	EPOXIDE(950 cm^{-1})	BF_3:MEA(1050 cm^{-1})
254-1	+17.7	+1.0	-10.5	0.0
254-2	+13.7	+9.4	+ 3.5	0.0
254-3	+ 3.6	+7.5	-	<254-1A

III. DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

A. Experimental

Differential scanning calorimetry (DSC) analysis was performed on the formulations described in Table 1 under the following conditions:

Atmosphere	Heating Rate, (deg C/min)
air	5
air	10
air	20
nitrogen	5
nitrogen	10
nitrogen	20

The instrumentation utilized was a duPont 990 thermal analyzer system with a duPont cell base module. The heat of reaction (cure) ΔH was calculated utilizing the following formula:

$$\Delta H \text{ (mcal/mg)} = \frac{A}{m} (60BE\Delta qs)$$

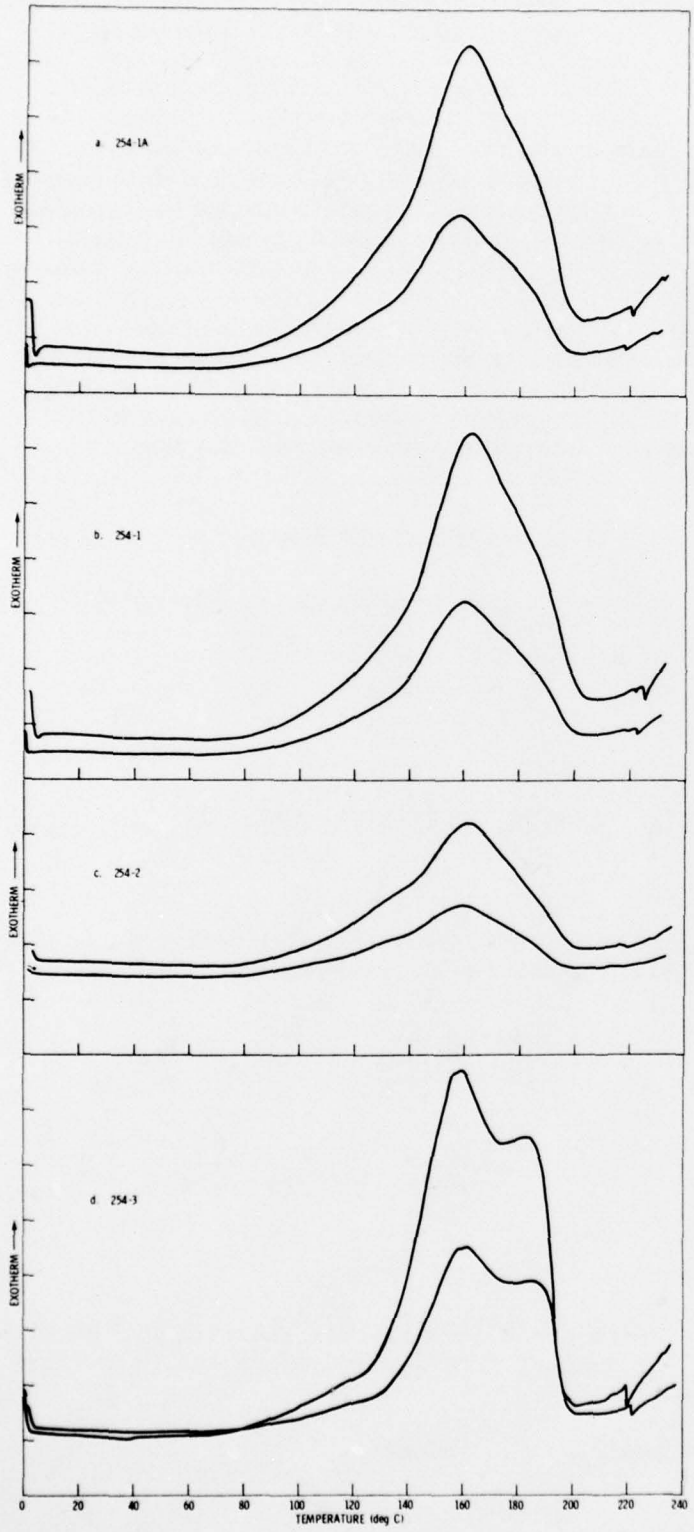


Figure 16. DSC thermograms for various samples (air atmoshere, heating rate of 5 C/min).

where A = peak area (sq in.); m = sample mass (mg); B = time base setting (min/in.); E = cell calibration coefficient at the temperature of experiment (dimensionless); Δqs = Y-axis range ((mcal/sec)/in.)

The value of E was calculated to be 0.956 using indium as a standard. The areas were obtained by digitizing the curves and applying the trapezoidal rule approximation.

DSC thermograms are illustrated in Figure 16. The values obtained for the heats of reaction for samples 254-1A, 254-1, 254-2, and 254-3 are presented in Table 8. The values obtained for the peak exotherm temperatures are presented in Table 9.

B. Results and Discussion

DSC is a technique which can establish differences in cure reactions, heat of cure, maximum exotherm temperature, and glass transition temperatures. For prepreg and resin formulations, DSC analysis can detect batch-to-batch changes in the relative amounts of starting constituents and differences in respective resin

advancement or B-staging of prepreg systems. From the results in Table 8, DSC has potential in monitoring small differences in formulations of the epoxy, hardener, and catalyst substances.

Sample 254-1A is considered to be the standard or control sample in the following discussions.

The main difference in the heat of reaction transition was detected in sample 254-3. The exotherm which occurred illustrated two major transitions which are shifted to higher temperatures. Samples 254-1A, 254-1, and 254-2 show one major transition followed at higher temperatures by a weak second transition. The 254-3 heat of reaction also has a greater ΔH than the other three samples. The only difference between this sample and the control 254-1A is the fact that sample 254-3 has 50% less BF_3:MEA catalyst than the control. Certainly this fact is critical and the DSC data illustrates this more distinctly than either the LC or FTS-IR measurements.

Resin advancement or B-staging lowers the heat of reaction as illustrated in Table 8. This is expected and is detected by DSC analysis. A change in the stoichiometry of the epoxy system to curing agent is more difficult to assess by DSC from the ΔH values in Table 8.

Table 8. HEAT OF REACTION (ΔH) FOR EPOXY RESIN FORMULATION SAMPLES MEASURED IN AIR AND NITROGEN ATMOSPHERES, ΔH IN MCAL/MG

Atmosphere	Sample Identification	Heating Rates, deg C/min 5	10	20
Air	254-1A	114.56	118.35	119.81
	254-1	112.69	109.11	124.17
	254-2	116.77	116.44	121.24
	254-3	131.83	127.90	135.36
Nitrogen	254-1A	120.48	122.15	129.22
	254-1	108.17	112.39	103.09
	254-2	114.52	117.96	119.01
	254-3	134.80	134.66	134.98

Table 9. EXOTHERM PEAK TEMPERATURES FOR EPOXY RESIN FORMULATION SAMPLES AT VARIOUS HEATING RATES IN AIR AND NITROGEN ATMOSPHERES (DEG C)

Atmosphere	Sample Identification	Heating Rates, deg C/min 5	10	20
Air	254-1A	197	204	204
	254-1	198	203	207
	254-2	202	205	203
	254-3	202,233	214,248	222,263
Nitrogen	254-1A	195	203	207
	254-1	193	203	207
	254-2	192	203	205
	254-3	203,235	214,250	224,267

A change in the heating rate and also the atmosphere of measurement does not seem to have a major effect on the results. Again, the values are consistent for the heat of exotherm, sample 254-3 yielding a higher exotherm temperature than the other three samples.

The exotherm peak temperatures are listed in Table 9. The exotherm peak temperature shows no significant change in samples 254-1A, 1, and 2. Resin advancement does not show any significant change in the peak exotherm. Sample 254-3 illustrates a two-phase change with the exotherm temperature shifting to higher temperatures. The elimination of a portion of the catalyst shifts the exotherm as expected to higher temperatures. Again, the heating rate change does affect the peak exotherm temperature; the more rapid the heating rate, the higher the peak exotherm temperature.

C. Conclusions

1. DSC analysis is able to detect minor differences in batch-to-batch variations in relative amounts of starting constituents.
2. Resin advancement or B-staging with the prepreg system can be evaluated from the total heat of cure.
3. DSC analysis is very sensitive to changes in accelerator concentration.
4. Altering the heating rate and the atmosphere for the measurement of heat of reaction and peak exotherm temperature has only a minor effect on detecting formulation and resin advancement changes.

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