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QUANTITATIVE ANALYSIS OF RESINS USED IN FIBER-REINFORCED COMPOSITES BY REVERSED-PHASE LIQUID CHROMATOGRAPHY

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SUMMARY

An improved reversed-phase liquid chromatographic method has been developed to analyze the epoxy resin present in a typical fiber-reinforced composite system, Narmco Rigidite 5208/WC3000. After solvent extraction of the resin from the prepreg (continuous-fiber reinforcement preimpregnated with partially cured resin) using tetrahydrofuran, acetophenone is added as an internal standard in order to obtain reproducible quantitative results. The separation is achieved with a linear water–acetonitrile gradient (50% to 100% acetonitrile in 15 min). The peak area or peak height is measured and normalized with respect to the acetophenone peak and the weight of the extracted epoxy resin. A reproducibility of less than 3% relative standard deviation was obtained for quantitative measurements of the main peaks. A smaller standard deviation was obtained with peak height than with peak area measurements but the latter is recommended for definitive quantitative analysis since the results are less column-dependent and permit easier interlaboratory comparison. The main peaks in the Narmco 5208 chromatogram have been identified by comparison of their retention times with those of individual components and by infrared spectroscopy of collected fractions. Several batches of Narmco 5208 prepreg have been analyzed and their compositions estimated by comparing the results with those obtained for the individual components of the system.

INTRODUCTION

Fiber-reinforced polymer-matrix composites are widely used in the aerospace industry to make sophisticated structural parts[1,2]. At the present time, the most common materials employed are epoxy resin as matrix and carbon or polyamide fibers as reinforcement. Variations in the chemical composition of the polymer matrix can have significant effects on the processing and on the final properties of these composites. Analytical techniques such as infrared spectroscopy or liquid chromatography must be used to obtain reliable information on the organic matrix composition of these products[3].

High-performance liquid chromatography (HPLC) appears to be one of the most useful techniques for characterizing such systems[4–6], and experiments involving different modes of separation have established reversed-phase liquid chromatography (RPLC) as the most widely used method. LC can be used to check the batch-to-batch reproducibility of neat epoxy resin or of prepreg (continuous-fiber reinforcement preimpregnated with partially cured resin), to determine the composition of an epoxy system, or to follow the aging of a prepreg. Epoxies have often been characterized by a "fingerprint" analysis to reveal the presence and relative amounts of different components on a chromatogram[4]. However, this technique is of limited usefulness for precise quantitative definition of such systems. Hagnauer and Setton[5] and Hagnauer[6] have calculated the weight percent of major components (epoxy or hardener) in epoxy systems by performing calibration with standard solutions of components corresponding to individual peaks. This requires the isolation of the pure compounds from the commercial products, a tedious and time-consuming procedure. An alternative is to perform calibration with the commercial resins used to formulate the prepreg system. This procedure is complicated by the fact that these resins are usually mixtures involving a number of different molecules, and the samples used for calibration may not have exactly the same composition as those used in the prepreg. The methods just described have been used to qualitatively follow the advancement of the curing reaction on a short-term basis. However, to compare batches of epoxy resin over a long time interval, accurate quantitative methods must be developed. This paper describes the optimization of the separation of an epoxy resin by RPLC and compares various methods for the quantitation of the peaks in the chromatogram. The use of an internal standard is proposed, and parameters influencing the quantitative analysis are carefully examined in order to obtain the most reproducible results and hence to facilitate quality control over a long period of time or comparison of results among different laboratories. A common commercial system, Narmco Rigidite 5208, has been chosen for this purpose.

EXPERIMENTAL

Apparatus

The chromatography system consisted of a Varian Model 5000 liquid chromatograph (Varian, Palo Alto, CA, U.S.A.) with an automatic universal injector (10 μl loop) Model 7216 (Rheodyne, Cotati, CA, U.S.A.). The detector was a Varian variable-wavelength detector Model UV-100 with a 4.5-μl flow cell. Chromatograms were recorded on a Varian Vista 401 data station and transferred to an Apple II+ computer (Apple, Cupertino, CA, U.S.A.) via an RS-232 interface to perform additional data processing. The columns used were purchased pre-packed and are as follows: MCH-5-n-CAP (Varian), 30 cm × 4.0 mm I.D., 5 μm particles; and Hypersil MOS-1 (Shandon), 25 cm × 4.6 mm I.D., 5 μm particles. Infrared spectral measurements were done on a Nicolet 170SX Fourier transform instrument equipped with a mercury cadmium telluride detector.

Chemicals

Water, acetonitrile and tetrahydrofuran (THF) were Fisher HPLC-grade (Fisher Scientific, Fair Lawn, NJ, U.S.A.). Epoxy resin Araldite MY 720 and Hardener HT 976 were obtained from Ciba-Geigy (Hawthorne, NY, U.S.A.). Epoxy resin

Epi-Rez SU-8 was from Celanese Polymer Specialities (Louisville, KY, U.S.A.). These products were stored in a refrigerator. Carbon-epoxy prepregs Rigidite 5208/WC3000 were obtained from Narmco Materials (Anaheim, CA, U.S.A.). They were stored in a freezer at all times except for sampling and performance of experiments.

Procedure

In the case of prepreg samples, the epoxy resin system was extracted at room temperature from a piece of prepreg about 5 cm × 5 cm with three consecutive extractions (about 15 min each) using 50, 30, and 20 ml of THF. This is the most effective solvent to dissolve the resin[7]. The resin concentration in the combined extract was about 6 mg/ml. The exact weight of resin extracted was determined by recovering, drying, and weighing the carbon fibers, and subtracting this weight from the initial prepreg weight. A known quantity of acetophenone (*ca.* 100 μg/ml) was added to the extract as internal standard. In the case of neat resin, solutions were prepared in THF. All solutions and extracts were filtered through a Millex-SR 0.5-μm filter unit (Millipore, Bedford, MA, U.S.A.) before injection on the column. For the resin separation, the eluent composition was changed linearly from 50% acetonitrile in water to 100% acetonitrile over 15 min, maintained at 100% acetonitrile for a further 15 min, and then returned to the initial composition over a 1-min period. The flow-rate was kept constant during the gradient run at 1.0 ml/min. The wavelength of detection was 230 nm and the column was kept at 25°C. In order to obtain infrared spectra of the major components, peaks were collected manually. They were analyzed by attenuated total reflection after depositing the solution on a KRS-5 prism and evaporating the eluent to leave a thin film.

RESULTS AND DISCUSSION

Separation and identification of peaks

Several isocratic and gradient elution methods involving various mixtures of water and organic solvents, such as acetonitrile, methanol or THF, were tested using an MCH-5-n-CAP column. Separations with isocratic eluents were always poor and gradient elution was found to be the best way to achieve an efficient separation in a reasonable time. Fig. 1 shows a typical chromatogram of the Narmco 5208 resin obtained with the linear acetonitrile–water gradient described in the Experimental section. The separation is realized in about 25 min with an excellent resolution of the main peaks.

It is very difficult to identify all the peaks in the chromatogram but the main ones must be known in order to properly characterize the system. Narmco Rigidite 5208 has been reported[8–10] to contain three main components: the principal epoxy resin, based on tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM), about 67% by weight; an amine hardener, 4,4′-diaminodiphenylsulfone (DDS), about 23% by weight; and a second epoxy resin, based on bisphenol A Novolac, about 10% by weight. Both epoxy resins are complex mixtures of monomer, higher oligomers, and by-products.

The identity of the most important peaks was established by running samples of the individual components present in the resin, by performing Fourier transform

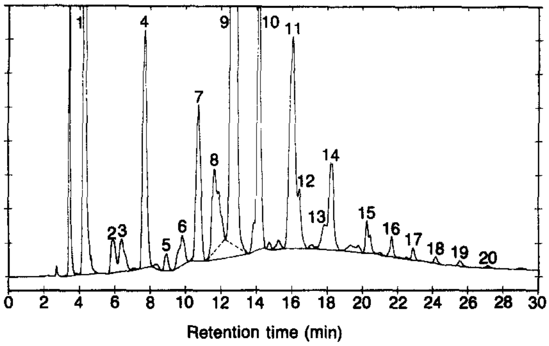

Fig. 1. Chromatogram of the extract of Narmco 5208 prepreg, batch 1103. Column: MCH-5-n-CAP, 30 cm × 4.0 mm I.D. See Experimental section for other details. Identification of major peaks: (1) DDS; (4) acetophenone; (7) reaction product; (9) TGDDM; (10) DGEBA.

infrared spectroscopy on recovered fractions, and by examining chromatograms of prepreg samples which had been partially polymerized by heating for periods up to 4 h at 100°C. In the latter case, peaks 1, 9, and 10 decreased steadily with heating time. They can be assigned respectively to DDS monomer, TGDDM monomer (from the major epoxy), and diglycidyl ether of bisphenol A (DGEBA) monomer (from the minor epoxy). Peak 7 was the only one or any importance to show an increase with heating, and its infrared spectrum showed bands characteristic of both TGDDM and DDS. It is therefore assigned to the initial reaction product of these two species. After some time, the quantity tends to stabilize because this molecule reacts further to form the polymer. Peak 4 corresponds to acetophenone added as internal standard. Peak 6, which is not found in any of the three starting materials, does not change significantly on heating, indicating that it is not a reaction product.

Fig. 2 shows the chromatogram and peak assignment obtained with the Hypersil MOS-1 column. The resolution is even better than with the MCH-5-n-CAP column, and the separation is achieved in a shorter time. The two peaks marked with an asterisk were not observed in any of the three starting materials. They could be due to an impurity in one of the particular batches used to make the prepreg or they

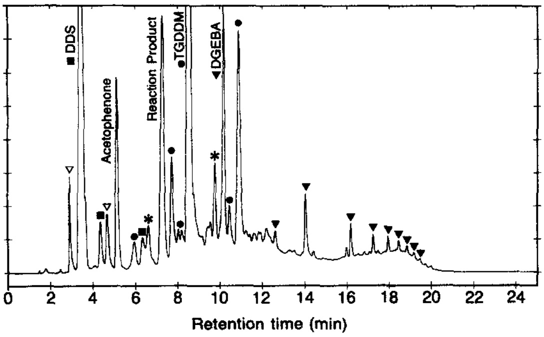

Fig. 2. Chromatogram of the extract of Narmco 5208 prepreg, batch 1103. Column: Hypersil MOS-1, 25 cm × 4.6 mm I.D. See Experimental section for other details. Symbols indicate origin of peaks: (▽) THF; (●) MY 720; (■) HT 976; (▼) SU-8; (✱) unknown.

could result from a coupling agent used to treat the surface of the carbon fiber reinforcement. They do not appear to be due to a reaction product since they do not become more intense when the prepreg is heated.

Internal standard

There are various methods for the quantitation of the peaks in the chromatogram: the ratio of the peak area with respect to the TGDDM peak, the relative area with respect to the total area, and the internal standard. The method using an internal standard is the most precise because it gives a result which is directly related to the percentage by weight of the compound in question. It could detect even foreign components which do not appear in the chromatogram, if they are present in significant amounts. However, this method is more complicated, requires more care, and is more subject to weighing errors during the preparation of solutions.

To find a suitable internal standard for use with Narmco 5208, several compounds (*p*-xylene, toluene, benzene, benzaldehyde, acetophenone) were tested using the chromatographic conditions described previously. The first three are inappropriate as regards the retention time; they are eluted in the same region as other peaks. Benzaldehyde has a suitable retention time but seems difficult to obtain commercially with sufficient purity, since injection of this product gave a chromatogram with several impurity peaks. The best internal standard was acetophenone. To account for variations in the weight of resin, after the peak areas or peak heights are divided by that of acetophenone they are normalized to a standard resin weight of 100 times the acetophenone weight:

$$\text{Normalized response} = \frac{\text{Response of peak}}{\text{Response of acetophenone}} \cdot \frac{\text{Wt. acetophenone}}{\text{Wt. resin}} \cdot 100$$

This gives normalized peak intensities in the range of 0.2 to 20.

Reproducibility

Regardless of the method of calculation, the baseline used for the evaluation of the peak area or the peak height must be clearly established to avoid quantitation differences between the chromatograms. This requirement, which is often neglected, is particularly important for comparing results obtained over a long time interval or even for comparing results obtained on different columns. Fig. 1 shows the baseline selected for this work. The ideal case consists of well-resolved peaks where baselines are drawn from valley to valley. In a complex chromatogram such as that of an epoxy resin system, it is not always possible to apply this principle unequivocally. For example, if the baseline is drawn from valley to valley for peaks 8 and 9 as shown in Fig. 1 by dotted lines, the peak area or height will be sensitive to the degree of resolution of the two peaks. Thus, it is advisable to draw a baseline closely following the base level of the chromatogram in order to minimize the variation in the measurement of peak area or peak height.

In the first experiment performed, a known quantity of acetophenone (10 μl, 10.28 mg) was added directly to the prepreg extract with a microsyringe. The reproducibility with respect to the extraction was checked by analyzing three different extracts of resin from the same sheet of prepreg. The percentages by weight of resin extracted were respectively 40.15%, 39.23%, and 38.82%. Four injections were then performed for each extract, giving a total of twelve chromatograms for averaging. An MCH-5-n-CAP column was used. The data were analyzed by the three different methods using both peak area and peak height. Table I (columns 2 to 4) reports the results obtained for the most important peaks using peak area.

Chen and Hunter[7] have proposed the use of the strongest epoxy peak (TGDDM) as a reference. The ratio DDS–TGDDM can be used to evaluate the resin composition and the ratio of the reaction product peak against the TGDDM peak serves to follow the advancement of the resin. When the results are calculated in this way, as shown in the second column of Table I, the relative standard deviations are generally quite low. While this method may be adequate for quality control of a well-characterized prepreg system, it may not be sensitive to all variations in composition which may occur, since it uses only the ratios of a few well-defined peaks.

The results calculated in terms of relative peak areas, defined as the peak area divided by the total area of the chromatogram (sometimes called internal normalization), are given in the third column of Table I. The relative standard deviations are similar to those of the peak ratio method. However, when applied to different batches over a longer interval, this method is subject to complications. The problem is that the results are affected by all the peaks in the chromatogram, and these can have different response factors. Consequently, when changes occur in the chromatogram, their magnitude may not be truly indicative of the importance of the compositional variations.

TABLE I

QUANTITATIVE RESULTS FOR NARMCO 5208 PREPREG, BATCH 1103, BASED ON PEAK AREAS

Relative standard deviations are reported in parentheses. In experiments 1 and 2 the columns MCH-5-n-CAP (30 cm × 4.0 mm I.D.) and Hypersil MOS-1 (25 cm × 4.6 mm I.D.) were used, respectively. ACP = Acetophenone (internal standard), RP = reaction product.

Peak No.	*Experiment 1*			*Experiment 2 Normalized area ACP solution*
	$\frac{\textit{Peak area}}{\textit{TGDDM area}}$	*Relative peak area*	*Normalized area ACP direct addition*	
1 (DDS)	0.3548	15.86	4.810	3.43
	(1.7%)	(1.6%)	(1.6%)	(4.7%)
7 (RP)	0.0888	3.968	1.204	1.738
	(2.5%)	(2.0%)	(3.8%)	(1.1%)
8	0.0949	4.244	1.288	0.550
	(1.4%)	(0.8%)	(1.8%)	(0.7%)
9 (TGDDM)	–	44.71	13.56	11.98
		(0.8%)	(3.1%)	(0.8%)
10 (DGEBA)	0.1385	6.194	1.879	1.042
	(0.7%)	(0.2%)	(2.5%)	(1.3%)
11	0.1470	6.573	1.994	1.335
	(1.6%)	(1.3%)	(3.6%)	(0.9%)
16	0.0083	0.369	0.112	0.064
	(9.9%)	(9.8%)	(7.7%)	(4.4%)

The use of an internal standard such as acetophenone overcomes many of the disadvantages associated with the other methods. The fourth column of Table I shows that with this method the relative standard deviation is slightly higher than for the previous two methods, but is under 4% for the main peaks. Thus, the normalization procedure with an internal standard is preferred for evaluating the chromatogram of an epoxy resin system. Its main advantage is to eliminate any effects of variation in instrumental response and loss of solvent. If pure components are available for calibration, it can be used to determine the actual percentage of these components in the resin.

Although the results just presented may be considered acceptable, direct addition of 10 μl of acetophenone with a microsyringe to the prepreg extract can produce a significant error in the amount of acetophenone. In order to improve the reproducibility of the LC method, a second experiment was subsequently performed using a different approach. A standard solution of acetophenone in THF was prepared and an aliquot of this solution was added to the prepreg extract. The standard solution consists of 0.5 ml of acetophenone in 50 ml of THF, and each component is accurately weighed to determine the percent by weight of acetophenone (about 1.1%). A 1-ml aliquot of this solution is added to an Erlenmeyer flask, with weighing before and after to allow calculation of the exact quantity of acetophenone added (about 10.2 mg). To this is added the prepreg extract, prepared as described in the Experimental section, containing a known weight of epoxy resin. This gives a solution in which the ratio of acetophenone to epoxy resin is precisely known. For this experiment, a Hypersil MOS-1 column was used.

TABLE II

QUANTITATIVE RESULTS FOR NARMCO 5208 PREPREG, BATCH 1103, BASED ON PEAK HEIGHTS

Relative standard deviations are reported in parentheses. In experiments 1 and 2 the columns MCH-5-n-CAP (30 cm × 4.0 mm I.D.) and Hypersil MOS-1 (25 cm × 4.6 mm I.D.) were used, respectively. ACP = Acetophenone (internal standard), RP = reaction product.

Peak No.	*Experiment 1*		*Experiment 2*
	Peak height / TGDDM height	*Normalized height ACP direct addition*	*Normalized height ACP solution*
1 (DDS)	0.7790 (0.8%)	10.78 (1.3%)	2.074 (3.0%)
7 (RP)	0.0777 (1.7%)	1.075 (1.2%)	1.217 (0.3%)
8	0.0441 (1.2%)	0.611 (1.6%)	0.4811 (0.3%)
9 (TGDDM)	–	13.84 (0.5%)	11.72 (0.2%)
10 (DGEBA)	0.1508 (2.0%)	2.088 (2.1%)	1.173 (2.3%)
11	0.1082 (0.2%)	1.498 (0.7%)	1.047 (1.0%)
16	0.0104 (5.2%)	0.144 (5.3%)	0.098 (2.7%)

The last column of Table I shows the results obtained using this procedure. Comparison of the relative standard deviations with those in the next-to-last column shows for the most part a significant decrease when a standard solution is employed instead of a direct addition of 10 μl of acetophenone.

In isocratic elution, it has been shown that peak height measurements are more precise than peak area measurements[11]. Peak heights are less subject to interference by adjacent, overlapping peaks. For equivalent accuracy, a lower degree of resolution is required for quantitation by peak height than by peak area.

Table II reports results calculated from the same chromatograms as Table I using the peak height instead of the peak area. A comparison with Table I shows that in general this gives lower relative standard deviations. The chromatogram of the epoxy resin system being complex, there are many overlapping peaks. Thus, accurate measurement of the area is more difficult. As in Table I, the use of an acetophenone solution gives more reproducible results than direct addition. Although in the present case height measurements give a lower standard deviation than peak area, area measurements are recommended for quantitative analysis of an epoxy resin chromatogram on a long-term basis because peak areas are less sensitive to changes in column efficiency. Comparison of results obtained with different columns or in different laboratories will be facilitated with this procedure. However, peak height measurement is recommended for characterizing an epoxy resin when the same column is used to compare several different samples over a limited time interval.

Splitting of the DDS peak

Comparison of the normalized values (area or height) obtained in the two experiments just described shows significant differences between them, especially in the case of the normalized height for the DDS peak (peak 1). A period of 2.5 years separates the two analyses and the results show that the prepreg aged somewhat during this time, probably because it had been thawed several times for sampling. The significant changes which occur over time underline the importance of good quality control of these materials. The values of the normalized height decreased for the main epoxy TGDDM peak (13.84 to 11.72), the minor epoxy DGEBA peak (2.09 to 1.17), and the DDS peak (10.78 to 2.07), while the reaction product peak increased (1.075 to 1.217). Since the amount of TGDDM in Narmco 5208 exceeds the amount required for stoichiometric reaction with the DDS, it is not surprising that the free DDS disappears relatively fast compared to the TGDDM. However, the apparent decrease in DDS is quite substantial and is much greater when peak heights are used than when areas are used. A further unusual observation was that the relative standard deviation for the DDS peak is considerably worse with the Hypersil MOS-1 column than with the MCH-5-n-CAP column.

Since the efficiency of the Hypersil MOS-1 column is better than that of the MCH-5-n-CAP column, a splitting of the DDS peak was observed in some chromatograms. This is illustrated in Fig. 3 for two different injections of the Narmco 5208 system. In one case, there is only one peak with a small shoulder, but in the other, two peaks are detected in addition to the shoulder. It is difficult to establish the origin of the different peaks; they may result from the presence of different isomers in the industrial hardener. Since the resolution with the MCH-5-n-CAP column is not good enough to separate the two peaks, this phenomenon was not observed before.

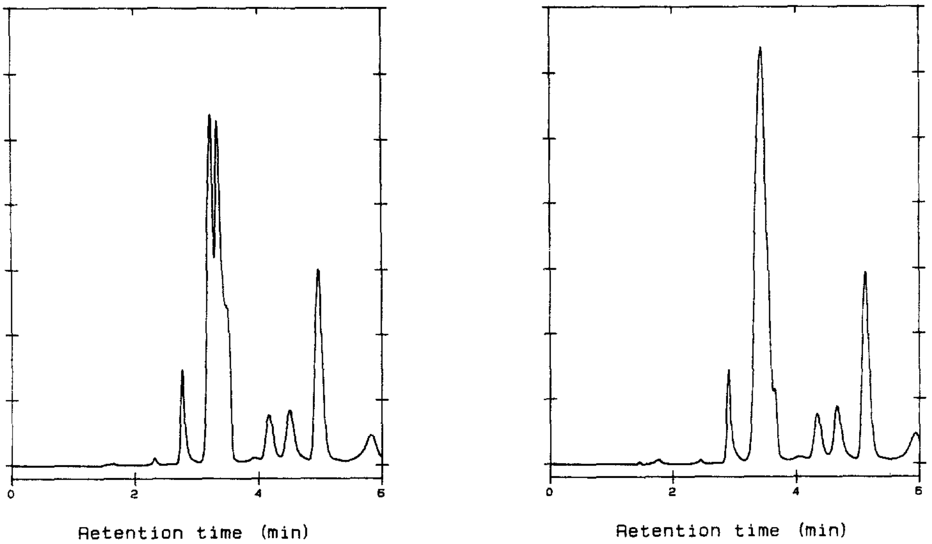

Fig. 3. Chromatograms of Narmco 5208 showing splitting of the DDS peak. Column: Hypersil MOS-1, 25 cm × 4.6 mm I.D. See Experimental section for other details.

This result underlines one of the main problems of gradient elution, namely the regeneration of the column. The splitting of the DDS peak is not always present and this is attributed to the initial conditions of the column. If, for some reason, the equilibrium between the stationary phase and the mobile phase is not always identical, certain experimental conditions can favour the separation of the DDS components whereas in other conditions, they will be completely unresolved.

The splitting of the peak obviously influences the peak height to a significant extent. The major DDS peak seems to be the first one and its height was used for the calculation. This explains the unusually low value obtained for the normalized height with the Hypersil column. Thus, a column with excellent resolution has some advantages but it must be used with circumspection in the case of the DDS peak. For quantitative measurements, it is advisable to calculate the normalized area using the combined area of these peaks, since the different compounds are included in the single peak of DDS when the separation is not complete.

Comparison of different batches of Narmco 5208 resin

Different batches of the Narmco Rigidite 5208 epoxy resin system were analyzed by RPLC on the MCH-5-n-CAP column. They included five prepreg samples (batches 1010, 1014, 1101, 1103, 1104), one sample of neat resin on a plastic backing sheet (batch 1047) and one of neat resin in bulk form (batch 1023). The results are reported in Table III as normalized areas with respect to acetophenone internal standard. In addition, ratios with respect to the TGDDM peak are reported for the main peaks of interest. These ratios are independent of the presence of acetophenone.

An estimation of the actual percentages of the two epoxy resins and the hardener in Narmco 5208 was also performed by measuring chromatograms for the individual components Hardener HT 976, Araldite MY 720, and Epi-Rez SU-8. For each component, THF solutions were prepared containing a known concentration of acetophenone and varying known concentrations of the particular component. For each solution, the RPLC chromatogram was measured, and a normalized peak area calculated based on the main peak (DDS, TGDDM, or DGEBA, depending on the component). For a particular component, the response is effectively the same for all the solutions and the average value corresponds to a concentration of 100%. The respective values obtained for Hardener HT 976, Araldite MY 720, and Epi-Rez SU-8 are 27.7, 20.0, and 12.2. The ratio of the normalized area of the peak of interest in a sample of Narmco 5208 against that obtained for the corresponding pure component gives an estimate of the percentage of the particular component in the resin. The calculation is somewhat approximate since it is based on only the major peak of each component, and it assumes that each component in the epoxy mixture has the same composition as the product used for calibration. It should be noted that the percentages determined correspond to unreacted material, so the sum will be less than 100% if the resin is advanced. Table IV reports the values obtained for the different batches of Narmco 5208.

Examination of Tables III and IV shows that appreciable variations can be observed. For example, batch 1047 is the least advanced since it has high values for free DDS and TGDDM (peaks 1 and 9) and the lowest value for peak 7, which is the product of the reaction between TGDDM and DDS. However, the content of free DGEBA (peak 10, from the Novolac epoxy) is abnormally low compared to the other batches. The low value calculated for Novolac in Table IV underlines this fact. It appears that this batch is unbalanced with respect to the usual composition. Batch 1023 lies at the other extreme, having low values for free TGDDM, DDS and DGEBA, and the highest value for the reaction product. Although it consists of neat resin, it is more advanced than all the prepreg samples, probably the result of undue heating at some point in this history. In Table IV, the sum of the three components is only 78% and this also indicates a high degree of advancement.

TABLE III

RPLC RESULTS FOR DIFFERENT BATCHES OF THE NARMCO 5208 SYSTEM; NORMALIZED AREAS WITH RESPECT TO ACETOPHENONE, AND AREA RATIOS WITH RESPECT TO TGDDM

Column: MCH-5-n-CAP (30 cm × 4.0 mm I.D.).

Peak No.	*Batch No.*						
	1047	*1103*	*1104*	*1014*	*1101*	*1010*	*1023*
1 (DDS)	4.795	4.810	4.311	4.130	3.600	3.719	3.034
7 (RP)	1.110	1.204	1.336	1.623	1.742	1.785	2.406
8	0.836	1.288	0.690	0.831	0.612	0.638	0.830
9 (TGDDM)	13.54	13.56	13.19	13.37	12.72	12.70	12.33
10 (DGEBA)	0.792	1.879	1.626	1.552	1.324	1.185	0.709
11	0.898	1.994	1.899	–	1.474	0.668	0.567
16	0.136	0.112	0.101	0.127	0.082	0.107	0.026
1/9	0.354	0.355	0.327	0.309	0.283	0.293	0.246
7/9	0.082	0.089	0.101	0.121	0.137	0.141	0.195
10/9	0.058	0.139	0.123	0.116	0.104	0.093	0.057

TABLE IV

PERCENTAGE (BY WEIGHT) OF EACH COMPONENT IN DIFFERENT BATCHES OF NARMCO 5208 EPOXY RESIN

Batch No.	*HT 976*	*MY 720*	*Novolac*	*Sum*
1047	17.3	67.7	6.5	91.5
1103	17.4	67.7	15.5	100.6
1104	15.6	65.9	13.4	94.9
1014	14.9	66.9	12.8	94.6
1101	13.0	63.5	10.9	87.4
1010	13.5	63.4	9.7	86.6
1023	11.0	61.4	5.8	78.2

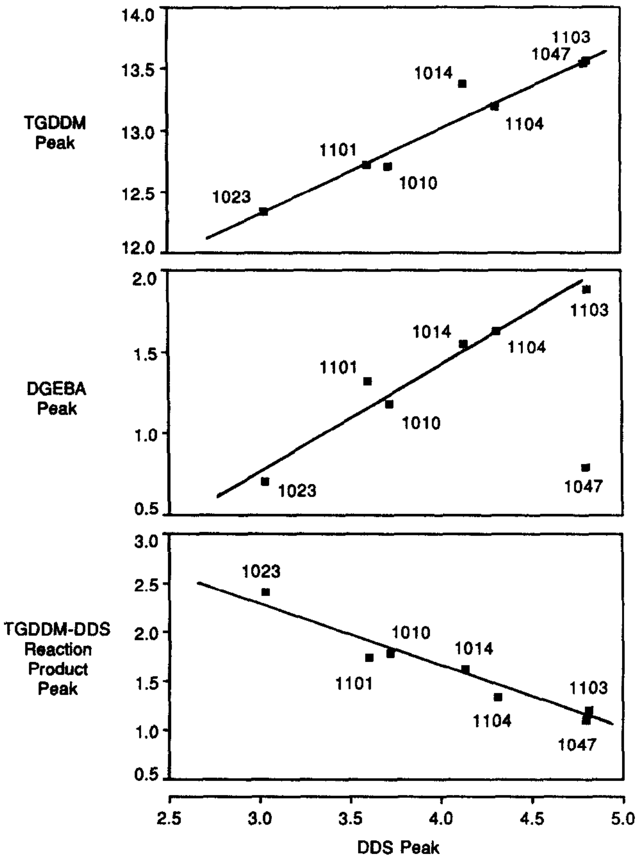

Fig. 4. Variation of the normalized peak area of the TGDDM peak, the DGEBA peak, and the reaction product peak as a function of the normalized peak area of DDS, for different batches of Narmco 5208.

Comparison of the five prepreg samples shows results which are in better agreement. Generally speaking, batches 1101 and 1010 are very similar to each other, while the other three (1103, 1104 and 1014) are also similar to each other but somewhat less advanced than the first two. In Table III, the batches are arranged approximately in order of increasing degree of advancement. The relationships between some of the main peaks are shown graphically in Fig. 4, where the normalized peak areas for the reaction product, DGEBA, and TGDDM are plotted against those of DDS. There are obvious correlations. In general, a decrease in free DDS correlates with a decrease in TGDDM and DGEBA and an increase in reaction product, as expected based on the nature of the curing reaction. These results indicate that the batches differ mainly in degree of reaction advancement and not in initial composition. One exception is batch 1047, which deviates considerably from the linear relationship in the case of the DGEBA peak. This batch appears to have a low Novolac content.

The same trends are evident whether the normalized peak intensities or the peak ratios are used as an indicator. However, the normalized peak intensities provide a more complete picture of the variations in composition.

CONCLUSION

RPLC is an excellent technique for analyzing epoxy resin systems such as Narmco 5208. The separation has been optimized by using a gradient elution method with acetonitrile–water with UV detection at 230 nm. The addition of acetophenone as an internal standard permits accurate quantitative analysis using a normalization of the peak area or peak height with respect to the weight of the extracted resin and the weight of added acetophenone. A lower relative standard deviation is obtained with a standard solution of acetophenone rather than a direct addition of acetophenone to the prepreg extract. For interlaboratory comparison and for comparison of analyses involving different columns, peak area measurements are recommended, even though the standard deviations are slightly higher than for peak height measurements. However, the baseline used for the evaluation of the peak area or the peak height must be clearly established to avoid quantitation differences between the chromatograms. A Hypersil MOS-1 column gives excellent resolution, but care must be exercised in analyzing the DDS peak because of a splitting observed in some chromatograms.

The main peaks in the chromatograms have been identified, including that of the reaction product between TGDDM and DDS. This peak is useful for following the aging of a prepreg.

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