High-Speed Reverse-Phase Liquid Chromatography with 3 μm Packing for Analysis of Fiber-Reinforced Epoxy Composite Formulations

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Synopsis

A high-speed reverse-phase liquid chromatography column packed with 3 μm particles has been used to separate different epoxy resin formulations used in manufacturing fiber-reinforced composites. The mass transfer of the solute between the stationary phase and the mobile phase is improved with the decrease of the particle diameter, and the height equivalent to a theoretical plate remains low even at higher flow rates of eluent. The separation of a typical epoxy resin was achieved with good resolution in less than 6 min on a short column 4 cm long packed with 3 μm particles, as compared to about 30 min on a 30 cm long column packed with 5 μm particles. Moreover, the regeneration time with gradient elution is considerably reduced with a short column. Separations of different formulations are shown and the advantages and disadvantages of these 3 μm packings for a quality control laboratory are discussed. In addition, the ageing of Narmco Rigidite 5208/WC3000 prepreg at room temperature in a controlled atmosphere has been quantified using these high-speed columns.

INTRODUCTION

In recent years, the use of fiber-reinforced organic-matrix composites has grown substantially. One of the most important areas of application is the aerospace industry, where such composites provide a significant reduction in weight as compared to metals, without a concomitant loss of mechanical strength.[1,2] Variations in chemical composition of the organic matrix cannot always be detected by mechanical performance tests, but can have important effects on the long-term performance of the part. Consequently, chemical composition of the composites must be determined by modern physicochemical characterization techniques such as high performance liquid chromatography, Fourier transform infrared spectroscopy, and differential scanning calorimetry.[3]

One of the most useful techniques for characterizing such systems is high performance liquid chromatography (HPLC). It can be used to check the batch-to-batch reproducibility of the neat epoxy resin or of the prepreg (woven fiber reinforcement preimpregnated with partially cured resin), to determine the composition of a chemical system, or to follow the aging of a prepreg. Separations of epoxy resins have been done in both normal-phase HPLC (polar stationary phase with nonpolar eluent)[4,5] and in reverse-phase HPLC (nonpolar stationary phase with polar eluent).[6-8] An excellent review

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on the chromatography of epoxy resin systems, covering the years 1970–1984, has been published by Mestan and Morris.[9]

Most epoxy resin separations are achieved in reverse-phase liquid chromatography (RPLC) using octadecyl (C_{18}) bonded silica gels with gradient elution, because epoxy resin systems contain many compounds with different hydrophobicities. In RPLC, the more hydrophobic the solute is, the greater the chromatographic retention. Thus, a stronger eluotropic strength of the mobile phase is necessary to efficiently elute highly hydrophobic solutes. The eluotropic strength of the eluent is increased during a gradient run by gradually increasing the organic solvent content in the mobile phase. However, the column must be regenerated to its initial condition after the completion of the gradient run. With a column 30 cm long packed with 5 or 10 μm particles, this operation requires an important consumption of time and solvent. In addition to the regeneration requirement, the chromatographic separation must be optimized to obtain a compromise between the peak resolution and the analysis time. The introduction of commercially available short reverse-phase columns packed with 3 μm particles has resolved this problem by substantially decreasing the separation time.[10,11]

The purpose of this paper is to demonstrate the usefulness of short columns packed with 3 μm particles for reducing the analysis time and the solvent consumption without a significant loss of resolution in the analysis of epoxy resins. It will be shown that these columns can be used advantageously to quantify the aging of an epoxy–graphite prepreg. As the instrumental parameters are more critical with a 3 μm packing,[12] the basic parameters involved in separations using this type of column will be discussed.

EXPERIMENTAL

Apparatus

The chromatography system consisted of a Varian Model 5000 liquid chromatograph (Varian Instrument Group, 611 Hansen Way, Palo Alto, CA 94303) with an automatic universal injector (10 μL loop), Model 7126 (Rheodyne Inc., P.O. Box 996, Cotati, CA 94928). With the 3 μm packing, an automatic loop injector (1 μL loop) from Rheodyne, Model 7410, was used. 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. The columns used were purchased prepacked from Varian and were as follows: MCH-10-n-CAP, 30 cm length × 4.0 mm i.d., 10 μm particles; MCH-5-n-CAP, 30 cm length × 4.0 mm i.d., 5 μm particles; Ultra-fast C_{18}-3, 4.0 cm length × 4.6 mm i.d., 3 μm particles. Guard columns were used in order to protect the packing in analytical columns.

Chemicals

Water, acetonitrile (ACN), and tetrahydrofuran (THF) were Fisher HPLC grade (Fisher Scientific Co., Fair Lawn, NJ 07410). Epoxy resin Epi-Rez SU-8 was from Celanese Polymer Specialties (Louisville, KY 40232). Epoxy

resins Araldite MY 720 and Araldite 6010, and Hardener HT 976 were obtained from Ciba-Geigy Corp. (3 Skyline Drive, Hawthorne, NY 10532). Epoxy-graphite prepregs Rigidite 5208/WC3000 and Narmco 3203/WC3000 were obtained from Narmco Materials, Inc. (1440 N. Kraemer Blvd., Anaheim, CA 92809).

Procedure

In the case of prepreg samples, the epoxy resin system was extracted at room temperature from a piece of prepreg of 5 × 5 cm with three consecutive extractions (about 15 min each) using 50, 30, and 20 mL of tetrahydrofuran. The resin concentration after extraction was about 6 mg/mL. The exact weight of resin extracted was determined by recovering, drying, and weighing the graphite fibers, and subtracting this weight from the initial prepreg weight. A known quantity of acetophenone ($\simeq$ 100 μg/mL) was added to the extract as internal standard. In the case of neat resin, solutions were prepared in tetrahydrofuran. All solutions and extracts were filtered through a Millex-SR 0.5 μm filter unit (Millipore Corp., Bedford, MA 01730) before injection on the column. The retention time of unretained solute was determined for each chromatographic column at 220 nm by injection of a sodium nitrite solution in tetrahydrofuran. In order to evaluate the column efficiency, a solution of anthracene in methanol (0.008 mg/mL) was injected in an isocratic eluent 60%/40% ACN/H_2O. For separations of epoxy resins on the 30 cm long column packed with 5 μm particles, the eluent composition was changed linearly from 50%/50% ACN/H_2O to 100% ACN over 15 min, maintained at 100% ACN 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. For separations on the 4 cm long column packed with 3 μm particles, the initial eluent 20%/80% ACN/H_2O was increased linearly to 100% ACN over 3 min at a flow rate of 2.0 mL/min, kept at this composition for two additional minutes, and returned to the initial state within 0.1 min. In both cases, the wavelength of detection was 230 nm and the column temperature was kept at 25°C.

RESULTS AND DISCUSSION

Column Efficiency

Various parameters have been defined in chromatography theory in order to evaluate the quality of a separation. Some of them will be briefly described as a basis for comparing the performance of different chromatographic stationary phases. The efficiency of a chromatographic column is expressed quantitatively as the number of theoretical plates per unit length or its inverse, the height equivalent to a theoretical plate (HETP):

$$H = L/N \tag{1}$$

where L is the column length and N is the total number of theoretical plates. The parameter H is preferable to the number of theoretical plates

alone to describe adequately the efficiency of a chromatographic column.[13] In the calculation of H, N is obtained by measuring the retention time t_R and the half-height width W_h of a given peak:

$$N = 5.54(t_R/W_h)^2 \tag{2}$$

The degree of resolution of two peaks is influenced by the magnitude of the relative band spreading, which is related to the HETP. Thus, for a column of length L, a decrease in HETP corresponds to an increase in the number of theoretical plates N and hence an increase in the resolution. Consequently, it is very important to minimize the HETP value to obtain a good separation.

There are four sources of band spreading in liquid chromatography: (1) eddy diffusion; (2) longitudinal diffusion; (3) mass transfer; and (4) extra-column tubing. The overall HETP can be expressed as the sum of all these contributions.

Assuming that extra-column volumes are kept constant and as low as possible in a chromatographic system, the fourth parameter can be neglected. Mathematical expressions have been developed to relate the remaining three factors to experimental parameters such as solvent linear velocity and the particle size of the packing.[14]

Figure 1 shows a plot of the height equivalent to a theoretical plate vs. the flow rate as measured for anthracene in 60% acetonitrile–40% water with three columns having different particle diameters. The variation of H is expressed as a function of the flow rate instead of the linear velocity

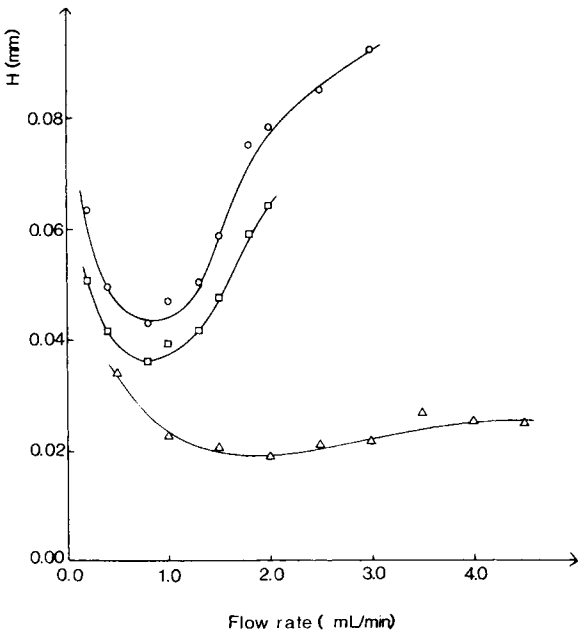

Fig. 1. Variation of the height equivalent to a theoretical plate as a function of the flow rate for anthracene in 60% acetonitrile–40% water with three columns having different particle diameters: (○) 10 μm; (□) 5 μm; (△) 3 μm.

to facilitate the comparison of different columns. With the 3 μm particles, the height equivalent to a theoretical plate remains almost constant as the flow rate increases whereas H increases rapidly with the flow rate for the 5 and 10 μm packings. Eddy diffusion, which corresponds to flow paths of different lengths in the column, is not highly dependent on the linear velocity of the mobile phase. This term can be minimized by decreasing the particle diameter and maintaining a uniform packing.[14] At high linear velocity, the longitudinal diffusion contribution, which is related to the dispersion of a sample under the influence of molecular diffusion, becomes negligible, since it is inversely proportional to the velocity. The mass transfer term is the most important in liquid chromatography. Mass transfer describes the time taken by a solute to leave the particle by diffusion. The mass transfer contribution is proportional to the product $d_p^2 u$, where u is the mobile phase linear velocity and d_p is the particle size of the stationary phase. Consequently, a decrease of the particle diameter of the stationary phase permits the use of a higher linear velocity (or flow rate) without increasing the height equivalent to a theoretical plate. As shown in Figure 1, the range of optimum flow rates is about 0.8–1.0 mL/min with the 10 μm packing whereas this range is about 1.5–4.5 mL/min with the 3 μm stationary phase. Consequently, a column packed with 3 μm particles can be used at a higher flow rate without a significant loss of efficiency.

The possibility of using higher flow rates means that the analysis is completed in less time and that the solvent consumption is decreased substantially. This can amount to substantial savings on a long-term basis for a quality control laboratory as shown in the next section.

Separation of Epoxy Resins

Figure 2 shows the separation of an extract of Narmco Rigidite 5208/WC3000 prepreg on a MCH-5-n-CAP column and on an Ultra-fast C_{18}-3 column. Both stationary phases are octadecyl bonded phases. Acetonitrile has been selected because it is a solvent with a good eluotropic strength in reverse-phase mode and because epoxy resins are highly soluble in this solvent. Moreover, as opposed to tetrahydrofuran, acetonitrile shows negligible UV absorbance at the detection wavelength (230 nm), and hence gradient elution is possible with ACN.

Several experiments were done with the two columns in order to obtain the maximum resolution in the shortest time. It was found that the separation is superior on the 4 cm column packed with 3 μm particles if the starting eluent contains a larger proportion of water in comparison to the 30 cm long column. This is probably caused by the need to reduce the mass transfer efficiency with the 3 μm particles by using a weaker eluent.

With the 3 μm packing, the separation time is reduced from 25 to 6 min. The resolution is almost as good as with the 30 cm column. Peak #1, which is well separated from other major peaks, corresponds to an aromatic diamine, 4,4′-diaminodiphenylsulfone (DDS). This curing agent accounts for about 23% by weight of the Rigidite 5208 epoxy resin.[15] As this peak is free of chromatographic interferences, it can be used to quantify the amount of DDS. Peaks #4 and 5 are the main peaks arising from the two epoxy

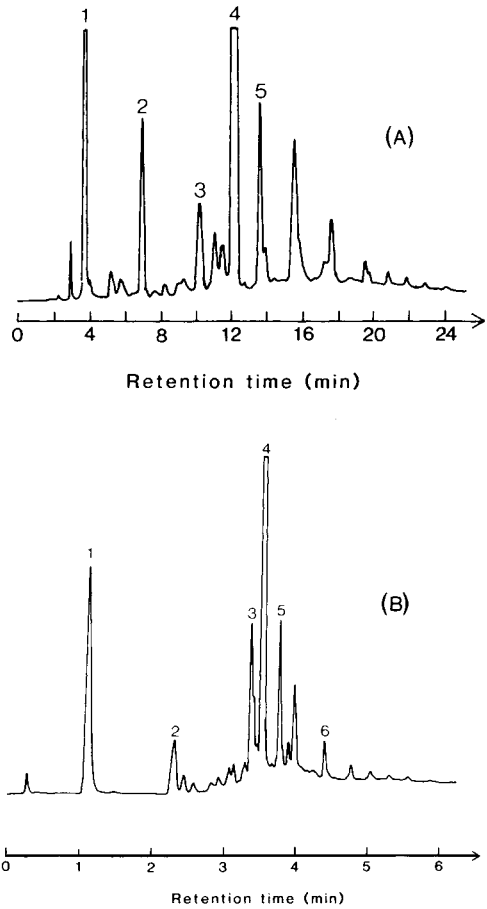

Fig. 2. Separation of the extract of Narmco Rigidite 5208/WC3000 prepreg (A) on the 30 cm long column (5 μm particles) and (B) on the 4 cm long column (3 μm particles). See the Experimental section for details.

components. The major epoxy, which accounts for about 67% by weight of the Rigidite 5208, has as its main component (peak #4) the tetrafunctional molecule tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM). The minor epoxy, which accounts for the remaining 10% of the 5208, is a bisphenol A Novolac epoxy. Its main component (peak #5) is the diglycidyl ether of bisphenol A (DGEBA). Peak #3 is the initial reaction product of TGDDM and DDS. This compound is formed from one molecule of TGDDM and one molecule of DDS by the reaction of one epoxy ring with an amine group of the DDS.[16] The identity of the main peaks was confirmed by comparison with chromatograms of the individual resins and hardener and by FTIR spectroscopy of collected fractions. Acetophenone can be added as an internal standard (peak #2) to serve as a reference for quantifying the various peaks of the chromatogram.

The column regeneration time is also considerably reduced with the 4 cm long column. Figure 3 shows the effect of the regeneration time on the retention time of the TGDDM peak in the Narmco Rigidite 5208 resin for both columns. With the 5 μm packing, a regeneration time of about 30 min

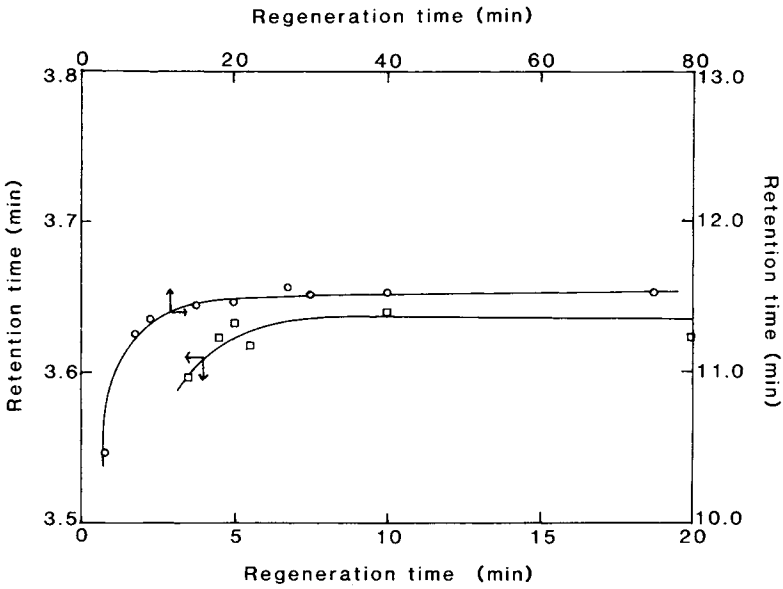

Fig. 3. Retention time of the main epoxy peak as a function of the regeneration time for the 30 cm long column (5 μm particles) (○) and for the 4 cm long column (3 μm particles) (□).

is necessary to obtain good reproducibility in the retention time whereas a regeneration time of 4 min is enough with the 3 μm packing. Thus, the overall analysis on the 4 cm column is accomplished in 10 min at a flow rate of 2 mL/min, whereas the 30 cm column with 5 μm packing requires 60 min at 1 mL/min. Consequently, the use of the high-speed columns reduces solvent consumption by a factor of 3 and overall analysis time by a factor of 6.

Figure 4 shows the separation of the resin extracted from the Narmco 3203/WC3000 prepreg, which is also used in the aerospace industry, on the same two columns. This epoxy system contains dicyandiamide as hardener (peak #1) and the diglycidyl ether of bisphenol A (DGEBA) as the main epoxy (peak #2). As previously, the separation is almost as good with the 4 cm column as with the 30 cm long column, but the analysis time is reduced to 6 min with the short column.

The time required for quality control testing of raw materials can be significantly reduced by the use of high-speed reverse-phase columns with 3 μm particles. For example, impurities in the hardener 4,4'-diaminodiphenylsulfone can be detected in less than 3 min (Fig. 5), while those in dicyandiamide are detected in less than 1 min. The different components of DGEBA epoxy resin can be separated within 5 min with excellent resolution, as illustrated by Araldite 6010 in Figure 6.

Aging of the Narmco Rigidite 5208/WC3000 Prepreg

Sheets of Narmco Rigidite 5208/WC3000 prepreg were suspended in a room maintained at 22°C and a relative humidity of 50% for 66 days. At periodic intervals, a sample of the prepreg was taken, and the epoxy resin was extracted in tetrahydrofuran. The extract was injected three times on

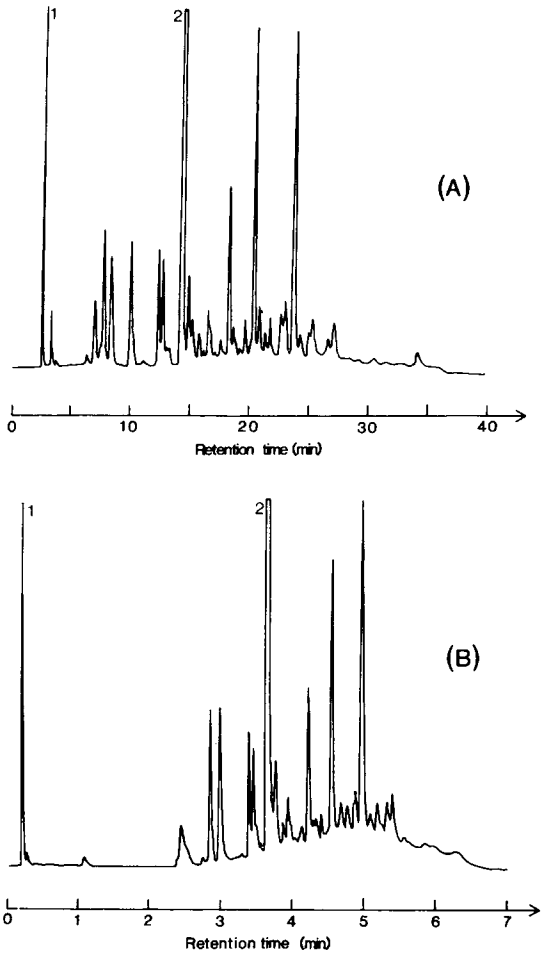

Fig. 4. Separation of the extract of Narmco 3203/WC3000 prepreg (A) on the 30 cm long column (5 μm particles) and (B) on the 4 cm long column (3 μm particles). See the Experimental section for details.

the 4 cm long column packed with 3 μm particles. For selected peaks in the chromatogram, the peak area was ratioed against that of acetophenone internal standard according to the following formula:

$$\text{Normalized area} = \frac{\text{peak area of the solute}}{\text{peak area of acetophenone}} \times \frac{\text{mass of acetophenone}}{\text{mass of resin}} \quad (3)$$

This normalization has the advantage of permitting a quantitative comparison between different formulations of epoxy resins or between different chromatographic columns.

The normalized area of many peaks varied with the exposure time but only the three most interesting ones are reported here. The first is the peak of the hardener DDS which is peak #1 in Figure 2. Figure 7 illustrates the variation of the normalized area as a function of the number of days of exposure. The variation is linear and the peak area decreases continuously

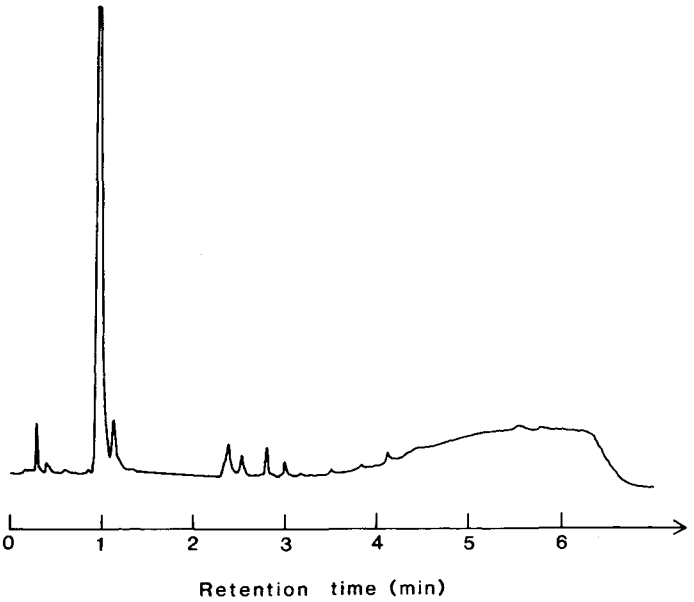

Fig. 5. Separation of Hardener HT 976 (DDS) on the 4 cm long column (3 μm particles). See the Experimental section for details.

with time indicating a reaction of this product with another compound. The decrease can be represented by the following equation:

$$\text{Normalized area} = (4.5 \pm 0.1) - (0.048 \pm 0.003)(\text{no. of days}) \quad (4)$$

This corresponds to a decrease of 1.1% per day. As the relation is linear

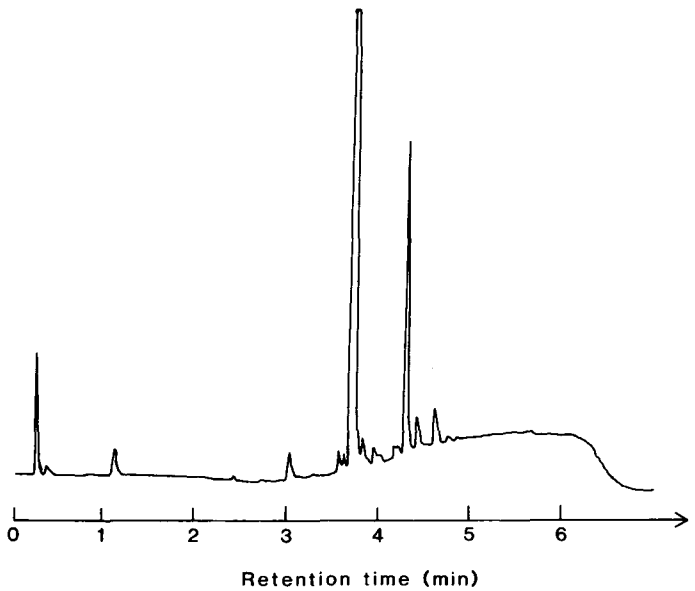

Fig. 6. Separation of Araldite 6010 epoxy resin (DGEBA) on the 4 cm long column (3 μm particles). See the Experimental section for details.

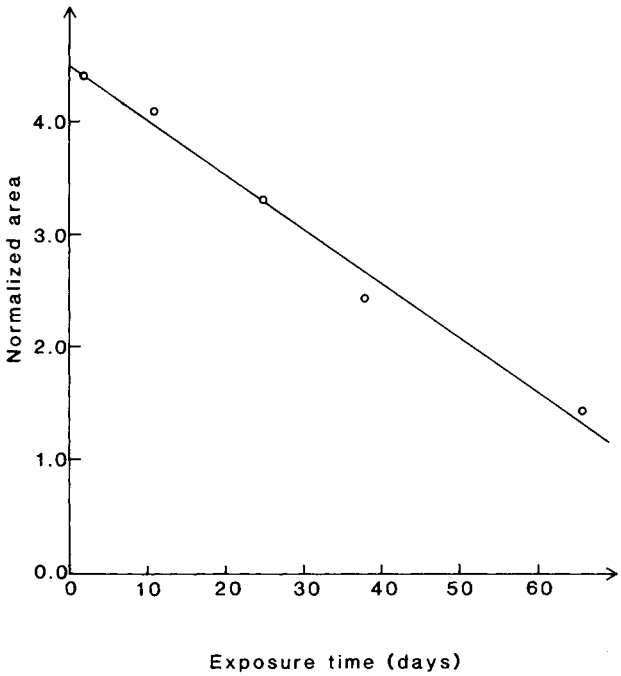

Fig. 7. Narmco 5208/WC3000 aging test (22°C, 50% RH). Variation of the normalized area for peak #1 (DDS) as a function of exposure time.

and as this peak is well separated from other components of the resin, it is a good choice to monitor the aging of a prepreg.

Figure 8 shows the variation of the normalized area for the initial reaction product between TGDDM and DDS (peak #3). The area increases up to about 25 days and then decreases regularly. Thus, before 25 days, a certain amount of the initial reaction product is formed and after this period, the amount decreases due to further reaction with epoxies or with the hardener to form compounds of higher molecular weight.

At the same time, peak #6 in Figure 2(b) shows a net increase of the normalized area after 25 days, as illustrated in Figure 9. Unfortunately, this peak has not yet been identified, but it is probably a reaction product between the initial reaction product and the main epoxy, which also decreased faster after 25 days. Thus, high-molecular-weight compounds are formed after 25 days, and the chromatograms show that the aging of the prepreg is highly advanced after this period of time.

Instrumental Considerations

In this work, short columns with 3 μm particles were used without modification of the chromatographic system. It is well known that extra-column volumes (e.g., capillary tubing connections, flow cell, etc.) must be minimized to reduce the extra-column dilution.[9] The standard cell with the UV-100 detector has a volume of 4.5 μL, and it was not found necessary to change the flow cell for a smaller one to obtain an acceptable bandwidth. Of course, a decrease of the volume of the flow cell would improve the number of

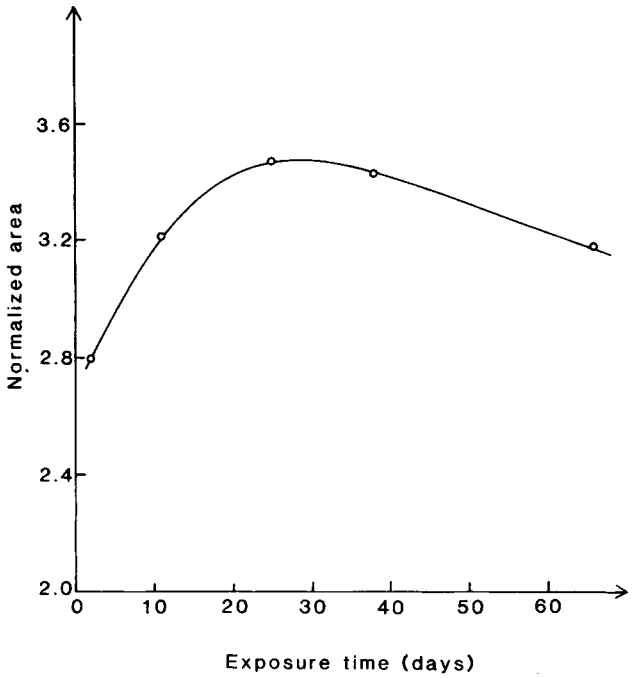

Fig. 8. Narmco 5208/WC3000 aging test (22°C, 50% RH). Variation of the normalized area for peak #3 (reaction product) as a function of exposure time.

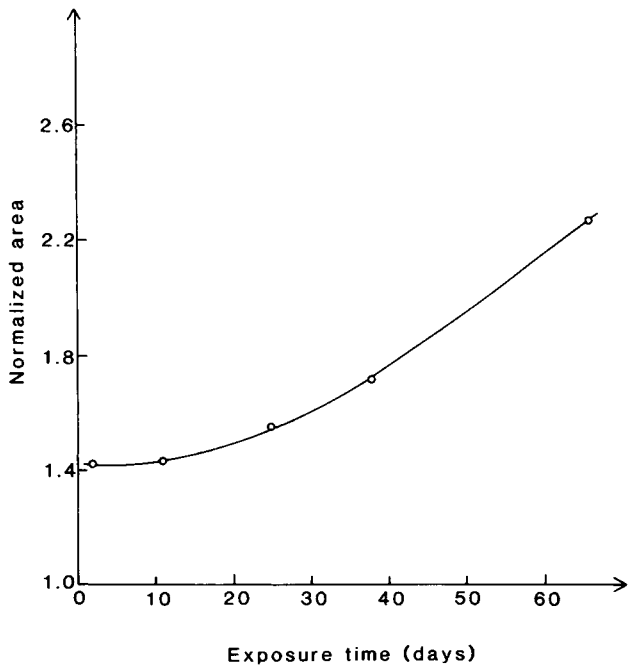

Fig. 9. Narmco 5208/WC3000 aging test (22°C, 50% RH). Variation of the normalized area for peak #6 as a function of exposure time.

theoretical plates, but if the instrument is used also with conventional columns, it is more convenient to use a medium size detector flow cell. If a small volume injector is available, it is preferable to use it in order to reduce the band broadening. Also, it is recommended not to inject a sample volume greater than 6 μL to avoid damaging the column. The 3 μm packing is more fragile than 5 μm particles but the improvement in analysis time is considerable. As stipulated elsewhere,[11] it is recommended to carefully clarify the sample and the mobile phase before injection.

CONCLUSION

Short columns packed with 3 μm packing are useful when the separation does not need a high number of theoretical plates and when the rapidity of analysis is important. It has been shown that these high-speed columns can be used advantageously to analyze and to follow the aging of an epoxy–graphite prepreg. The variation of the hardener peak with time is linear and is useful for quantifying the advancement of a prepreg. The results obtained with the high-speed columns correlated well with those found using other analytical techniques such as Fourier transform infrared spectroscopy, gel permeation chromatography, pyrolysis gas chromatography, and differential scanning calorimetry. This will be discussed in forthcoming papers.

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