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FINGERPRINTING EPOXY RESIN SYSTEMS USING TWO-DIMENSIONAL REVERSED-PHASE THIN-LAYER CHROMATOGRAPHY

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SUMMARY

Obtaining reproducible strengths from composites and adhesives composed of complex epoxy resin systems requires a close control of resin formulations. Commonly used liquid chromatographic procedures can be time consuming and do not always provide complete separations. The use of two-dimensional reversed-phase thin-layer chromatography can provide a well-resolved fingerprint of complex resin systems, without many of the drawbacks of other chromatographic methods.

INTRODUCTION

Fiber-reinforced plastics are rapidly replacing metals in many aircraft structural parts because of their superior strength-to-weight ratios. Graphite- and Kevlar-reinforced thermoset epoxies are now extensively used on both commercial and defence aircraft. Although most of the strength in fiber-reinforced epoxies is provided by the reinforcing fibers, problems with the organic matrix are responsible for many failures. In particular, poor resin formulation or impurities in the matrix can result in an inferior composite structure. As well, if uncured sheets of fiber-reinforced one-part epoxy composite resins (prepreg) is allowed to stay at room temperature for more than a few days it will "age", resulting in a change in the chemical composition of the resin. The use of overage resin can produce voids during curing with a resultant loss of strength. Therefore, methods for determining resin composition before it is used in the manufacture of composite parts are necessary.

Epoxy resin systems are also being used extensively as adhesives to replace conventional rivetting and welding in a wide variety of aircraft applications. The advantages of adhesive bonding over rivetting and welding are numerous, especially in terms of stress dissipation, aerodynamics and corrosion prevention. As in composite epoxy resins, obtaining desired properties from epoxy adhesives requires good knowledge and close control of resin compositon.

A number of methods using high-performance liquid chromatography (HPLC) have been developed to analyse epoxy resins[1–8]. Among them the most commonly used are gel permeation chromatography (GPC) and reversed-phase liquid chromatography (RPLC). GPC has been used to correlate molecular weight distributions in epoxy resins with composite properties, and this technique can be used to estimate age in prepreg resins. However, the lack of chromatographic resolution in GPC does not allow it to be used for identifying most of the components in a complex resin mixture[1,3,5-8]. When higher resolution is desired, RPLC or normal-phase chromatography with a solvent program can be used[1-8]. However, the analysis of a complex resin system generally takes more than 1 h and cycle times between samples is usually about 2–3 h. Further, the requirement of a solvent gradient precludes the use of "universal" detectors and a fixed-wavelength UV detector must be used. Since all components will not have absorption bands at any particular wavelength, some components may be missed by the detector. This problem can only be alleviated by monitoring more than one wavelength using expensive diode-array detectors or multiple fixed-wavelength detectors. Finally, the sticky nature of the resins being analysed usually results in frequent column replacement and substantial downtime for cleaning equipment.

Unidirectional thin-layer chromatography (TLC) has been used previously in conjunction with HPLC to isolate some components in epoxy resins[1]. These experiments indicated that although some components could be identified, TLC in a single dimension lacked sufficient resolution to analyse complex mixtures. However, the recent introduction of high-performance plates has improved the resolution obtainable as well as reduced the development time[9]. The TLC technique also has the advantage of using each plate only once, so recycling times of liquid chromatography are eliminated and cleaning is not necessary. The technique is also relatively inexpensive, and is faster than gradient liquid chromatography since many samples can be run simultaneously in a single chamber.

The present report shows how the advantages of TLC can be combined with a two-dimensional development technique using different solvent systems to fingerprint complex epoxy resin systems. We also demonstrate that reversed-phase two-dimensional TLC (2D-TLC) can provide as much information as reversed-phase chromatography (*e.g.* prepreg age, resin composition) with a substantial saving of time and cost of equipment.

EXPERIMENTAL

RPLC

For the liquid chromatographic separations a Waters 660 solvent program system combining a Waters M45 pump and a Waters 6000 pump was used. A Whatman Partisil 10 $_8$ column and a 40-min slightly concave gradient (gradient number 7) of 40–100% acetonitrile in water at a flow-rate of 2 ml/min were utilized to achieve the best separation of components for a variety of epoxy systems. Detection was via a Varichrome UV detector set at 254 nm.

TLC

Reversed-phase 2D-TLC was performed using Whatman KC18F reversed-phase plates (10 × 10 cm) containing a fluorescent indicator. Separation in the first dimension was achieved via development with an acetonitrile–water (70:30) mixture and in the second dimension with chloroform. thus the first dimension development mimics the separation on RPLC while the second dimension provides additional separation via a different mechanism through the use of a more non-polar system. An UV lamp set at 254 nm was used to visualize spots of the fluorescent background of the plates.

Analysis of eluents and TLC spots

Although all of the components separated either by RPLC or by 2D-TLC were not analysed, a number of the major components were identified by Fourier transform infrared spectroscopy (FT-IR) or mass spectrometry. For these analyses, spots were scraped from the plates and washed with chloroform before being centrifuged and filtered through 0.2 Millex filters. The chloroform was allowed to evaporate and the residue was ground with about 20 mg of potassium bromide in an agate mortar. Pellets of 7 mm diameter were prepared and analysed in a Nicolet 6000C Fourier transform infrared spectrometer. Some samples were analysed by mass spectrometry (MS) using the chloroform extract from above. RPLC peaks were collected with a Gilson peak collector, dried with a stream of nitrogen and analysed as pellets in potassium bromide in the same manner as were the thin layer spots.

Sources of epoxy resins

Commercial grade resins used came from the following sources:

tetraglycidyl ether of methylenedianine (TGMDA), Ciba Geigy MY 720 (Ciba Geigy, Mississauga, Canada)

triglycidyl ether of *p*-aminophenol (TGPAP), Ciba Geigy 0500

diglycidyl ether of bisphenol A (DGEBA), Shell Epon 828 (Shell Canada, Vancover, Canada)

novolac resin, Ciba Geigy ECN 1139.

The composite resins used were extracted from prepregs from the following sources using acetone as the solvent:

Narmco 5208 (Narmco Materials, Costa Mesa, CA, U.S.A.)

Hercules 3501-6 (Hercules, Magna, UT, U.S.A.)

Finally, the adhesive resin analysed was a commercial formulation (EA 9321) obtained from Hysol Dexter (Pittsburg, CA, U.S.A.). It was chosen because of its ability to produce strong bonds using room temperature curing.

RESULTS

Since failures associated with composite resins are usually related to either the initial resin formulation or the use of overage resin, the ability of reversed-phase 2D-TLC to differentiate between resin compositions was compared to that of RPLC. In particular, comparisons were made to determine differences in the various types of epoxy resins used in composite and adhesive systems, batch-to-batch variations in the same composite prepreg resins, aging in a composite prepreg and differences between similar prepreg resins from different manufacturers.

Reversed-phase 2D-TLC fingerprints compared to RPLC chromatograms

Differentiation of epoxy resin types. Commercial resins containing TGMDA, TGPAP, DGEBA and phenol–formaldehyde novolac were fingerprinted by reversed-phase 2D-TLC and the results were compared to those using RPLC.

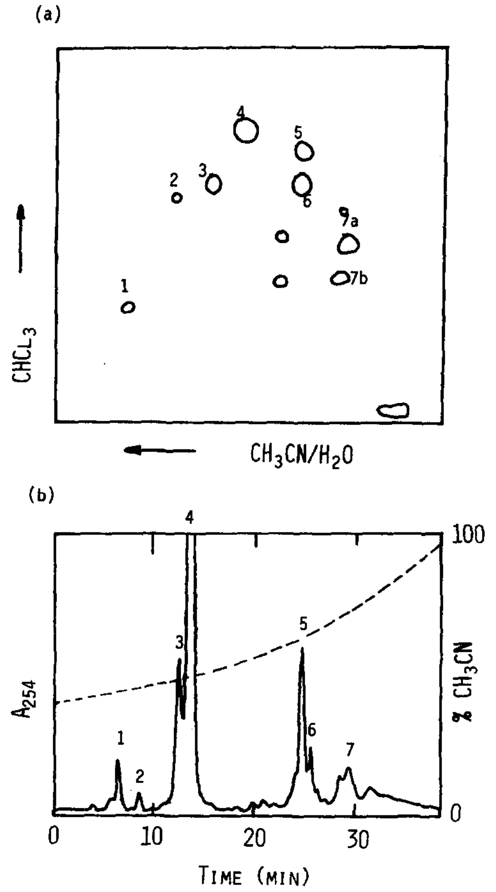


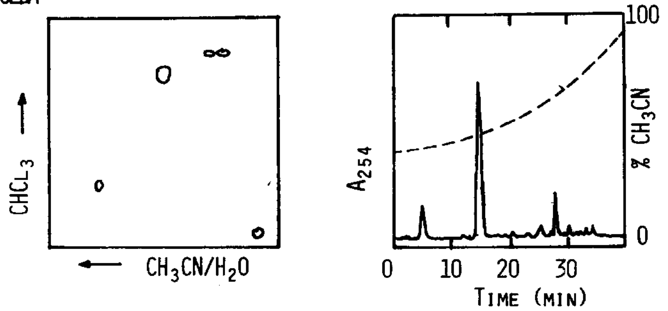
Fig. 1. Reversed-phase 2D-TLC fingerprint (a) compared to the RPLC profile (b) for Ciba Geigy MY 720 resin. Note the superior resolution obtained by reversed-phase 2D-TLC.

Fig. 1 shows that all of the major peaks in the reversed-phase chromatogram of commercial grade TGMDA are readily visible in the reversed-phase 2D-TLC plates. Further, many of the peaks which are only partly resolved in the RPLC are well resolved by reversed-phase 2D-TLC. For example the two components co-eluting as peak 7 from the liquid chromatographic run are resolved into two spots by the use of a different solvent system in the second dimension on the 2D-TLC plate. This demonstrates the value of the reversed-phase 2D-TLC technique for analysing complex systems where resolving all components in a singel solvent system is very difficult or impossible. This fact will become more evident during the analysis of Hercules 3501-6 composite resin which is described later. Therefore, the reversed-phase 2D-TLC technique can enhance the resolution of many components over the conventional reversed-phase chromatographic methods.

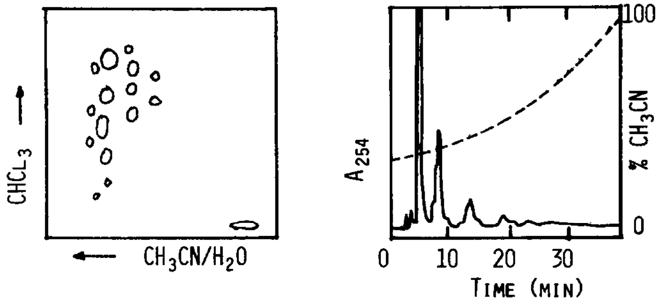
In the present example, the liquid chromatogram shows improved separation of high-molecular-weight components when compared to reversed-phase 2D-TLC. However, a simple solvent change to higher acetonitrile concentrations in the first dimension of the reversed-phase 2D-TLC fingerprint improves the separation of higher-molecular-weight components with a slight loss of resolution of faster moving components. Extraction of spot 4 from the reversed-phase 2D-TLC chromatogram and subsequent FT-IR and MS analyses identified it as pure TGMDA, while similar analyses of spots 5, 6, 7a and 7b were identified as polymers of TGMDA.

Similar chromatographic comparisons between RPLC and reversed-phase 2D-TLC for commercial DGEBA, TGPAP, and novolac resins were performed (Fig. 2). The reversed-phase 2D-TLC chromatograms show a distinctive pattern for each epoxy resin type, and the different types can be easily distinguished. In some cases, such as TGPAP, the resolution in the reversed-phase 2D-TLC is superior to that

(a) DGEBA



(b) TGPAP



(c) NOVOLAC

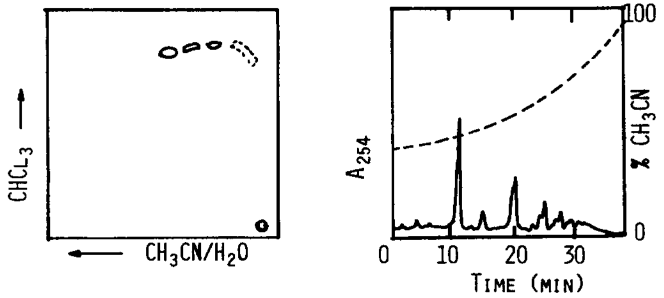


Fig. 2. Comparisons of reversed-phase 2D-TLC fingerprints and RPLC profiles for three commonly encountered commercial grade epoxy resins: a, DGEBA; b, TGPAP; c, glycidylether of phenol-formaldehyde novolac (novolac).

from the liquid chromatogram, while in others containing a larger proportion of high-molecular-weight components (*e.g.* novolac) the reversed-phase liquid chromatogram has slightly better resolution.

Analyses of resin mixtures. to test the ability of the reversed-phase 2D-TLC method to identify components in mixtures of epoxy resins, two epoxy resin systems were chosen: one, a common commercial 350°C-curing composite resin (Hercules 3501-6); and the other, a commercial rubber-toughened epoxy adhesive (Hysol EA 9321). In Hercules 3501-6 resin, both the epoxy and the amine curing agent are present, while in Hysol EA 9321, two distinct epoxy resins are present. Fig. 3 compares the reversed-phase 2D-TLC chromatograms with the reverse-phase liquid chromatograms of the two resins.

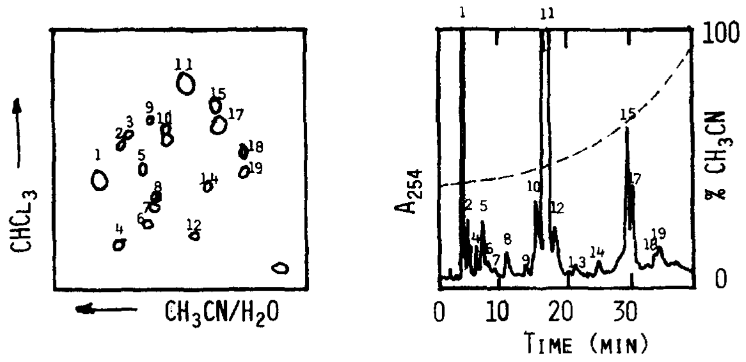
For Hercules 3501-6, the reversed-phase 2D-TLC chromatogram provides an excellent fingerprint of the resin system. At least nineteen different components are readily identified on the reversed-phase liquid chromatogram. The two most intense spots of the reversed-phase 2D-TLC (spots 1 and 11) were eluted from the chromatographic plate and identified by IR and mass spectrometry as the diaminodiphenylsulphone (DDS) and the tetraglycidylether of methylenedianiline (TGMDA), respectively.

Comparison of the reversed-phase 2D-TLC chromatogram and the RPLC profile indicates the superior resolution obtained for faster eluting components by reversed-phase 2D-TLC. In the reversed-phase 2D-TLC fingerprint, peak 1 from the reversed-phase liquid chromatogram is well isolated while peaks 2 and 3 are completely resolved. In fact, the resolution via reversed-phase 2D-TLC is superior on all components up to peak 12. The importance of this high resolution when determining batch-to-batch variations and prepreg aging will be demonstrated later. For components after peak 12 only a slight loss in resolution for some spots is seen in the reversed-phase 2D-TLC chromatograms, while others (spots 15, 17, 18 and 19) are better resolved. A comparison of the patterns of spots in Figs. 3a and 1 indicate that all components in Ciba Geigy MY 720 resin are also found in the Hercules 3501-6 resin which must therefore contain Ciba Geigy MY 720. Thus, the reversed-phase 2D-TLC fingerprint can be used to identify the base epoxy resin as Ciba-Geigy MY 720 without the necessity of IR or MS analyses.

Hysol EA 9321 part A epoxy resin produced the reversed-phase 2D-TLC and RPLC chromatograms contained in Fig. 3b. As can be seen, the reversed-phase 2D-TLC method produces better resolution of components in this mixture than does the RPLC profile. A comparison with Fig. 2b indicates that TGPAP is a major component of Hysol EA 9321 resin and that the other component is a novolac resin similar to Ciba Geigy ECN 1139. Using RPLC, the presence of the novolac in small concentrations is difficults to detect, but with reversed-phase 2D-TLC, the fingerprint pattern is fairly clear. Therefore, the reversed-phase 2D-TLC method can be used successfully to identify mixtures of epoxy resins and the intensities of the spots can be used to estimate proportions of each resin type.

Although not shown here, other commercial resins including numerous film adhesives were also successfully fingerprinted with the reversed-phase 2D-TLC method. These resins are one-part film adhesives used to bond skin plates to honeycomb substructure in advanced aircraft, and contain both the epoxy resin and curing agent as a mixture impregnated in a cloth backing material. In each case the reso-

(a) 3501-6 Resin



(b) EA 9321

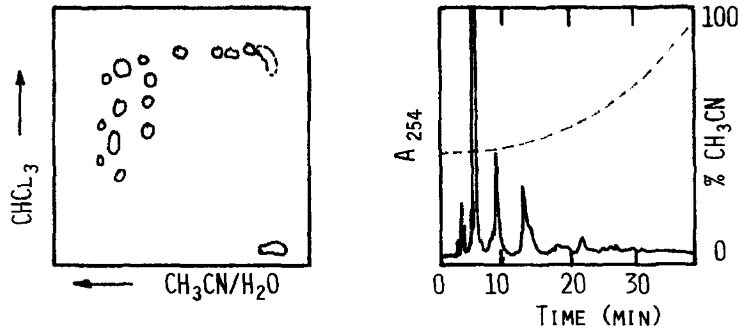


Fig. 3. Comparisons of reversed-phase 2D-TLC fingerprints and RPLC profiles for two important commercial resin systems: (a) Hercules 3501-6 resin used extensively in high temperature composite parts; (b) Hysol EA 9321 resin characteristic of numerous cold-set epoxy adhesives.

lution was at least equal to that produced by RPLC indicating that virtually all commercial epoxy resins can be analysed quickly and accurately by this method.

Discriminating between similar resin systems

Two composite resin systems, both composed of TGMDA epoxy resin and DDS as the hardener (Hercules 3501-6 and Narmco 5208) and curing at 350°C were compared by reversed-phase 2D-TLC to determine if the technique could distinguish between similar resins from different sources. Fig. 4 contains the reversed-phase 2D-TLC fingerprints of each of these resins with its corresponding RPLC profile.

From the reversed-phase liquid chromatogram it is evident that 3501-6 resin has two early eluting peaks (peaks 4 and 6) not found in Narmco 5208 resin. These peaks are readily visualized as well-isolated spots (spots 4 and 6) on the reversed-phase 2D-TLC fingerprint. As well, peak 5 is substantially larger in the liquid chromatogram of Hercules 3501-6 and is similarly more intense in the reversed-phase 2D-TLC fingerprint. Finally, the reversed-phase 2D-TLC fingerprints resolve more components than the RPLC profiles, especially in the early eluting region. This result again correlates well with fingerprints of the pure components and confirms the usefulness of reversed-phase 2D-TLC for identifying minor differences between similar resins for quality control purposes.

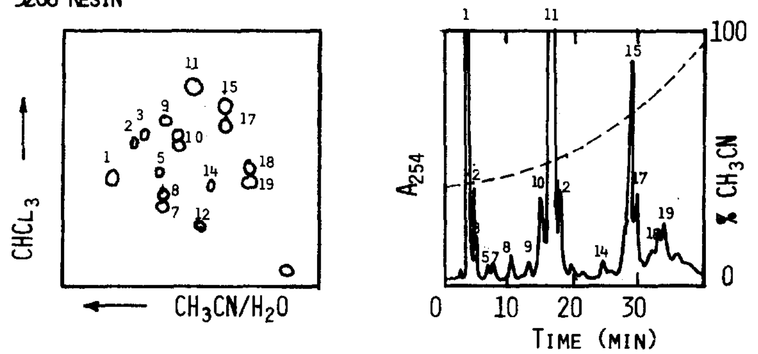
Finally, the reversed-phase liquid chromatogram indicates a substantially higher area of peak 17 relative to peak 15 in Hercules 3501-6 resin when compared to Narmco 5208 resin. This difference can also be seen in the reversed-phase 2D-TLC fingerprints of the resins where spot 17 is substantially more intense in the Hercules 3501-6 resin sample.

Batch-to-batch variations in a singele resin formulation

In order to be useful for monitoring quality control in epoxy prepreg manufacture, the reversed-phase 2D-TLC method must be able to distinguish batch-to-batch variations in resin formulations. Therefore, reversed-phase 2D-TLC fingerprints of two different batches of Hercules 3501-6 resin were compared to their corresponding RPLC curves (Fig. 5).

The RPLC curve indicates that there are only two distinguishable differences between the two batches: the presence of peak 14, and the higher proportion of peak 17 relative to peak 15 in batch 1. These differences are again visible in the reversed-phase 2D-TLC chromatogram. Spot 14 is readily visible in batch 1 while the relative

(a) 5208 Resin



(b) 3501-6 Resin

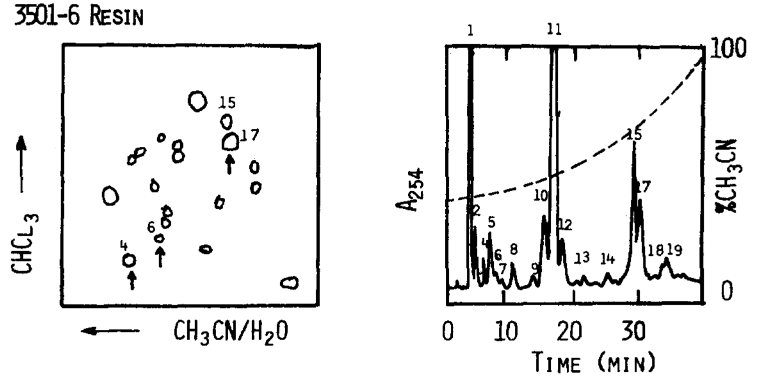
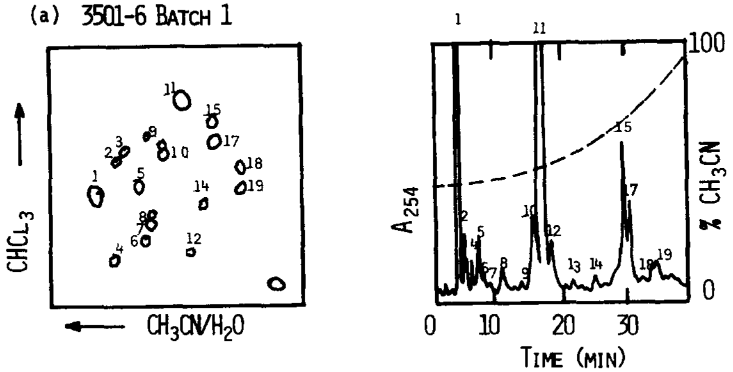


Fig. 4. A comparison of reversed-phase 2D-TLC fingerprints from similar epoxy resin systems from two manufacturers to show the ability of reversed-phase 2D-TLC to identify minor differences in composition of complex mixtures: (a) Narmco 5108 resin; (b) Hercules 3501-6 resin.

(a) 3501-6 Batch 1



(b) 3501-6 Batch 2

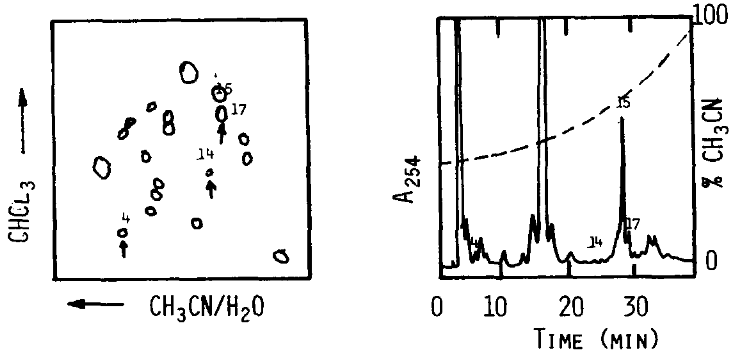


Fig. 5. A comparison of reversed-phase 2D-TLC fingerprints from different resin batches of Hercules 3501-6 to show the utility of reversed-phase 2D-TLC for quality control of resin formulation.

intensity of spot 17 is also increased. Therefore, the reversed-phase 2D-TLC technique can be used to monitor batch-to-batch variations in a single resin system.

Aging in epoxy prepreg resins

As mentioned in the introduction, a major concern during the manufacture of parts from prepreg resins is that the resin ages when kept at room temperature and loses desired properties. Therefore, a good resin analysis technique should be able to determine resin age. Previous experiments have suggested that Hercules 3501-6 resin aging produced some specific components, and that the major component of aging produces peak 12 in the RPLC curve. This peak corresponds to spot 12 in the reversed-phase 2D-TLC fingerprint. Samples of Hercules 3501-6 resin were aged between 0 and 33 days at room temperature before being fingerprinted by reversed-phase 2D-TLC. Although not shown here, the result of these experiments indicate that a visual inspection of the relative intensity of peak 12 to peak 11 can give a qualitative estimate of resin age. The use of available TLC scanners may result in quantitative estimates and the method, therefore, shows promise as a quick alternative to other methods for determining resin age.

DISCUSSION AND CONCLUSIONS

From the above experiments it is evident that reversed-phase 2D-TLC is a valuable alternative to liquid chromatography for the analysis of epoxy resins used in adhesives and composites. In most cases the resolution of components, especially in complex samples, exceeds that obtained by RPLC. Not only could minor variations in composition of similar resins be determined, but the age of the epoxy composite resins could also be estimated, as could the amounts of the various component resins in mixtures. As well, a number of other advantages are obvious. First the use of fluorescent plates allows all components to be visualised regardless of whether they absorb light at a particular frequency, in contrast to detection of gradient elutions by RPLC. Since the size and intensity of the spot in reversed-phase 2D-TLC is roughly proportional to the amount present, one can estimate amounts by visual inspection or through the use of a commercial TLC scanner. During the present experimental work, it was also noted that the reversed-phase 2D-TLC method could be used to detect components which were not detected by the use of a fixed-wavelength liquid chromatographic detector.

The second advantage of the reversed-phase 2D-TLC method, which is most important for laboratories performing a large number of analyses, is the speed with which analyses can be done. In the present experiments a reversed-phase 2D-TLC fingerprint could be obtained easily in 1 h and many could be run simultaneously, while a single RPLC analysis requires a 1-h run and a 1-h recycle time. Therefore, more samples can be run via the reversed-phase 2D-TLC method.

Third, the cost of equipment for reversed-phase 2D-TLC is minimal and only small amounts of solvents are used. By contrast, gradient elution by liquid chromatography requires a relatively expensive set-up and uses substantial amounts of solvents. As well, the necessity of re-using the column in liquid chromatography diminishes reliability for samples like epoxy resins which tend to contaminate the reversed-phase silica gel.

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