

Identification of Some Boron-Based Curing Agents in Cured Epoxy Systems by Computer-Assisted Infrared Spectroscopy

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Synopsis

The use of computer-assisted infrared spectroscopy has allowed identification of three different boroxines and a boron trifluoride complex used as curing agents in cured epoxy resins. Boroxines were distinguished from a boron trifluoride complex by the B—O stretch absorption near 1400 cm^{-1} in the solid state. Detection of this absorption was enhanced by spectral subtraction methods in which the reference spectrum was that of the parent resin, or a suitably cured system of similar structure. Distinction between different boroxines was achieved by analysis of the gases evolved from samples heated at 300°C in nitrogen. Identification of the alcohol fraction of the original boroxine was improved by subtraction of the spectrum of water vapor. Boron trifluoride was detected in the gases evolved at $450\text{--}500^\circ\text{C}$ from BF_3 -cured systems, and also in the liquid pyrolyzates. Further simplification of the 300°C gas spectra by subtraction of alcohol and carbon dioxide revealed the presence of acrolein in the gases from boroxine-cured systems while BF_3 -cured systems yielded acetaldehyde. These differences may be associated with different end groups in the cured resins.

INTRODUCTION

Epoxy resin based systems are widely used as adhesives and in structural composites, especially in the aerospace industry. Analysis of uncured systems, in terms of quality control, has received considerable attention,¹⁻³ but identification of the components of cured material, other than in general terms appears to have been largely neglected. This aspect will undoubtedly assume greater importance in future, as, for instance, in the examination of defective components. The most general method for characterization of cured systems is some form of pyrolysis, followed by analysis of the gaseous and liquid products, and much work has been done along these lines, mainly to determine thermal stability or to elucidate thermal degradation mechanisms. The topic was reviewed in 1966 by Bishop and Smith⁴ and in 1975 by Paterson-Jones.⁵ Not surprisingly, degradation temperature and rate of temperature rise were found to affect the composition of the products, and it also appears that catalytic influences of the substrate play a significant role in the degradation.

The most popular method for the analysis of the pyrolyzates has been gas-liquid chromatography and in recent years gas chromatography-mass spectrometry.⁶⁻⁹ Analysis of the pyrolyzates by IR spectroscopy has not been generally used, possibly because of the low resolving power of the technique compared with chromatographic methods. Sugita and Ito¹⁰ were able to identify parent resins and several anhydride curing agents from the IR spectra of liquid pyrolyzates obtained at temperatures between 300°C and 500°C . Morimoto

and Enomoto^{11,12} examined the gaseous products from high temperature pyrolysis of cured epoxy systems and found that the components of the gases were characteristic of the resins and curing agents under investigation. IR analysis of cured epoxy systems as solid dispersions in KBr will usually give useful indications of the type of epoxy resin present, but the curing agent often cannot be identified.

The information contained in IR spectra can be more readily obtained if the spectra are in digital form, suitable for computer processing. Koenig¹³ has demonstrated the applicability of computer data processing to IR spectra, and Lin, Bulkin, and Pearce used these techniques to follow the course of degradation of some cured epoxy systems.¹⁴ Thus, some indication of the identity of components other than the epoxy resin might be obtained by subtraction of the parent resin spectrum from that of the cured system. Successive subtraction of recognizable components of a pyrolysis gas mixture (e. g., water) might yield useful information about both resin and curing agents. The advantages of such a system have been described by Liebman, Ahlstrom, and Griffiths,¹⁵ who examined the products of pyrolysis and combustion of PVC and ureaformaldehyde resins, and Lephardt and Fenner,¹⁶ who used an on-line FT-IR spectrophotometer to analyze the gases evolved from cellulose and tobacco.

This paper presents the results of an investigation into the use of computer-assisted IR spectroscopy for the analysis of some cured epoxy systems. The analytical aspect has been stressed, and no attempt has been made here to interpret the data in terms of curing or degradation reactions. The results show that the technique can be used to distinguish between four different boron compounds in cured systems, and may be used for the analysis of unknown materials. The materials chosen for the initial study were three cyclic borate esters (boroxines) and a boron trifluoride-monoethylamine complex ($\text{BF}_3\text{-MEA}$), and two commonly used glycidyl ether type epoxy resins. The use of boroxines as curing agents for epoxy resins yields materials having good transparency and resistance to heat and ultraviolet radiation.^{17,18} Boroxines and BF_3 complexes may be used as the sole curing agent for epoxy resins, and the BF_3 complexes are often used as catalysts for more conventional curing systems. In this work, the boron compounds have been used as the sole curing agents.

EXPERIMENTAL

Apparatus

All spectra were recorded on a Perkin-Elmer Model 580B Double Beam, Ratio Recording Spectrophotometer, interfaced with a Perkin-Elmer Model 3500 Data System. Spectra were stored on microfloppy disks and retrieved for manipulations as required.

A small tube furnace, 20 cm \times 2.5 cm was used for pyrolysis work. The pyrolysis tube (Pyrex, 25 cm \times 1.5 cm diameter) was connected to the gas cell (20 cm path length) by 2 mm i.d. capillary tubing and a spherical joint. The gas cell remained *in situ* in the spectrophotometer during the experiments. A bypass line was provided via a three way tap ahead of the furnace.

Materials

Epoxy resins were Epon 828 (Shell) and DEN 431 (Dow) and were used as received. Epon 828 is based on Bisphenol A, and DEN 431 on a phenol novolak resin.

Trimethoxyboroxine (TMB, Aldrich) and $\text{BF}_3\text{-MEA}$ (Ciba-Geigy, HT973) were used as received. Tri-*n*-butoxyboroxine (TBB) and tribenzyloxyboroxine (TZB) were prepared by the reaction of boric acid with the appropriate alcohol with concurrent removal of water.¹⁹

Resin and curing agent were mixed at 80°C, then cured for 3 h at 80°C, 3 h at 135°C, and 2.5 h at 180°C. The proportion of curing agent, by mass was 5 phr for TMB and $\text{BF}_3\text{-MEA}$, 7 phr for TBB, and 15 phr for TZB. These levels were calculated to give approximately the same concentration of boron in the final mixtures. Solvents were laboratory grade and were distilled in glass before use.

Methods

Solid State Spectra

Cast samples were sawn into slices about 1 mm thick. The "sawdust" was incorporated into KBr discs and the slices retained for pyrolysis work. Liquid epoxy resins were prepared as films between KBr plates. All solid state spectra were recorded under conditions which gave 3 cm^{-1} resolution at 1700 cm^{-1} ; data were recorded at 1 cm^{-1} intervals.

Spectra of Pyrolysis Gases

Spectra of pyrolysis gases were recorded between 300°C and 500°C at 50°C intervals as follows:

1. Cured resin, 0.1–0.2 g, was inserted into the pyrolysis tube in a porcelain boat and positioned at the center of the furnace. The system was thoroughly flushed with nitrogen, and with nitrogen passing through the bypass only, at 100 mL/min, the temperature of the furnace was raised to 300°C at 20°C/min and then held at 300°C for 5 min.

2. The "blank cell" spectrum was recorded, and the evolved gases were then flushed into the IR cell. The optimum time required for this transfer was determined by observing the increase in absorption of the water vapor band near 1557 cm^{-1} (Fig. 1).

3. At the point of maximum absorbance, the nitrogen flow was turned off and the spectrum of the gases in the cell recorded under conditions which gave 4 cm^{-1} resolution at 1700 cm^{-1} ; data was collected at 5 cm^{-1} intervals, scan time 2 min.

4. The temperature of the furnace was then raised to 350°C at 10°C/min and held for 5 min. At the same time, the cell was flushed with nitrogen at 500 mL/min via the bypass. At 100 mL/min, more than 5 min were required for complete flushing of the cell (Fig. 1).

5. The spectrum was corrected for the "cell blank," by digital subtraction, and stored on disk.

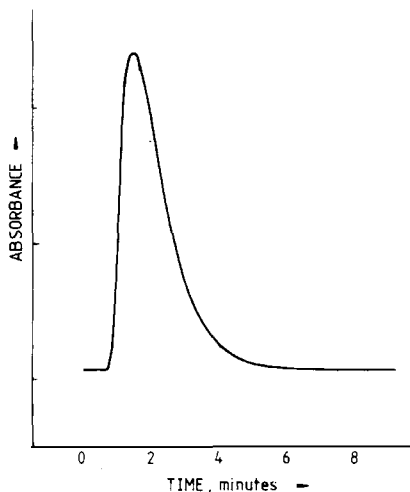


Fig. 1. Rate of flow of gases through gas cell at a nitrogen flow of 100 mL/min.

6. The series of operations from step 2 was repeated at furnace temperatures of 400°C, 450°C, and 500°C.

Analysis of Liquid Pyrolyzates

At temperatures below the onset of complete pyrolysis (400°C), some samples yielded a liquid pyrolyzate which condensed in the cooler parts of the tube. When this occurred, a separate experiment was performed at 350°C and the liquid was removed for analysis.

In a separate series of experiments, samples were heated in the apparatus from ambient to 500°C at 20°C/min. The liquid pyrolyzates were extracted from the tube by successively refluxing with petroleum spirit (40–60°C) and acetone. After removal of the solvent on a water bath the residues were analyzed by TLC and IR immediately, and after standing for several days.

Merck precoated TLC plates (silica gel F₂₅₄, 0.25 mm, on glass) were used as received. Eluants were various mixtures of acetone and petroleum spirit (40–60°C) from 1 + 1 to 3 + 7 by volume. A spray reagent, 2,6-dichloroquinone-4-chloroimine (1% in toluene), was used to detect compounds on the TLC plates. Plates were sprayed with the reagent, dried with a hot air blower to remove toluene, then exposed to UV radiation (254 nm) for 30 min. Phenolic compounds produced pink colors and amines yielded various colors from purple to green.

RESULTS

Solid State Spectra

The spectra of the cured materials retain many of the characteristics of those of the uncured resin, so that the resin component is readily identified (Fig. 2). The main differences are the expected loss of epoxide absorption near 3000, 910

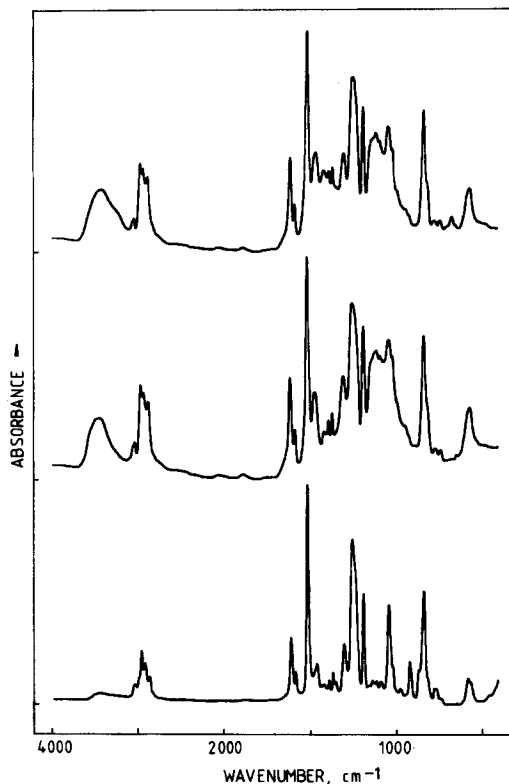


Fig. 2. Resin spectra: top: 828/TMB-cured; middle: 828/BF₃-MEA-cured; bottom: 828 resin, uncured.

and 850 cm⁻¹, the appearance of noncyclic CH₂ stretching bands near 2920 and 2830 cm⁻¹, and broad absorption near 1100 cm⁻¹ attributed to C—O—C stretching in aliphatic ethers, as a result of homopolymerization. There is little evidence of the presence of the boroxines, other than a general broadening near 1400 cm⁻¹. There is no evidence of the BF₃-MEA curing agent.

In order to emphasize the changes that occur in the spectrum on curing, the spectrum of the appropriate epoxy resin is subtracted from that of its cured system. The boroxines are indicated by broad absorption near 1400 cm⁻¹, attributed to B—O stretching vibrations (Fig. 3). The out-of-plane bending vibrations of the aromatic C—H bonds in TZB are clearly visible near 700 and 750 cm⁻¹, but there is no useful distinction between the boroxines in the 1400 cm⁻¹ region. A small band near 660 cm⁻¹ is present in boroxine-cured systems but not in the BF₃-MEA system. Strong negative bands near 1500 and 1240 cm⁻¹ are due to changes in band shape on curing, with the result that the subtraction is imperfect. The loss of epoxide, the increase in noncyclic CH₂, and the formation of aliphatic ether bonds are also more clearly indicated than in the original spectra. There is no evidence of the BF₃-MEA curing agent.

A somewhat clearer view of the differences between the boroxine cured systems can be obtained by subtracting the spectrum of the appropriate BF₃-MEA system from those of the boroxine systems. The technique simplifies the dif-

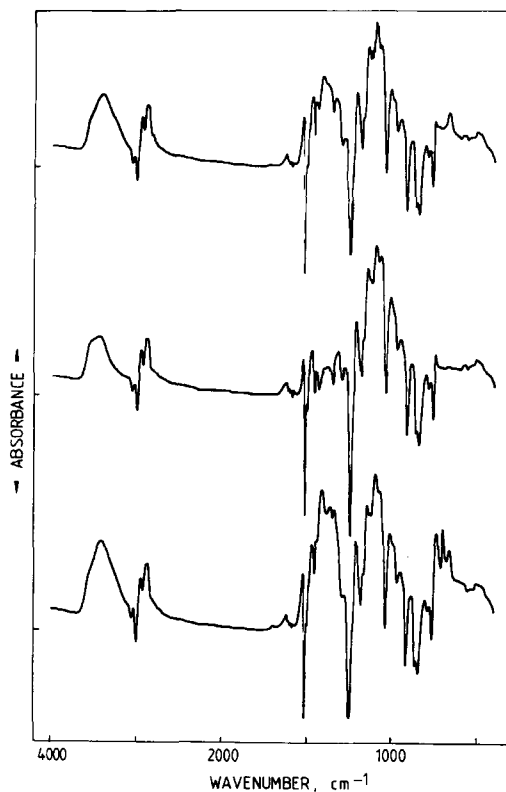


Fig. 3. Solid state difference spectra: uncured 431 resin used as reference; normalized on band near 1600 cm^{-1} . Top: 431/TMB-cured; middle: 431/ BF_3 -MEA-cured; bottom: 431/TZB-cured.

ference spectrum so that only bands associated with the presence of boroxine are evident. Thus negative bands due to epoxide, and positive bands due to aliphatic ether are more or less cancelled, as are the imperfect subtractions near 1500 and 1240 cm^{-1} . There is still little difference between the three boroxine spectra near 1400 cm^{-1} , but the spectrum of the TBB system appears to contain less hydroxyl (OH str , 3400 cm^{-1}) and less aliphatic ether. There is also evidence of residual unreacted epoxide (Fig. 4).

Spectra of Pyrolysis Gases

The spectra of gases evolved from either type of cured resin system at 300°C allowed clear differentiation between all four curing agents (Fig. 5). Methanol and *n*-butanol from the TMB and TBB systems, respectively, were readily identified after subtraction of the water vapor spectrum. No volatile alcohol was observed in the 300°C gas spectrum from TZB systems, but benzyl alcohol was identified, by its IR spectrum, in a liquid which appeared in the pyrolysis tube at this low temperature. The boroxine systems yielded gas spectra which differed only in the alcohol present, but the spectra of the gases evolved from the BF_3 -MEA systems were significantly different. After subtraction of water, alcohol, CO and CO_2 from each gas spectrum, the boroxine systems all yield a

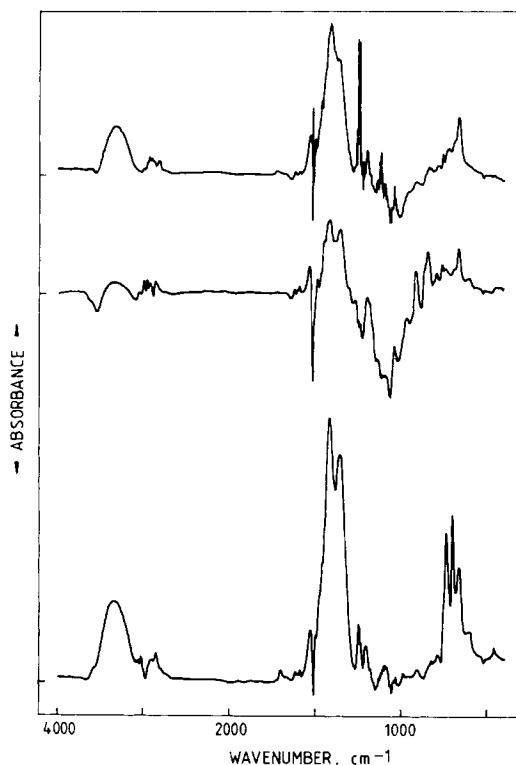


Fig. 4. Solid state difference spectra: 431/BF₃-MEA-cured resin used as reference; normalized on band near 1600 cm⁻¹. Top: 431/TMB; middle: 431/TBB; bottom: 431/TZB.

spectrum consistent with that of acrolein. By contrast, acrolein was not positively identified in the residual spectrum of the BF₃-MEA systems. The carbonyl absorptions in the spectra of the latter are more complex, and are consistent with the presence of acetaldehyde. The ratio of CO₂ to carbonyl is higher than for boroxine systems. A small band near 1600 cm⁻¹ may be associated with the amine fraction of the curing agent (—NH₂ deformation); otherwise, there is no indication of its presence.

As the temperature is raised above 350°C, more extensive decomposition occurs, and liquid products appear in the pyrolysis tube. The gas spectra become very similar for all samples (Fig. 6) and do not appear to be characteristic of either resin type or curing agent. In some experiments with BF₃-MEA systems, a band near 730 cm⁻¹ was observed, usually at temperatures above 450°C, and there appeared to be some reaction with the cell window material. The species responsible has been identified from its IR spectrum as fluosilicate, and may be derived from the reaction of BF₃ with silica.²⁰ This phenomenon was not constant, and therefore not a reliable indicator of the presence of fluorine compounds. The reaction appeared to be related to the length and diameter of the tubing between the pyrolysis tube and the gas cell, and to the gas flow rate. Short, wide-bore tubing favored the reaction in the cell, more than longer, narrow-bore tubing. A narrow-bore tube was used in our experiment to reduce dilution of the sample with inert gas.

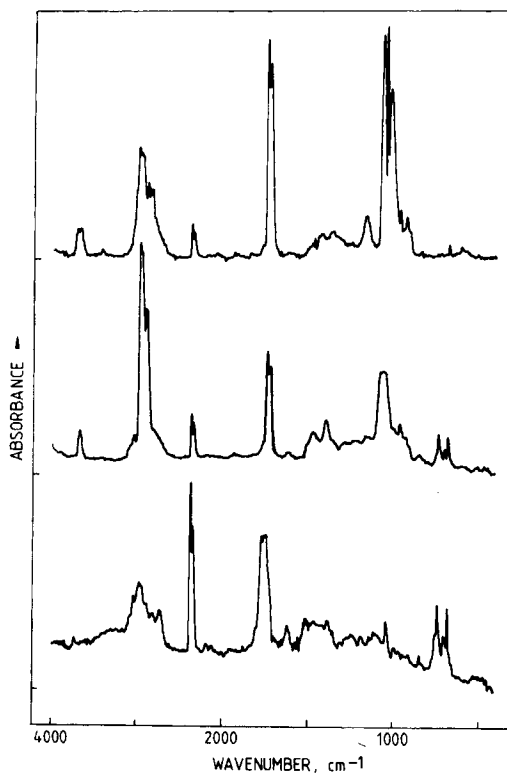


Fig. 5. Gas spectra: gases evolved at 300°C from cured resins, corrected by subtraction of water vapor spectrum. Top: 828/TMB; middle: 828/TBB; bottom: 828/BF₃-MEA.

Spectra of Pyrolyzates

The spectra of the liquids obtained from pyrolysis at 500°C gave IR spectra which were similar to those of the phenols from which the epoxy resins were made. The difference between petroleum-spirit-soluble and acetone-soluble fractions was reflected in the greater hydroxyl content of the latter fractions. TLC analysis showed, as expected, that the pyrolyzates were complex mixtures, with the more polar materials in the acetone fraction.

The spectra of the acetone soluble fractions from BF₃-MEA systems contained a band near 1040 cm⁻¹. A reaction with the KBr window was observed, and after removal of the organic material the residue was identified as potassium fluoborate (KBF₄). It appears that BF₃ is present in the pyrolyzate in a very loosely bound form, since the spectrum of the BF₃-MEA in KBr does not contain bands due to BF₄⁻. This phenomenon is reproducible, and can be used as a reliable indicator of the presence of BF₃-MEA complexes in the cured system. There was little difference in the spectra of the pyrolyzate fractions when fresh and after exposure to the atmosphere, other than some indication of oxidation (carbonyl bands near 1700 cm⁻¹). TLC analysis of the BF₃-MEA pyrolyzates yielded colored compounds, indicative of amines, when the plates were sprayed with 2,6-dichloroquinone-4-chloroimine and exposed to UV radiation. Attempts to separate and identify these compounds were not successful.

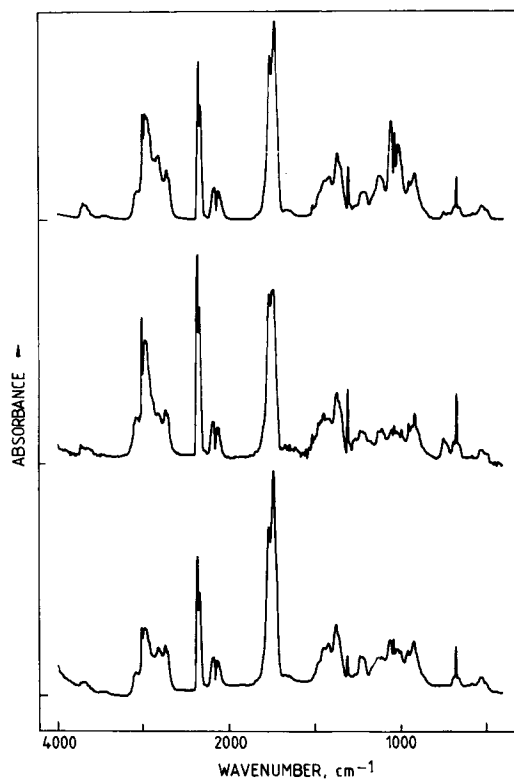


Fig. 6. Gas spectra: gases evolved at 400°C from cured resins, corrected by subtraction of water vapor spectrum. Top: 431/TMB; middle: 828/BF₃-MEA; bottom: 431/TZB.

A liquid pyrolyzate evolved from TBB cured systems at 300°C was identified, from its IR spectrum, as low-MW unreacted epoxy resin. This is consistent with the difference spectra obtained from the solid samples (Fig. 4). Boric acid was identified in the liquid pyrolyzates obtained at 500°C from boroxine cured systems.

Cerco²¹ found that spectra of epoxy pyrolyzates changed significantly on standing, and attributed this to oxidation and the loss of volatile components. Since our procedure involves evaporation of solvents on a water bath, the volatiles would no doubt be removed at the same time. The only change of significance was the gradual disappearance of the BF₃, indicated by the BF₄⁻ band at 1040 cm⁻¹, and the formation of boric acid, in the BF₃-MEA pyrolyzates.

In all samples, solid carbonaceous residue left in the pyrolysis boat was found to contain boric acid after exposure to the laboratory atmosphere for several days, probably by hydration of boric oxide.

DISCUSSION

If boron has been detected in a sample, for instance, by emission spectrography, then the techniques described can be used to distinguish between boroxines and BF₃ complexes and between different boroxines.

Boroxines can be distinguished from BF₃-MEA by the absorption near 1400

cm^{-1} due to B—O stretching vibrations. The identity of the resin component will usually be evident from the solid state spectrum of the sample, and subtraction of the resin spectrum from that of the sample will give reasonably clear indication of B—O bands. This difference spectrum is complicated by the presence of both positive and negative bands as a result of chemical and physical changes that occur on curing. One way to enhance detection of bands due to the curing agent is to use a suitably cured sample of parent resin as the reference material in the spectral subtraction. Ideally, the curing agent used in this reference sample should produce a cured structure that is chemically similar to the system under investigation so that maximum cancellation of absorption bands occurs in the subtraction process, but naturally should not contain any interfering IR absorption. The spectra of resins cured with BF_3 -MEA are similar to those of resins cured with boroxines (Fig. 2) in that extensive etherification occurs.²² The difference spectra in which BF_3 -MEA cured systems are used as the reference are thus much simpler than those in which the uncured parent resin spectrum has been subtracted. In addition, differences in degrees of cure are more readily seen in terms of residual epoxide and extent of etherification. Even if the identification of the parent resin is imperfect, the subtraction still gives adequate results; Figure 7 shows the result of subtraction of 431/ BF_3 -MEA from 828/TMB. A clue to the presence of boroxine is provided by the band near 660 cm^{-1} , which is usually visible in the solid state spectrum of the sample (Fig. 3). This band has not been assigned, but appears to be a constant characteristic of

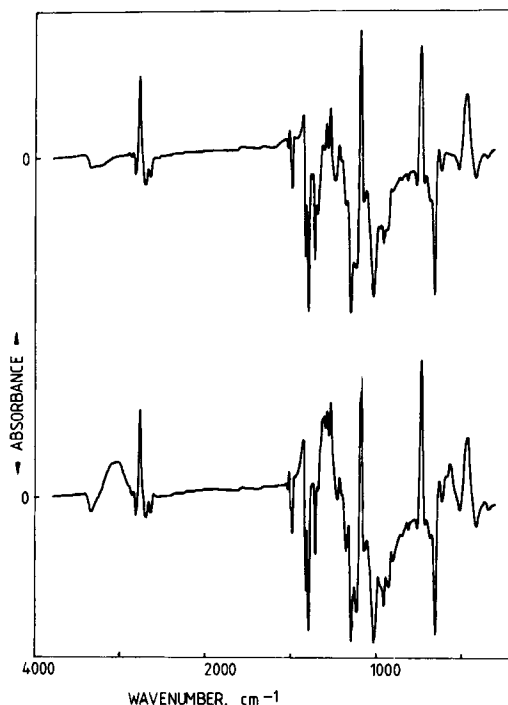


Fig. 7. Solid state difference spectra: subtractions performed with an unmatched sample of cured resin: 431/ BF_3 -MEA used as reference for cured 828 resins. Normalized on band near 1600 cm^{-1} . Top: 828/ BF_3 -MEA; bottom: 828/TMB.

boroxine cured systems, and occurs in borate esters but not in boroxines or polyborates.²³ Confirmation of boroxines, and further identification, is provided by the evolution of the alcohol of the original boroxine at 300°C. Under the conditions used in this work, the amount of alcohol evolved was well below that expected from the amount of boroxine used. This could be due to insufficient pyrolysis time at 300°C, with other reactions occurring at higher temperatures, or perhaps some of the alcohol is chemically different from the remainder, as, for instance, in end groups in which bonds are more easily broken than in the polymer chain.

The various forms in which the boron and fluorine were found in the pyrolyzates of BF₃-MEA-cured systems indicates that a complex series of reactions occurs during pyrolysis. These pyrolysis products are more sensitive to experimental conditions than those of boroxine cured systems. Although there were indications of the presence of amines in the TLC analyses of BF₃-MEA pyrolyzates, the presence of ethylamine was not confirmed; if organic carboxylic acid is present in the 300°C gas from BF₃-MEA systems, then it is to be expected that ethylamine would react to form a protonated species, which is unlikely to be volatile at room temperature.

Spectra of gases evolved from the various samples at temperatures above 400°C all show the same trends. Methane and CO become more evident, and the oxygenated species decrease. Although there are small differences between the various systems, there is enough variation between runs to render the spectra unreliable for identification purposes.

The similarity of the spectra of the three boroxines in the cured systems suggests that boron is present in each in the same state of chemical combination. The 300°C pyrolysis gas spectra of the boroxine systems differ only in the alcohol component, which suggests that the same pyrolysis reactions occur in each system on heating. That a single carbonyl compound, acrolein, should be the major species that contains oxygen is noteworthy, especially by contrast with the gases evolved from the BF₃-MEA system, which contain acetaldehyde. It is possible that the production of acrolein is associated with the release of alcohol from the system; not only is acrolein not specifically detected in the BF₃-MEA systems, but the overall amount of carbonyl compounds is considerably lower. There is no doubt that for the systems studied, the spectra of the gases evolved at 300°C are characteristic of the curing agents, and do not appear to be affected by the resin. These gaseous products may reflect differences in end groups.

The application of this technique to other epoxy/curing agent systems is presently being investigated, as is a more detailed examination of the gases evolved in low temperature pyrolysis.

CONCLUSION

Computer-assisted IR spectroscopy has been found to be a useful technique for characterization of cured epoxy resin systems. Boron-based curing agents may be identified by using spectral subtraction methods on the solid samples and on the products of pyrolysis. The speed and sensitivity of a ratio recording dispersive IR spectrometer can be used to produce low-resolution gas spectra of considerable diagnostic value.

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