Thermochimica Acta, 230 (1993) 293–308
Elsevier Science Publishers B.V., Amsterdam
SSDI 0040-6031(93)01099-O

The characterization of amine-activated epoxies as a function of cure by using TGA/FT-IR

David J. Johnson[a], David A.C. Compton[a,*], Richard S. Cass[b] and Philip L. Canale[b,1]

[a] *Bio-Rad, Digilab Division, 237 Putnam Ave., Cambridge, MA 02139 (USA)*
[b] *Bacon Industries, Inc., 192 Pleasant Street, Watertown, MA 02172 (USA)*

(Received 8 December 1992; accepted 23 February 1993)

Abstract

The physical and chemical properties of cured diglycidyl ether of Bisphenol A (DGEBA) are greatly affected by the initial and final cure temperatures and cure schedule. These properties are also affected by the deviation from the stoichiometric ratio of curing agent used. Analysis of a previously cured epoxy for these parameters has usually involved large samples and an inordinate amount of time. In this work, a cured epoxy is studied as it decomposes using a combination of two analytical techniques: thermogravimetric analysis and simultaneous analysis of the evolved gases by Fourier transform infrared spectroscopy, a combination known as TGA/FT-IR. During the TGA/FT-IR experiment, evolution profiles for specific gases are obtained, as well as the normal TGA weight loss profiles. Using this information, both the cure schedule and epoxy/activator cure ratios could be established from the analysis of the cured polymer. The particular material studied, a DGEBA polymer cured using a primary cycloaliphatic diamine, showed a curing mechanism similar to that obtained using an aromatic diamine. However, the decomposition behavior of the studied sample was more reminiscent of an epoxy cured by using an aliphatic diamine system. This work demonstrates that a cured polymer can therefore be characterized in terms of both thermal history and activator–resin ratio in a single TGA/FT-IR experiment.

INTRODUCTION

Changes in activator–resin ratio and/or the cure schedule of an epoxy resin adhesive will greatly affect the operating performance of the finished product. As a result, the ability to monitor quickly and reliably the processing variations and, therefore, to predict performance has become a major goal in today's polymer industry.

Prior to the advent of commercially available thermal analysis equipment, hardness and lap-shear strength measurements were performed to

---

* Corresponding author at Sonoco Products Company, N. Second St., Hartsville, SC 29550, USA.

[1] Present address: W.R. Grace, 25 Hartwell Avenue, Lexington, MA 02173, USA.

monitor the quality of the cured system. Great care was needed when performing these tests and often the results were unreliable. Recently, analysis by DSC, TMA and DMA have contributed greatly to the overall characterization of these materials. The thermal stability, hardness, solvent resistance and long-term dimensional stability of the epoxy system analyzed in this study have been studied extensively as functions of concentration and degree of cure [1,2]. The research described in this paper utilizes a combined TGA/FT-IR method to characterize the processed materials further. The thermogravimetric analyzer (TGA) records the loss of weight of a sample as a function of temperature, or time, under various purge gas conditions. The Fourier transform infrared spectrometer (FT-IR) can be used to obtain spectra of the evolving gases and correlate these to the detected weight losses.

The epoxy resin system under study was a near-monomeric diglycidyl ether of Bisphenol A (2-di-[4-(2,3-epoxy-1-propoxy)-1-phenyl]propane) with an epoxy equivalent weight of 173. The curing agent was composed of a mixture of 10% tertiary amine catalyst and 90% primary cycloaliphatic diamine. The primary diamine curing agent is very alkaline and its active amine hydrogens are sterically hindered. If the tertiary amine catalyst is removed from the system and the primary amine is used in stoichiometric amounts with the epoxy resin, a stable pre-polymer (B-state) will be formed at temperatures below 70°C. Even with the tertiary amine catalyst, a less stable B-staged pre-polymer can be formed below 40°C. This similar pre-polymer B-stage phenomenon is normal for most epoxy/primary aromatic diamine systems [1,3], and is attributed to steric hindrance and pH effects.

The cycloaliphatic diamine used in this study is similar to most primary aromatic amines in that the primary amine polymeric addition is favored [3]. This preference for the primary amine hydrogen reaction is well documented, and supported by other studies [4,5]. These studies have indicated the difference in kinetics between primary, secondary, and tertiary amine reactions. A differential scanning calorimetry (DSC) study of the epoxy system discussed in this paper [3] shows two distinct DSC peaks during the cure reaction, when the formulation used has an under-stoichiometric amount of activator. These peaks, representative of high heats of reaction, were assumed to be reactions involving the primary and secondary amine hydrogens, respectively.

It is known that aromatic-diamine-cured epoxy resins are more thermally stable than materials cured by aliphatic amines [6,7]. However, the decomposition of cycloaliphatic-amine-cured DGEBA epoxies has not been completely studied. It has been suggested [6] that the aliphatic-diamine-cured systems are less thermally stable than aromatic-diamine-cured systems, due to their strong nucleophilic nature. If so, this should also be the case for the more nucleophilic cycloaliphatic diamines.

Our research had two initial objectives. The first was to subject the same epoxy system to various cure schedules and to differentiate between the resultant materials using TGA/FT-IR. To accomplish this, the uncured activated epoxy was cured in two distinctly different manners. The first set of specimens was cured for four hours at 150°C. This cure will be referred to as a "zap" cure. The second set of samples was cured for eight hours at 57°C, sixteen hours at 70°C, followed by 24 hours at 110°C, which will be referred to as a "step" cure. These two types of cure are attractive processes for different reasons. The production-line foreman would naturally prefer the "zap" cure since it would produce a high volume of parts in a short period of time. The polymer engineer favors the slow "step" cure since research has shown that this schedule produces the more thermodynamically (and thus dimensionally) stable product.

The second objective of this research was to investigate whether TGA/FT-IR could measure the activator/resin ratio for each material *regardless* of thermal history. This was considered important information for a supplier of resins, because a customer finding a problem with a formulation would most probably return the cured material for analysis, rather than the resin. The analyst is then faced with the challenge of deciding whether the resin supplied caused the problem, or whether the activator was added at the wrong level. Infrared analysis is known to be able to yield quantitative results, since the absorbance of a component in a mixture is related to its concentration in a linear fashion, and so it was felt that the TGA/FT-IR combination would be able to meet this object as well.

TGA records the weight loss of a sample as a function of temperature. The first derivative of the weight loss profile can also be calculated to highlight subtle changes in the *rate* of weight loss during the experiment. While a TGA experiment is in progress, an inert purge gas typically passes over the sample. In a TGA/FT-IR experiment, we can use this purge gas to sweep any evolved gases to the FT-IR spectrometer for infrared analysis. The spectrometer records spectra continually as the composition of the evolved gases changes; each spectrum is displayed on the data station screen as it is obtained. The FT-IR data station also calculates a series of evolved gas profiles in real time, which we call the total evolved gas profile (EGP), functional group profiles (FGPs), and specific gas profiles (SGPs). The evolved gas profile measures total IR absorbance as a function of time; this profile is often very similar to the first derivative of the weight loss. A functional group profile measures IR absorbance within specific frequency regions as a function of time. Many infrared absorbances can be correlated to a particular function group, such as bands in the 3000–2850 cm^{-1} region, which arise from the C–H stretching mode of aliphatics. A specific gas profile is a special type of FGP, where it is known that only one evolved gas absorbs infrared energy within the frequency window selected. This allows the experimentalist to isolate and monitor the evolution of that specific gas, even in the presence of a mixture of other species being evolved. It should be noted here that even through TGA is an excellent quantitative tool, it is unable to measure the loss of an individual component when evolved as part of a complex mixture.

A comparison of the various evolved gas profiles obtained from samples of similar materials often allows for differentiation of similar, but different, polymer systems. This is directly analagous to the way in which first derivative weight loss profiles are routinely compared, but with significantly more information being available. In the past we have examined many types of systems by TGA/FT-IR [8–12], such as poly(vinyl chloride) and paper pulp [8], solvent retention [9], poly(tetrafluoroethylene), polybutadiene, rubber, epoxy resin, silicone, and poly(vinyl acetate) [10], photodegradable polyethylene concentrate [11], and gunpowder [12], among others, Other workers using TGA/FT-IR [13–15] have studied fire retardant mechanisms [13, 14] and synthetic fibers [15]. So far, however, no one appears to have studied the very important epoxy materials by this technique. The TGA/FR-IR approach has been so successful that we have recently also investigated other combinations of thermal analysis with spectroscopy, notably DSC/FT-IR (3), and simultaneous TGA/DSC/FT-IR [16]. In the DSC/FT-IR study, we examined the curing of the epoxy system being discussed in this work, as well as that of poly(ethylene terephthalate). The STA/FT-IR study [16] in progress has been able to obtain valuable comparisons between samples of solder paste and encapsulant formulations purchased from different vendors.

In all of these TGA/FT-IR studies, and the STA/FT-IR study, the examination of the various evolved gas profiles was found to be very informative. In several cases [9, 12], we were able to obtain quantitative information from these profiles that was not available from TGA alone. It was our hope that such detailed study and comparisons of data from different epoxy formulations would allow us to differentiate those formulations in terms of their thermal history. Furthermore, we wanted to ascertain whether we could measure the activator/resin ratio that had been used in a particular formulation, by integration of suitable specific gas profiles.

EXPERIMENTAL

The data presented here were collected using an integrated TGA/FT-IR system from Bio-Rad, Cambridge, MA. This system combines a Bio-Rad FT-IR spectrometer and a TG 1000 thermogravimetric analyzer (PL Thermal Sciences, Epsom, UK), with a specially created optical interface bench for TGA/IR. Operation of the combined system was designed so that the Bio-Rad 3200 data station controls all TGA and FT-IR activity. The PL Computer Controlled Interface operates under the command of the 3200 data station; this allows the 3200 to control the temperature of the furnace and collect both weight loss and spectroscopic data. During an experiment, the 3200 displays simultaneously the evolved gas profile, the latest absorbance spectrum, and one of five functional group profiles in real time. One or two of these functional group profiles may be substituted with "percent weight remaining" and/or "temperature" as a function of time, so that the operator may display the weight profile in real time instead.

The TGA data were obtained using a PL Thermal Sciences TGA 1000. All epoxy samples were heated from 30 to 600°C at a rate of 20°C min^{-1}. Sample sizes ranged between 6.5 and 12.5 mg. All samples were run under a nitrogen purge of about 30 ml min^{-1}.

A heated transfer line allows for the efficient transfer of the nitrogen purge and any evolved gases from inside the furnace to a heated gas cell located inside the TGA/IR interface bench. The 1 mm i.d. transfer line is made of stainless steel with a thin silica lining. The stainless steel gas cell (Harrick Scientific Model TGC–S10, Ossining, NY) is 10 cm in length with a 6 mm internal diameter. The cell has double windows at both ends. The inside windows are made of zinc selenide, which is resistant to water vapor and other gases which commonly evolve during TGA experiments. The outside windows are made of potassium bromide and act as thermal shields to eliminate cold spots on the inside windows. Both the transfer line and gas cell are heated to ensure transfer of heavier molecular weight gases out of the furnace and through the cell. The transfer line was held at 200°C while the gas cell was maintained at 230°C.

All spectroscopic data were collected using a Bio-Rad FTS 40 infrared spectrometer equipped with a KBr beam splitter and a wide-band mercury cadmium telluride (MCT) detector. Spectra shown were collected at 4 cm^{-1} resolution, co-adding 16 scans per spectrum. With an MCT detector, this gives a time resolution of approximately 6 s. Because the majority of weight losses produced during a TGA experiment occur over a significant temperature range, this time resolution is more than adequate to capture all evolution events. It should be pointed out that most of the normal TGA/FT-IR work we have carried out and reported elsewhere [8–12] was performed using the lower-cost deuterated triglycine sulfate (DTGS) detector. The MCT detector was chosen for this work because it enables faster spectral scanning: it was not selected for its enhanced sensitivity.

RESULTS AND DISCUSSION

As expected for two such similar samples, the major gases evolved on pyrolysis of each cured epoxy were the same. Figure 1 shows a series of spectra recorded during the pyrolysis of the "step" cured sample. The spectra recorded at 337 and 378°C show absorbances near 3000 cm^{-1} that are due to the same hydrocarbon compound. The spectrum at 442°C shows a different absorbance pattern in this region, and the strong band at about

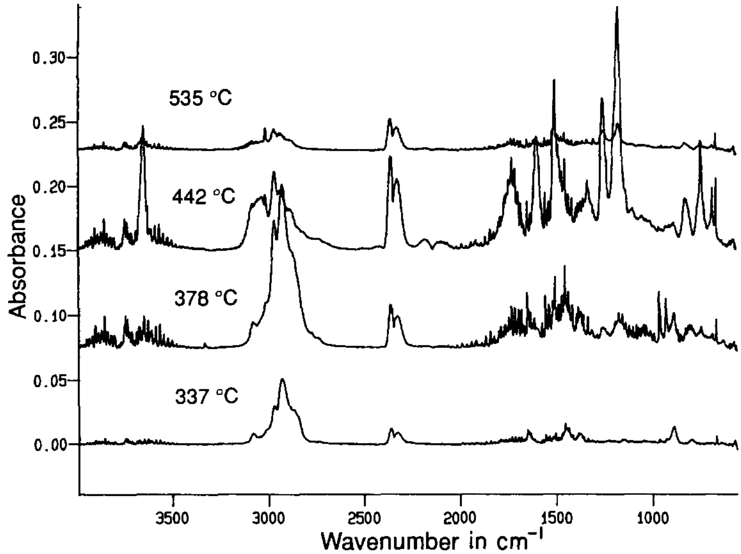

Fig. 1. Infrared spectra of gases involved from a slow "step" cured epoxy sample at various temperatures during a TGA/FT-IR run.

3650 cm^{-1} identifies this new material as an alcohol or phenol. The characteristic absorbance bands due to ammonia (3350, 980, and 905 cm^{-1}), water (complex absorptions in the regions 4000–3400 cm^{-1} and 1900–1300 cm^{-1}), and CO_2 (pair of bands at 2350 cm^{-1} and a single sharp band at 670 cm^{-1}) are also present in the spectra. These bands are commonly observed during TGA/IR experiments and thus the operator can easily identify their contributions.

The gases which evolved in this study were identified by computer match of their infrared spectra against a database of spectra, the Sadtler Vapor Phase Library, which contains spectra of 9,200 compounds. The search results which identify the two major gases as 4-isopropenyl-1-methyl cyclohexene (evolved first) and 4,4-isopropylidenediphenol (Bisphenol A) are shown in Figs. 2 and 3, respectively. The top three spectra represent the best three "matches" from the vapor phase library in order of their "hit quantity index" (HQI) value. A "perfect" match would give an HQI value of zero. The bottom spectrum represents the unknown material that is being searched, and the closest match is plotted above this "unknown" spectrum. To facilitate the best identification, spectral features due to water vapor were subtracted prior to each search. In addition, the regions of CO_2 absorbance were masked in all searches.

It is clear that the cyclohexene derivative evolved first, followed by evolution of Bisphenol A at elevated temperatures. These two dominant gases were evolved from both samples of the DGEBA epoxy, regardless of thermal history. The evolution of Bisphenol A is not unexpected because

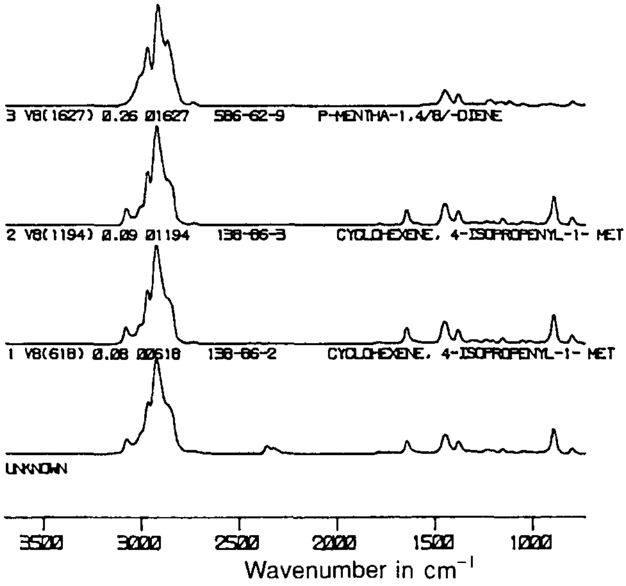

Fig. 2. Search report for the spectrum of gases evolved at 337°C from a "step" cured epoxy sample when heated under a nitrogen purge (bottom trace). Note that spectral contributions due to water and CO_2 were removed by spectral subtraction. The top three traces are the first three hits from the Sadtler Vapor Phase Library, plotted in ascending order of Hit Quality Index value.

this material comprised the resin for the formulation. The 4-isopropenyl-1-methyl cyclohexene species is extremely similar in structure to the cycloaliphatic primary diamine contained in the curing agent: it is essentially the curing agent with ammonia replaced by a double bond. The observation of ammonia in the evolved gases at a slightly higher temperature explains the formation of the cyclohexene on pyrolysis. It was therefore concluded that the evolution of the activator may be monitored by the loss of the cyclohexene derivative. Using similar logic, it was concluded that one may monitor the level of resin by following the loss of Bisphenol A.

The "zap" and slow "step" cured materials were quickly differentiated by TGA/FT-IR. The distinctions were not based on the types of gases evolved, but rather on the temperatures of maximum evolution and total temperature range of the loss of individual gases. Figures 4 and 5 show the weight loss profiles and first derivatives of the "zap" cured and slow "step" cured materials, respectively. Note that in the region of 350°C, two major weight losses appear to be much more resolved in the "zap" cured material relative to the slow "step" cured sample.

The first, very subtle difference between the two cured samples was noted at 278°C. Even though the TG weight loss profiles reveal no significant weight loss at this temperature, the infrared spectrum shows that

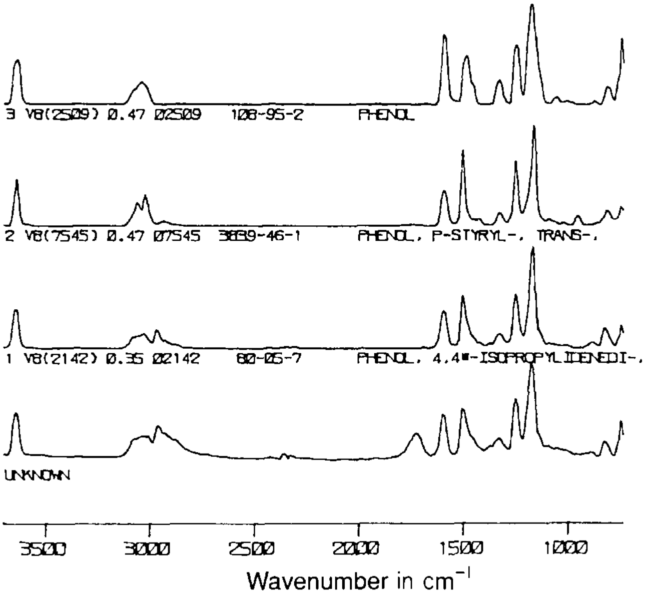

Fig. 3. Search report for the spectrum of gases evolved at 474°C from a "step" cured epoxy sample when heated under a nitrogen purge (bottom trace). The top three traces are the first three hits from the Sadtler Vapor Phase Library. Note the absorbance in the sample spectrum at about 1740 cm^{-1}. This indicates the presence of a small amount of an additional carbonyl compound, which is being evolved at this temperature along with the major component, Bisphenol A.

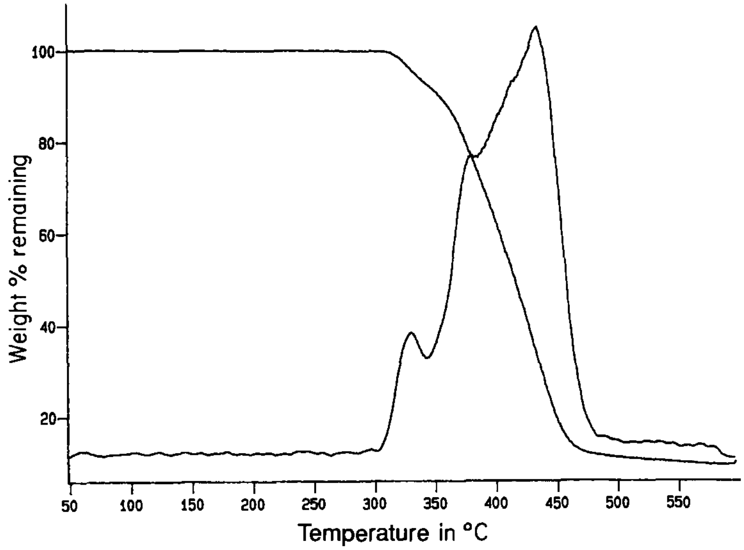

Fig. 4. The percent weight remaining and first derivative curves as a function of temperature for a "zap" cured epoxy sample.

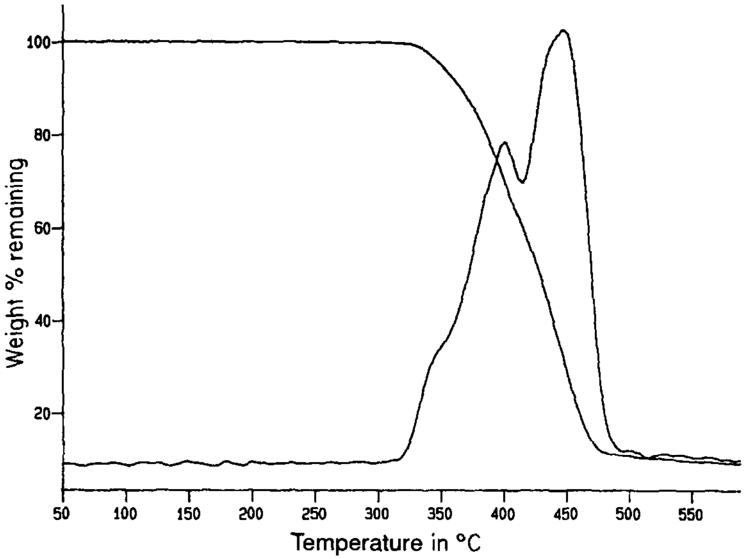

Fig. 5. The percent weight remaining and first derivative curves as a function of temperature for a slow "step" cured epoxy sample.

a low level of evolution is occurring. Figure 6 shows the spectra of the gases that evolved at this temperature from the two samples. The relatively strong absorbance band centered 2350 cm^{-1} is due to the evolution of CO_2, a common observation in TGA/FT-IR. Evidence for the evolution of a

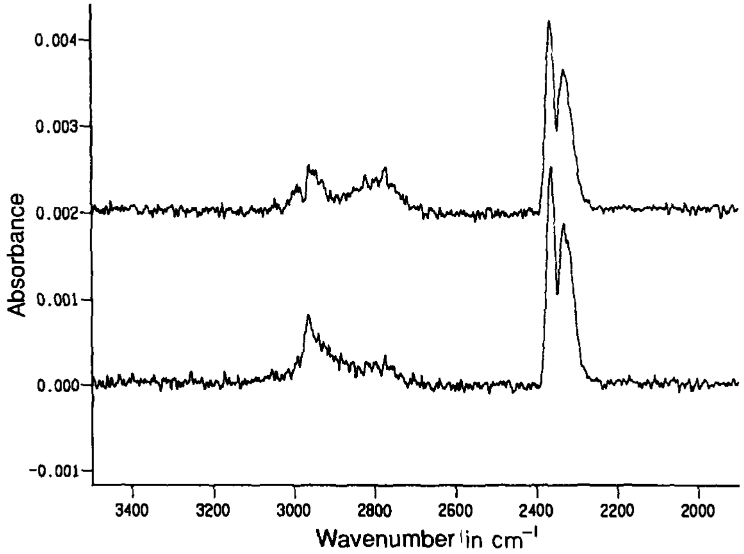

Fig. 6. Infrared spectrum of the gases evolved from a "zap" cured epoxy sample at 278°C (top), and from a "step" cured epoxy at the same temperature (bottom). Both spectra are plotted on the same absorbance scale, with the top spectrum offset for clarity.

second gas at low level is given by the weak absorbances in the C–H stretching region, between 2700 and 3000 cm^{-1}. Clearly, the hydrocarbon-containing species being evolved at this temperature are different for the two samples. The spectrum of the gas from the "step" cured sample, at the bottom of Fig. 6, shows a relatively sharp band at about 2960 cm^{-1}, typical of a methyl group in a hydrocarbon compound. In addition, however, there is evidence for a weaker, broad absorbance at lower frequencies, centered at about 2700 cm^{-1}. The spectrum at the top, however, shows a different pattern near 3000 cm^{-1}, and the broad band at 2770 cm^{-1} is more prominent. This spectrum was searched after masking the bands due to CO_2. Although a positive identification could not be made due to the poor signal-to-noise ratio of the spectrum, valuable functional group information was extracted. This unknown gas was characterized as probably being an *N,N*-dimethyl compound. The normal methyl group C–H symmetric stretching frequency is lowered significantly in such compounds by the electronegativity of the neighboring nitrogen atom [17]. Because of this, it was concluded that this material represents the loss of a product from the low-level tertiary amine activator.

It was theorized that the tertiary amine activator or its thermal degradation product evolves at higher temperatures in the "step" cured polymer relative to the "zap" cured material. In the case of the "step" cured polymer, the tertiary amine spectrum is not seen at the higher temperatures because a much stronger absorbing cyclohexene derivative (from the cycloaliphatic diamine) evolves at this time. The spectrum of the suppressed tertiary amine contribution is saturated by the stronger spectrum of the 4-isopropenyl-1-methyl cyclohexene. Even so, it should be pointed out that the materials used for the formulations were all industrial grade, and so these compounds evolved at low levels could simply be due to varying levels of impurities. This latter argument would also explain why the observed spectra, shown in Fig. 6, are significantly different.

Examination of spectra generated at 358°C from both samples, shown together on the same absorbance scale in Fig. 7, indicates that the evolution of 4-isopropenyl-1-methyl cyclohexene is taking place at a much greater rate in the "step" cured material relative to the "zap" cured sample. These spectra show that the weight losses detected at 358°C for both samples are due to the evolution of CO_2, ammonia, water and the cyclohexene derivative. The major contribution is due to the evolution of the cyclohexene species which shows a strong anti-symmetric methylene stretch at 2925 cm^{-1}. It was observed that the evolution of the cyclohexene material was slowing at 358°C in the case of the "zap" cured sample, whereas the rate of evolution of the cyclohexene in the "step" cured material was still increasing. This difference explains the relative loss in resolution observed in the first derivative of the weight loss profile for the "step" cured material.

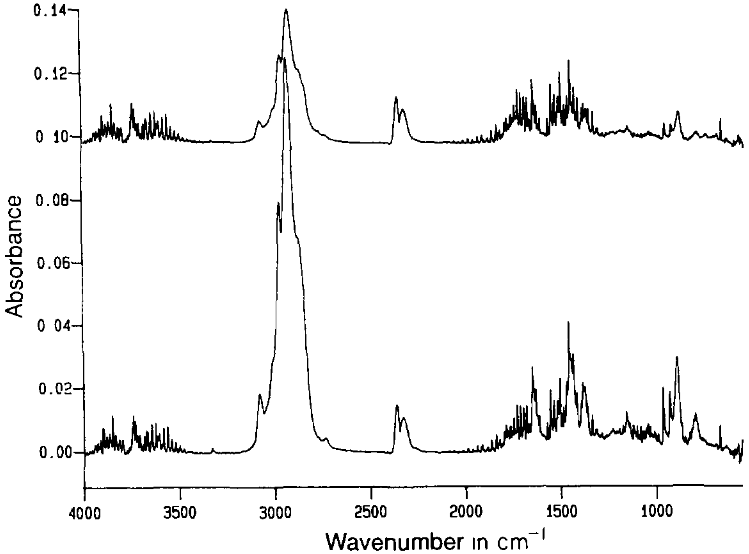

Fig. 7. Infrared spectrum of the gases evolved from a slow "step" cured epoxy sample at 358°C (top), and from a "zap" cured sample at the same temperature (bottom). Both spectra are plotted using the same absorbance scale, with the top spectrum offset for clarity.

To monitor the evolution of the individual gases released from the activator and the resin, and then to be able to quantify the activator–resin ratio, it was necessary to define the specific gas profiles that isolated the respective absorbances of these gases. Since the structure of 4-isopropenyl-1-cyclohexene is extremely similar to the structure of the cycloaliphatic diamine, the amount of activator was measured by monitoring the loss of the cyclohexene derivative. An 877–904 cm^{-1} SGP was set to isolate and monitor the loss of activator. In the same manner, a 1160–1185 cm^{-1} SGP was set to isolate and monitor the evolution of Bisphenol A and thereby measure the amount of resin. Note that the spectral features of ammonia, at 905 and 980 cm^{-1}, lie just outside the SGP region for the activitor.

The specific gas profiles for "activator" and "resin" generated from a slow "step" cured sample are plotted on a common time axis in Fig. 8, along with the evolved gas profile. Although there is a time when both activator and resin are evolving from the polymer, these SGPs are able to follow the evolution of the individual components. Even more revealing is a comparison of the SGPs obtained for samples having a different thermal history. Figure 9 shows two "activator" profiles plotted on a common time axis. The bottom profile was generated from a "zap" cured sample while the top profile was generated from a slow "step" cured polymer. When comparing these two profiles it is apparent that the activator from the "zap" cured material degrades first, i.e. at a lower temperature, relative to the slow "step" cured sample. The activator from the "zap" cured material

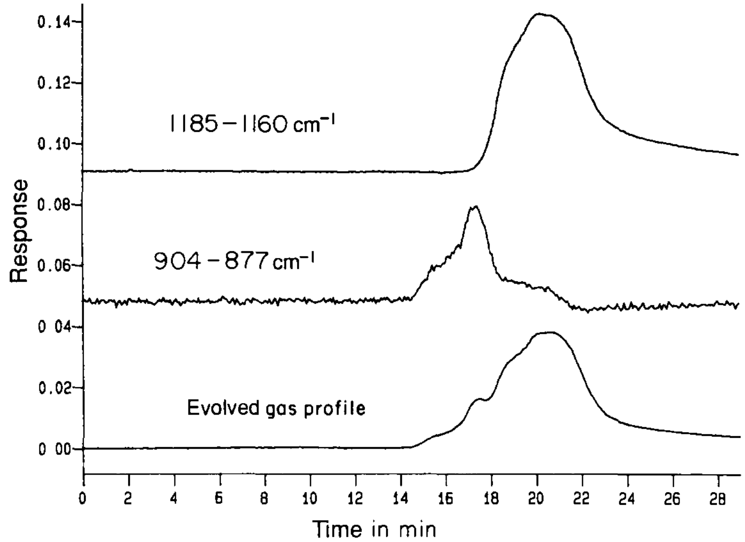

Fig. 8. The specific gas profiles for "resin" (1160–1185 cm^{-1}) and "activator" (877–904 cm^{-1}) and the total evolved gas profile generated during a TGA/FT-IR run of a slow "step" cured epoxy sample.

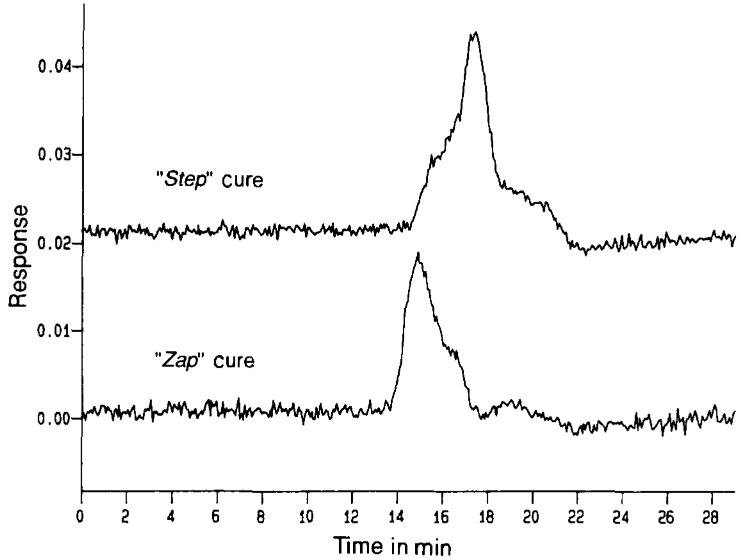

Fig. 9. The specific gas profiles for "activator" (877–904 cm^{-1}) generated from a slow "step" and "zap" cured epoxy sample, plotted on a common time axis.

also evolves within a slightly narrower temperature range. Note that these results are in agreement with the conclusions made earlier from a simple comparison of the individual spectra (Fig. 7).

The results described above indicate that the same epoxy system subjected to various cure schedule may be differentiated based on results obtained by TGA/FT-IR. It is equally important, however, to be able to monitor the activator–resin ratio because the relative amounts of materials present in the mix will also greatly affect the physical and chemical properties of the polymer. It is interesting to note that because the evolution of resin and activator overlap in time, stand-alone TGA could not be used to calculate the activator–resin ratio. The combined TGA/FT-IR approach, however, was found to be able to accomplish this goal. This technique would therefore aid significantly the quality control mechanism and ensure the predicted performance of the processed material.

Integration of the area of each SGP resulting from standard samples was carried out in order to relate integrated absorbance to the weight of activator and resin. Samples generated using known weights of activator and resin, cured in the slow, step manner, were used as standards for this study. For each standard sample, a complete TGA/FT-IR experiment was carried out, and the areas of the resulting SGPs for "resin" and "activator" were integrated using Bio-Rad's Quant-32 software. If the 875–904 cm^{-1} profile is successful in isolating the evolution of 4-isopropenyl-1-cyclohexene, then according to Beer's law, the area of this profile should be proportional to the weight of activator. The results of this study are shown in Fig. 10. In this figure, two sets of data are given together. The first experiments were carried out using a series of samples cured in the "step" fashion; these data points are shown as solid circles. This set of results confirms the expectation that Beer's law is obeyed, i.e. that absorbance is proportional to concentration, and that the calculated least-squares fit may be used to quantify the weight of activator in unknown samples. A further pair of experiments using "zap" cured standards was then carried out to establish whether the SGPs could be used to determine activator–resin ratio regardless of thermal history. The area of the profile should still remain proportional to the weight of activator, even though the evolution rate may vary as a function of cure. The data from these two experiments are also shown in Fig. 10, as open squares. The squares are very close to a straight line drawn through the circles, although perhaps offset a little in integrated response. Further data points could have been generated for the "zap" cured product by examining more standards in order to get a more precise plot for these materials. However, it was felt that the accuracy obtained from an averaged set including "step" and "zap" cured standards was sufficient to define whether an unknown sample had been created from the specified mixture. In any case, these results demonstrate that Beer's law is

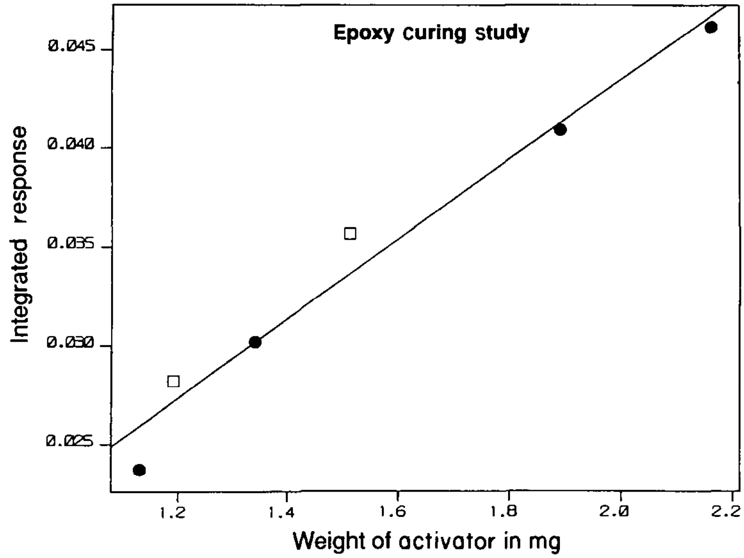

Fig. 10. A plot of integrated absorbance of the 875–904 cm^{-1} specific gas profile vs. weight of activator from known standards of slow "step" (●) and "zap" cured (□) epoxy samples. The least-squares fit shown is for the complete data set.

obeyed and that the activator content of a sample may be calculated reliably from the SGP, regardless of cure.

Similar results were obtained when the integrated absorbances of the SGP for "resin" (1160–1185 cm^{-1}) were plotted as a function of weights of resin from the same set of standards. These results are now shown for brevity, but they also demonstrated that the resin content of a sample can be measured from the SGP. When ratioed directly against the area of the "activator" SGP, an accurate measurement of the activator–resin ratio may be calculated, regardless of thermal history, from the results of a single experiment in an automatic manner.

Epoxy resins react with amines in three basic mechanisms: (1) primary amine to epoxy addition; (2) secondary amine to epoxy addition; and (3) tertiary-amine-catalyzed epoxy to epoxy addition. These mechanisms have been discussed in detail before (see Fig. 2 in ref. 3). Because, during slow cures, a higher percentage of the materials react in a more ordered manner, primary amine reacting first, secondary amine reacting second, and tertiary amine reacting last, the amine is more likely to be fully reacted. It should then not be surprising for the slow-step cured material to have the epoxy resin more completely reacted with the primary amine (cycloaliphatic amine) with less epoxy-to-epoxy addition. Consequently, the "zap" cured material should be less ordered and have less of the cycloaliphatic amine fully reacted with the epoxy resin, and thus be less stable and start to decompose at a lower temperature, relative to the slow cured material.

CONCLUSIONS

Results from this research have shown that the TGA/FT-IR may be used to determine qualitatively both the thermal history of an epoxy system and the activitor–resin ratio, in one run. The thermal history may be ascertained by monitoring the first derivative of the weight loss profile and the peak position and shape of specific gas profiles. The temperature at which individual gases evolve varies considerably according to the thermal history of the polymer. These variations will affect the calculation first derivative of the weight loss profile. "Reference" SGPs and weight loss profiles may be collected for various cures. These "reference" profiles may then be compared to those generated from unknown samples. Comparison to an accepted standard may provide the criterion for acceptance or rejection.

The same specific gas profiles may be integrated to determine activator–resin ratio. The area of these specific gas profiles are proportional to the weight of the individual components, independent of peak position and shape. Through the use of standards, integrated absorbance may be related to the weight of activator and resin regardless of thermal history.

The mixing and curing of epoxy resin adhesives must be strictly monitored in the production environment. Deviation from documented processing results in the product having poor physical properties, which may lead to rejection of a batch and thus prove costly. Verification of the thermal history and activator–resin ratio of a cured epoxy formulation by TGA/FT-IR can pinpoint the reason for a problem batch, and could therefore improve the quality control procedure.

The work contained herein can also be correlated very well with prior studies of this material [1] linking long-term stability with decomposition performance. Further work needs to be done to correlate this type of long-term physical property behavior with the kinetics and mechanism of decomposition. If this is accomplished, a quick and accurate way of determining the best resin-to-activator ratio, cure, and subsequent performance in an application would make the TGA/FT-IR a very valuable tool for studying the way many thermosetting polymers are used and processed.

REFERENCES

1 R.S. Cass and P.L. Canale, The Effect of Cure Schedules and Long-Time Ageing on Dimensional Changes and T_g of an Unfilled Epoxy System, Presented at the 9th Inertial Guidance Community Working Group Meeting, 1985.
2 P.L. Canale and R.S. Cass, The Evaluation of Activator Concentration and Cure Schedule on the Performance of Epoxy Resin Adhesives, Presented at the 9th Inertial Guidance Community Working Group Meeting, 1985.
3 D.J. Johnson, D.A.C. Compton, and P.L. Canale, Applications of simultaneous

DSC/FT-IR analysis, Thermochim. Acta, 195 (1992) 5–20. Available from Bio-Rad, Digilab Division, as FTS/IR Note No. 89.
4 C.A. May (Ed.), Epoxy Resins, Chemistry and Technology, Marcel Dekker, New York, 2nd edn., 1988, pp. 301–304.
5 S. Lunak and K. Dusek, Curing of epoxy resins II, curing of Bisphenol A diglycidyl ether with diamines, J. Polym. Sci. Symp., 53 (1975) 45–55.
6 J.C. Paterson-Jones, The mechanism of thermal degradation of aromatic amine cured glycidyl ether type epoxide resins, J. Appl. Polym. Sci., 19 (1975) 1539–1547.
7 H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967, pp. 6-3310–6-3337.
8 D.A.C. Compton, On-line FT-IR analysis of the gaseous effluent from a thermogravimetric analyzer: applications of an integrated TGA/FT-IR system, Int. Labmate, June (1987) 37–43. Available from Bio-Rad, Digilab Division, as FTS/IR Note No. 47.
9 D.J. Johnson and D.A.C. Compton, Solvent retention studies for pharmaceutical samples using an integrated TGA/FT-IR system, Spectroscopy, 3(6) (1988) 47–50. Available from Bio-Rad, Digilab Division, as FTS/IR Note No. 63.
10 D.A.C. Compton, D.J. Johnson, and M.L. Mittleman, Integrated TGA/FT-IR system to study polymeric materials-I, Res. Dev., February (1989); Integrated TGA/FT/IR system to study polymeric materials-II, Res. Dev., April (1989). Both articles available from Bio-Rad, Digilab Division, as FTS/IR Note No. 70.
11 T. Kumar, D.J. Johnson, and D.A.C. Compton, FT-IR and TGA/FT-IR characterization of a polyethylene photodegradable concentrate, Proc. 7th Int. Conf. on Fourier Transform Spectroscopy, SPIE Vol. 1145, June, 1989 pp. 570–573. Available from Bio-Rad, Digilab Division, as FTS/IR Note No. 71.
12 D.J. Johnson and D.A.C. Compton, Quantitative analysis of nitrocellulose and pulp using TGA/FT-IR, Am. Lab. Mag. January (1991) 37–43. Available from Bio-Rad, Digilab Division, as FTS/IR Note No. 79.
13 C.A. Wilkie, J.T. Leone and M.L. Mittleman, J. Appl. Polym. Sci., 42 (1991) 1133.
14 J.A.J. Jansen, J.H. Van der Maas, and A. Posthuma de Boer, Appl. Spectrosc, 46 (1992) 88.
15 J. Khorami, A. Lemieux, H. Menard, and D. Nadeau, Usefulness of Fourier transform infrared spectroscopy in the analysis of evolved gas from the thermogravimetric technique, in C.M. Earnest (Ed.), Compositional analysis by thermogravimetry, ASTM STP 997, American Society for Testing and Materials, Philadelphia, 1988, pp. 147–159.
16 K.A. Akinade, M. Cambell, and D.A.C. Compton, The use of a simultaneous TGA/DSC/FT-IR system for solving problems in materials science, manuscript in preparation.
17 G. Socrates, Infrared Characteristic Group Frequencies, Wiley-Interscience, Chichester, UK, 1980.