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Applications of simultaneous DSC/FTIR analysis

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Abstract

A combination of the standard laboratory techniques differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy is described. This simultaneous DSC/FTIR technique gives spectroscopic and thermodynamic information about a solid or liquid sample undergoing thermal modification. DSC measures the exothermic and endothermic responses of the samples, while the FTIR analysis observes their changes in chemical and physical composition. Reflectance infrared microspectroscopy was employed to examine the samples. Two epoxy samples were studied by DSC/FTIR. Both samples were mixtures of diglycidyl ether of Bisphenol A with a cycloaliphatic primary amine. The two samples differed only in the amount of primary amine used to crosslink the epoxy resin. The cure of each specimen was studied by using the reflectance/absorbance mode of infrared analysis, while simultaneously undergoing a DSC experiment. Samples were monitored as a function of secondary amine content, crosslink density, and hydroxyl formation. This information was used to examine whether the samples differed in their overall reaction rates.

The samples did in fact exhibit markedly different cure character, giving insight into the reaction routes and a prediction of the final molecular structures achieved by these small changes in the ratio of resin to amine activator. A sample of poly(ethylene terephthalate) (PET) was also analyzed by DSC/FTIR; in this case the specular reflectance mode of infrared analysis was employed. DSC was used to detect the glass transition, multiple melting endotherms and recrystallization of the polymer as it was heated and cooled. FTIR was used to monitor structural changes in the sample as it went through these thermal transitions. These experiments demonstrate the high potential of DSC/FTIR reflectance microspectroscopy when studying the thermal characteristics of materials.

INTRODUCTION

The study of polymeric materials by thermal analysis has become increasingly popular in today's analytical laboratory. Differential scanning calorimetry (DSC) in particular has been used for a wide variety of applications. DSC measures directly the endothermic or exothermic behavior of a material as a function of temperature, and provides the chemist with valuable information about the thermal properties and composition of a sample under investigation. Properties such as heat of cure, glass transition, percent crystallinity, melting point and degree of cure may all be calculated using the DSC technique [1]. From the material's observed data, it is often possible to draw conclusions about the materials purity, process history, and product quality.

At the same time, many laboratories study by infrared spectroscopy materials similar to those being examined by thermal analysis [2]. Almost all solids (except metals) and liquids exhibit absorption of infrared energy, and the use of Fourier-transform infrared (FTIR) spectroscopy to analyse these materials is commonplace and very powerful. The current state-of-the-art FTIR spectrometers can give a wealth of information about the composition, structure, crystallinity, and other properties of samples that can have sizes ranging from a few cm down to a few microns, if an infrared-transmitting microscope is used [3].

Both DSC and FTIR analyses are well suited to studying the thermal behavior of materials. The DSC instrument is, of course primarily designed to monitor changes in heat flow as a function of temperature, but is unable to identify the chemical nature of the observed transitions. The FTIR spectrometer is a general-purpose instrument, well suited to obtaining information about the chemical properties of a sample. Special accessories for FTIR are available to allow the study of samples at non-ambient temperatures [2], but these accessories generally do not allow for any thermal information (such as heat flow) to be recorded about the sample, except for its temperature. Thus, during a variable-temperature infrared spectroscopy study, any phase changes taking place must be inferred from changes observed in the infrared spectrum. Such spectral changes may be very subtle, in which case their physical interpretation can be ambiguous.

Performing FTIR analysis of a sample which is undergoing a simultaneous DSC experiment offers great promise in overcoming these limitations of the individual techniques when studying the thermal properties of materials. The combination of DSC and FTIR allows the chemist to monitor structural changes in the material as the sample passes through various thermal transition states, and potentially to obtain sufficient information by spectroscopic means to assign these different states to physical or chemical phenomena.

A similar approach in combining FTIR analysis of the gases evolved from a thermogravimetric analyzer (TGA) has proved very successful. The TGA measures sample weight as a function of temperature, or time, but can give no information as to the chemical basis for a weight change. The coupling of an FTIR to a TGA allows for the continuous collection of the infrared spectra of the gases which evolve during the heating of the sample. The chemist may then assign evolved gases to detected weight losses. Combined thermogravimetric analysis/Fourier transform infrared spectroscopy (TGA/FTIR) systems have been commercially available from Bio-Rad for a number of years [4]. As an example of the power of this technique, TGA/FTIR has been successfully used to identify the pyrolysis products of a number of polymers, including PTFE, polybutadiene, silicone rubber, polyvinyl acetate, and an epoxy resin [5]. In each case, a wealth of information was obtained to help characterize the polymer.

If the scientist wishes to monitor the structural changes in the material itself, rather than analyze the gases which evolve from the material, then combining FTIR analysis with DSC (instead of TGA) becomes the analytical approach that holds the most promise. Two groups of workers reported studies in 1986 that combined both FTIR and DSC [6–8], but such work was limited by the equipment available to the authors at that time. Both groups used transmission spectroscopy to obtain the infrared spectral data, which placed severe restrictions on the types of samples that could be studied. Now that improvements have been made to FTIR instruments, in both software and hardware terms, we are able to report experiments that show great promise for routine operation. By using reflectance infrared spectroscopy, we are able to examine more types of samples and obtain more accurate experimental results.

In all of the DSC/FTIR experiments reported, including those in this report, the DSC utilized has been a Mettler FP84 hot-stage microscopy cell. This particular DSC has been used because it is very small, designed to fit under a microscope objective, and also has a sample cup which is accessible to incoming infrared radiation. The various DSC/FTIR studies reported have differed significantly in the manner that the FP84 was mounted in the FTIR spectrometer.

Koberstein et al. [8] reported an experiment where the DSC was simply placed directly in the main infrared beam of the spectrometer sample compartment. To accomplish this it was necessary to remove the DSC sample cup, and place a thin sample of polyurethane film (mounted on a KBr window) over the hole. The simultaneous DSC data was recorded on a thicker sample of the polyurethane, placed in the DSC reference cup. This approach unfortunately means that the DSC and FTIR experiments examine different specimens, and it is well known that the thermal properties of a sample are often dependant on the sample morphology.

In order to obtain a better signal-to-noise ratio on the FTIR data, Mirabella used an infrared transmitting microscope accessory [6]. This accessory condenses the beam into the small opening of the DSC sample cup, thus giving much higher optical throughput. The infrared beam was transmitted through the sample in the cup; to achieve this special cups were fashioned from a sodium chloride or potassium chloride crystal. Again, it was necessary to examine a thin film of each sample in order to avoid the infrared absorbances becoming too high. Using this approach it was possible to monitor the structural changes in polypropylene [6] and polyethylene [7] during melting and recrystallization, and to study the degradation of poly(ethylene vinyl alcohol) [7].

When measuring a transmission infrared spectrum, the absorbance of the strongest bands of interest should not exceed about 0.8 absorbance units. To achieve this, a typical polymer sample must be only about 10 microns in thickness. Samples this thin generally have insufficient mass to generate an adequate DSC curve. As a result, both of the groups previously reporting DSC/FTIR work [6–8] placed a much thicker sample of the same material in the other cup, which is normally the reference cup. This produces a DSC trace with the *Y* axis reversed from the normal convention.

The present research was performed in a significantly different manner. The same FP84 DSC was employed, but we obtained the spectral data using an infrared microscope operating in the reflectance mode. In this case, the infrared beam is directed down onto the sample in the DSC cup; the reflected energy is then collected by the microscope objective, and focussed onto the infrared detector. Infrared spectra are recorded continuously during a standard DSC experiment.

There are several advantages to this experimental arrangement. It is not necessary to fashion DSC sample cups from a material (such as potassium bromide) that transmits infrared radiation; instead standard aluminum cups were employed. In many cases it is possible to study samples that have the normal thickness for the DSC experiment. Finally, the design of modern infrared-transmitting microscope accessories allows for spectra to be collected in the reflectance mode with excellent signal-to-noise ratio.

EXPERIMENTAL

All spectroscopic data were collected using a Bio-Rad FTS 40 spectrometer equipped with a KBr beamsplitter, high-temperature ceramic source, and UMA 300A infrared-transmitting microscope accessory. In order to give sufficient working depth with the DSC cell in place on the microscope stage, a 15X Cassegrainian objective was utilized for both infrared analysis and viewing with visible light. Spectra were collected continuously at 8 cm^{-1} resolution during the DSC experiment.

A Mettler FP84 TA microscopy cell was used to heat the samples and to obtain the DSC data. The cell temperature was controlled by a Mettler FP80 central processor. The temperature was programmed to ramp from 25 to 280 °C at 10 °C min^{-1}. In order to allow for the infrared beam to reach the sample, the glass cover slip normally positioned above the cell was removed. If necessary, this cover could be replaced with one fashioned from an infrared-transmitting material, but that was not done for this work.

RESULTS AND DISCUSSION

When collecting a reflected infrared beam, a variety of phenomena may occur depending on the surface, geometry and phase of the material under

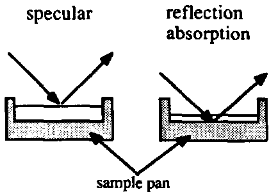

Fig. 1. Two possible interactions between the infrared radiation and sample when collecting IR spectra by micro-reflectance.

investigation. Two interactions, as shown in Fig. 1, between the infrared beam and sample were observed in this research. In some cases, the sample is relatively transmissive to infrared radiation, and the beam transmits down through the sample, reflects off the aluminum cup, and passes back up through the material. This type of analysis is called reflection/absorption spectroscopy, and can only be applied to a thin film of material in the sample pan. As a result, as in Mirabella's work [6,7], the bulk of the sample must be placed in the reference side of the sample cup. This type of behavior was exhibited by a sample of epoxy resin that we examined.

A different behavior was noted with a sample of poly(ethylene terephthalate), PET. That sample exhibited specular reflectance behavior, in which the bulk of the energy was reflected from the top surface of the sample, and hence the whole sample was placed in the sample cup. The advantage of this is that both the infrared spectrum and DSC trace can be obtained from the same sample. However, the infrared spectrum that is obtained by specular reflectance exhibits distorted or derivatized band shapes and requires a software correction to produce a normal absorbance spectrum. This correction, the Kramers–Kronig transformation [3], will be described in more detail below during the discussion of the results obtained for PET.

Epoxy study

Thin films of uncured amine-activated epoxies were placed in the sample pan of the FP84 and heated from 25 to 280 °C at 10 °C min^{-1}. Changes in the structure of the epoxy as a function of temperature were simultaneously recorded by infrared spectroscopy. The reaction mechanism of cure, as shown in Fig. 2, initially involves the reaction of a cycloalipahtic primary amine activator (4-amino-α,α,4-trimethyl-cyclohexanemethaneamine) with the epoxide group of the resin (2-di-[4-(2,3-epoxy-1-propoxy)-1-phenyl] propane) to produce a secondary amine. This secondary amine further reacts with an additional epoxide group to form a tertiary amine. Further reaction, catalyzed by water, hydroxyl, and tertiary amine concentration, continues the crosslinking activity. This same system was studied extensively by TGA/FTIR [9]. Results from this research showed that the

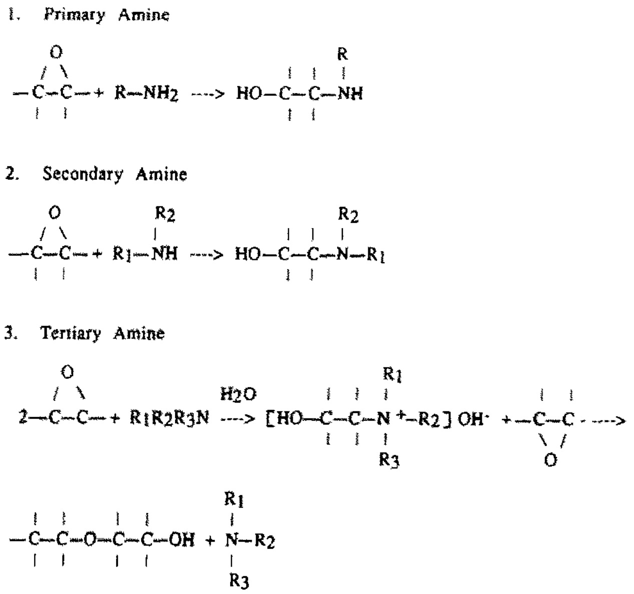

Fig. 2. The curing reaction mechanism of the amine-activated epoxy system.

TGA/FTIR technique may be used to quantify the activator/resin ratio and to determine qualitatively the thermal history of the polymer after cure.

The curing of an epoxy is an exothermic reaction. Research shows that the shape of the DSC exothermic peak changes considerably when varying the activator–resin ratio. Figure 3 shows the DSC trace when heating a

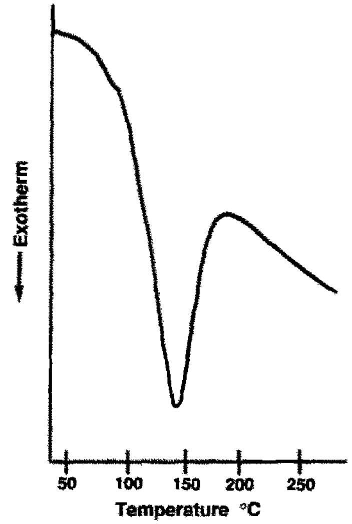

Fig. 3. The generated DSC trace during the cure of the 100 parts resin to 35 parts activator system. This uncured material was heated from 25 to 280 °C at 10 °C min^{-1}.

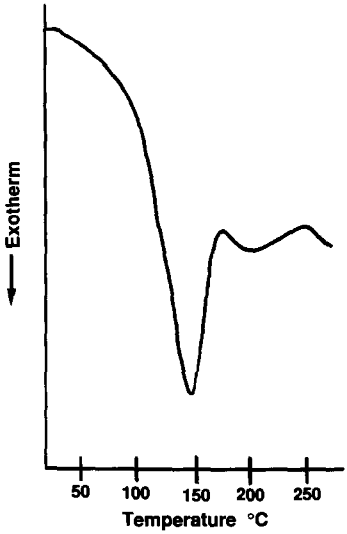

Fig. 4. The generated DSC trace during the cure of the 100 parts resin to 17 parts activator system. This uncured material was heated from 25 to 280 °C at 10 °C $\min^{-1}$.

mixture of 100 parts resin to 35 parts activator (41% over the stoichiometric primary and secondary amine concentration). Note that the ordinate is reversed because the DSC trace is generated from the bulk sample in the reference pan. This thermogram is a single-peak exotherm, and is used routinely to calculate heats of reaction or degree of conversion of epoxy systems. This curve may also be used to calculate various kinetic parameters which may predict the behavior of the reaction under isothermal conditions at different temperatures. When the same epoxy prepared with 100 parts resin to 17 parts activator (31% under the stoichiometric level of primary and secondary amines) is heated, a double-peak exotherm as shown in Fig. 4 is generated. This indicates a change in the reaction mechanism. By coupling the FTIR to the DSC these changes were studied and differentiated.

Thirty spectra were collected during each run, co-adding 128 scans per spectrum. Seven spectra generated at various temperatures during a typical experiment are shown in Fig. 5. Comparison of the spectra indicate that the changes in the relative peak heights of the 3030 cm^{-1} band to the 3048 cm^{-1} band can be used to monitor the degree of crosslinking. Both bands are due to aromatic C–H stretching in the polymer. A plot of this peak ratio as a function of temperature for both mixes (Fig. 6) shows that the rate of reaction is faster with the over-stoichiometric mix.

Band shifts in the infrared spectra may also be monitored to measure the rate of reaction. For example, the absorbance band at 1295 cm^{-1} shifts to lower frequencies as a function of cure. Comparing the slopes of these band shifts as a function of activator/resin ratio also confirms that the rate

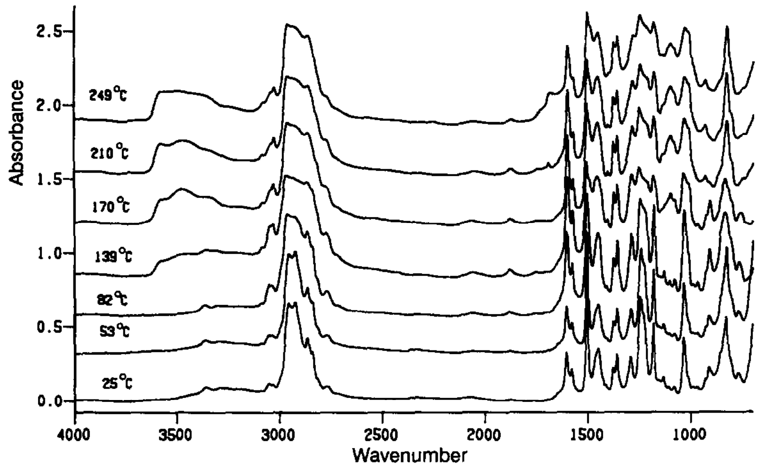

Fig. 5. A series of transmittance IR spectra generated at various temperatures during the heating of an epoxy sample containing 35 parts activator.

of the reaction with the over-stoichiometric mix is faster than the 17 parts activator system.

Not only does the rate of reaction vary, but the reaction mechanism itself changes as a function of activator–resin ratio. Figure 7 shows a series of spectra generated when the over-stoichiometric mix system was heated. The band at 3350 cm^{-1} in the top two spectra represents the N–H stretch

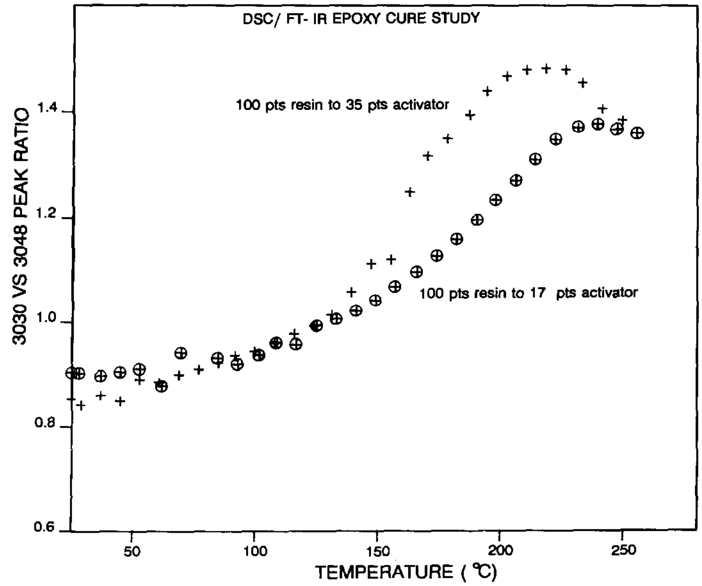

Fig. 6. A plot of 3030 cm^{-1} versus 3048 cm^{-1} peak ratio as a function of temperature for samples containing 35 parts and 17 parts activator.

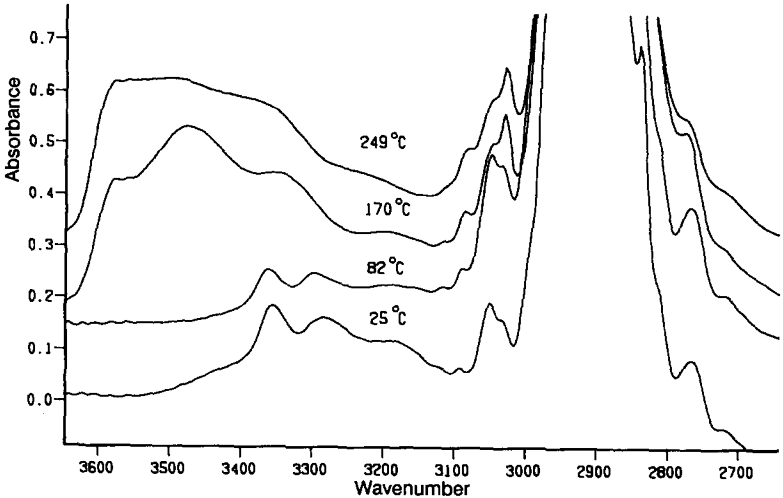

Fig. 7. Expanded portion of the IR spectra generated during the cure of the 100 parts resin to 35 parts activator mix at 25, 82, 170 and 249 ° C.

of a secondary amine. The presence of this band at 170 and 249 ° C indicates that even at elevated temperatures, the dominant reaction is primary amine to epoxy, producing secondary amine. Figure 8 shows that when less activator is used in the mix, as with the 100 parts resin to 17 parts activator system, the 3350 cm^{-1} band at elevated temperatures is noticeably absent. This indicates that due to lack of primary amine, the reaction between secondary amine and remaining epoxide groups becomes significant.

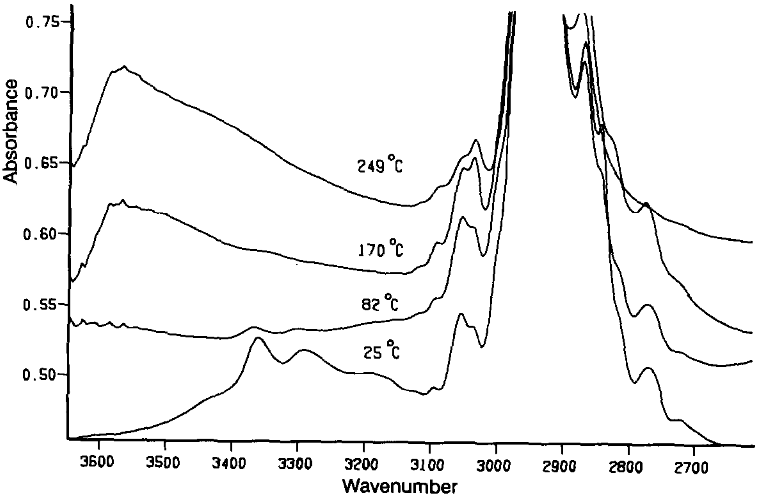

Fig. 8. Expanded portions of the IR spectra generated during the cure of the 100 parts resin to 17 parts activator mix at 25, 82, 170 and 249 ° C.

This interpretation explains the differences between Figs. 3 and 4. The single-peak character of Fig. 3 is almost completely due to the absence of any other reaction except that of primary amine adding to epoxide, generating a secondary amine group. Figure 4, however, has a double-peak nature where the first peak is due to consumption of primary amine. Because excess epoxide groups remain after the majority of the primary amine has been consumed, the less reactive secondary amine apparently then plays a major role in the formation of the second DSC peak.

The dominance of the primary amine reaction using aromatic curing agents is well documented [10] in work by Dusek et al. [11], Riccardi and Williams [12], Morgan et al. [13], and Mijovic et al. [14]. These authors showed that with aromatic amine curing agents the secondary amine reaction with epoxide has approximately one-tenth the reaction rate constant of that for a primary amine reacting with epoxide. In our work, it is apparent that the cycloaliphatic amine shows the same preference for primary amine reaction. Specifically, if excess primary amine is present, the reaction clearly dominating is that of primary amine with epoxide to generate a secondary amine. It is interesting to note that when using non-cyclic aliphatic amine curing agents, differences in reaction rate constants between primary and secondary amine reactions are minor [11,12,15].

Hydroxyl formation, resulting from either primary or secondary amine addition, was also monitored for the two activator–resin ratio systems. Figure 9 plots the intensity of the O–H stretching vibration at 3470 cm^{-1} versus that of the aromatic C–C stretching vibration at 1600 cm^{-1}, as a

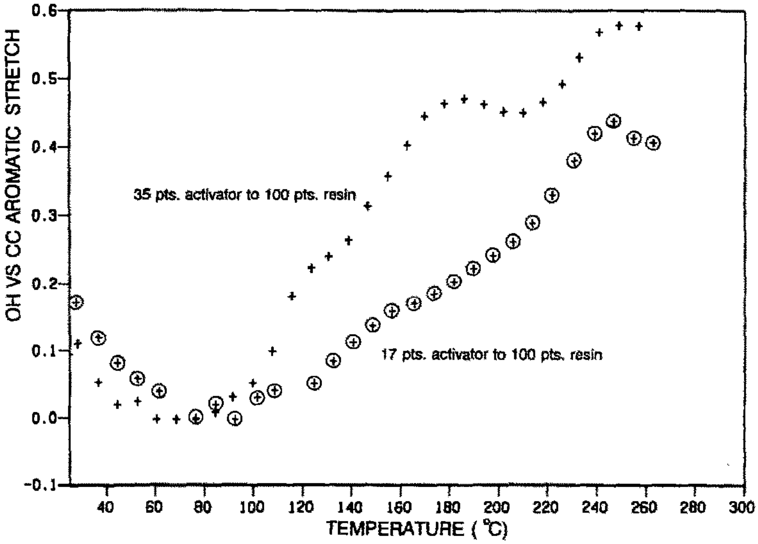

Fig. 9. Plot of the ratio of the infrared absorbance at 3467 cm^{-1} (hydroxyl group) divided by that at 1600 cm^{-1} (aromatic group) versus the temperature of cure (°C) for the two epoxy formulations.

function of temperature. The initial higher rate of hydroxyl formation in the mixture having the higher activator level reinforces the theory of the dominance of the primary amine.

It is interesting to note the decrease in the rate of hydroxyl formation in the over-stoichiometric mix at approximately 210 ° C. This may be due to an etherification/homopolymerization reaction, consuming hydroxyl groups, which competes with the secondary amine for epoxy sites. These competing reactions have been noted by Riccardi and Williams [12]. It should be emphasized that the DSC does not detect any significant change in this temperature range, but the infrared spectra do show significant changes.

Results from this study indicate that the simultaneous DSC/FTIR technique may be successfully used to monitor changes in reaction mechanisms during the cure of epoxy systems as a function of activator–resin ratio. Relative changes in the rates of reaction may also be monitored.

PET study

Polyethylene terephthalate (PET) was analyzed by DSC/FTIR to monitor the structural changes of the material as it was heated and cooled through its glass transition and multiple melting endotherm. The sample was heated in the FP84 from 25 to 280 ° C at 10 ° C min^{-1} and subsequently cooled at the same rate from 280 ° C to approximately 100 ° C. Infrared spectra were simultaneously collected, co-adding 256 scans per spectrum. Figure 10 shows the thermogram which was generated during the experiment. As mentioned earlier, due to the reflective surface of the PET, the generated IR spectra exhibited distorted or derivitized band shapes. This phenomenon occurs when a material undergoes a significant change in refractive index in frequency regions of strong IR absorbances. The distorted spectrum, as shown in Fig. 11, is actually a plot of extinction coefficient and refractive index as a function of frequency. A Kramers–Kronig correction may be applied to the spectrum to separate the index of

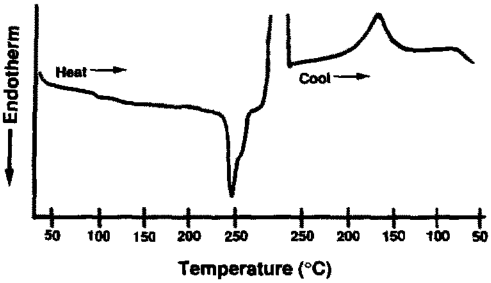

Fig. 10. The DSC trace generated during the heating and cooling of PET. The sample was heated from 25 to 280 ° C at 10 ° C min^{-1} and later cooled at the same rate from 280 to approximately 70 ° C.

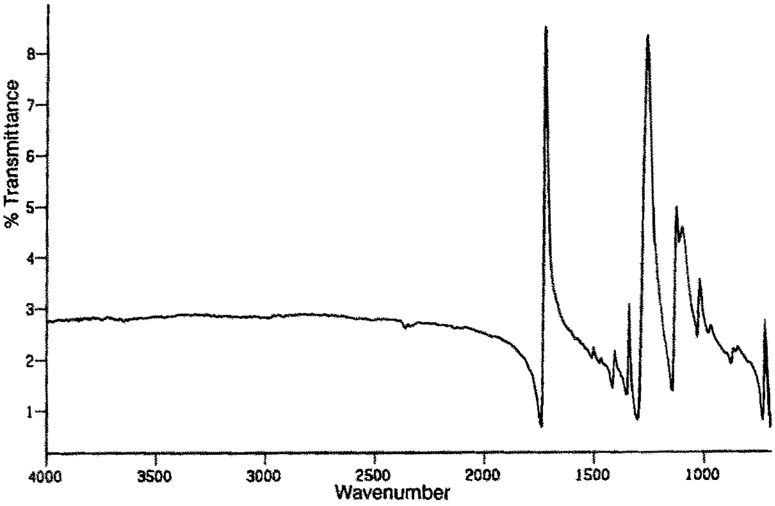

Fig. 11. Observed reflectance IR spectrum of PET at room temperature prior to Kramers–Kronig correction.

refraction component from the extinction coefficient component to produce a "K" spectrum which has the appearance of a normal absorbance spectrum. Figure 12 shows a reflectance spectrum of PET after a Kramers–Kronig correction.

Significant changes in the spectra were seen when the material was heating through its melting endotherm. Figure 13 shows four spectra generated before, during and after melting. Major changes in the relative peak heights of the 1111 cm^{-1} and 1128 cm^{-1} bands are evident. It was

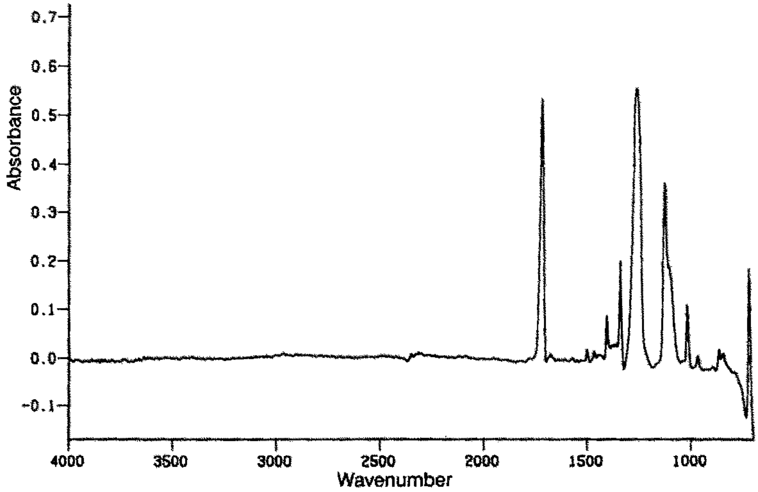

Fig. 12. IR spectrum of PET at room temperature after Kramers–Kronig correction.

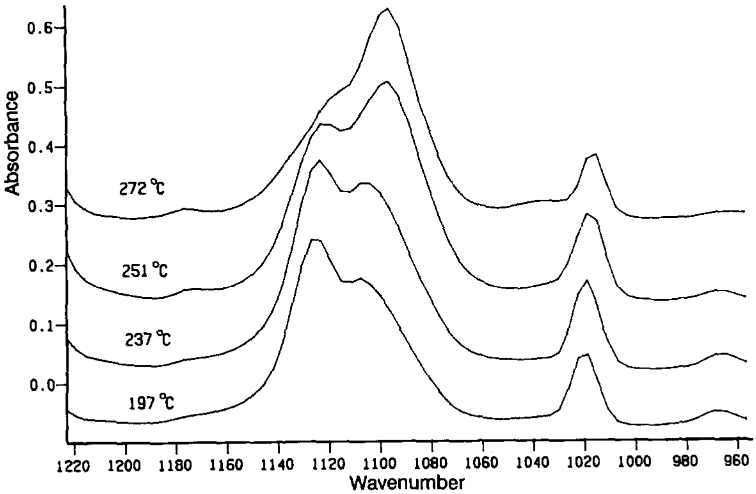

Fig. 13. A series of IR spectra generated at various temperatures as PET is heated through its multiple melting endotherm.

originally believed that these changes in relative intensity were related to rotational isomerism of the ethylene glycol segments in PET [16]. Although the position is not conclusive, normal coordinate calculations indicate that the observed changes are due to symmetry and resonance characteristics of the aromatic ring framework [16]. These results indicate that the PET framework is relatively rigid, even in the melt. In any case, examination of spectra during the recrystallization from the melt show that these changes are reversible. It is also interesting to note that the changes in relative

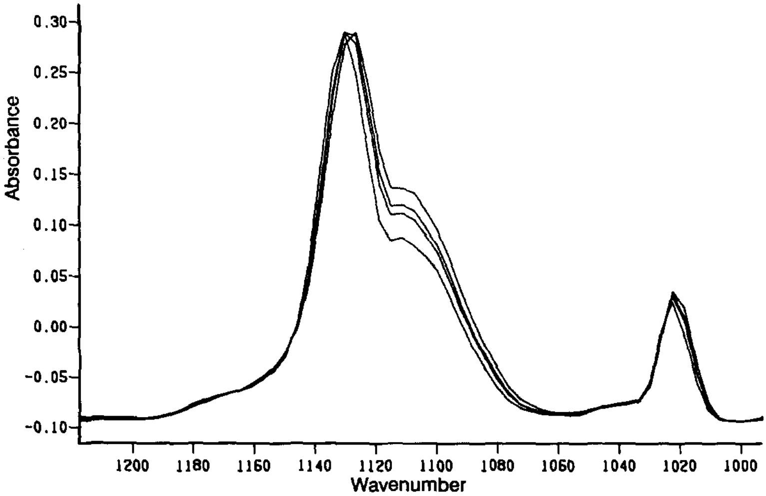

Fig. 14. A series of IR spectra generated at various temperatures as PET is heated through its glass transition.

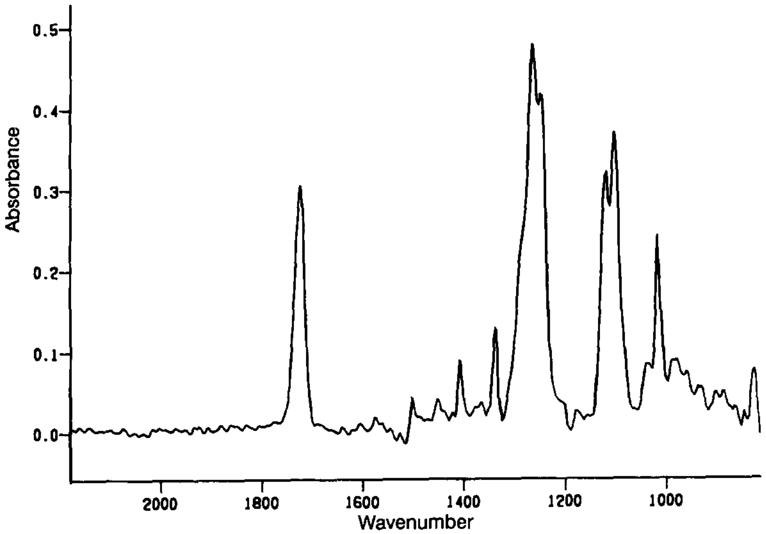

Fig. 15. Kramers–Kronig-corrected reflectance spectrum of a 40×80 μm^2 area of PET found in a pressure-treated multilayered tape.

intensities initiate during PET's glass transition at 80 °C. A series of spectra generated while PET was heated through its T_g is shown in Fig. 14.

A month after this work was completed, a section of high-pressure multi-layered tape came into the lab for analysis by IR microscopy. This tape was suspected of having experienced high temperatures. One layer of this material was composed of PET. An 80×40 μm^2 area of the PET was analyzed by micro-reflection. A Kramers–Kronig corrected spectrum is shown in Fig. 15. The relative band heights at 1111 and 1128 cm^{-1} indicate that this material had been heated in excess of 250 °C. It was theorized that the high-pressure environment prevented the sample from relaxing when cooled.

CONCLUSIONS

It is apparent from this research and from earlier work performed by Koberstein and Mirabella that the DSC/FTIR technique provides the chemist with a powerful tool for the characterization of polymeric materials. DSC has become a workhorse in the polymer lab for both research and quality control. By coupling an FTIR to the DSC, structural information about the sample as it passes through thermal transitions may also be gained, in the same way that TGA/FTIR gives information about any evolved gases. In particular, we have been able to demonstrate that the use of micro-reflectance techniques allows for the facile examination of the sample in a standard DSC microscopy cell, without any modification to the cell or microscope, except for the removal of the normal cover slip. Thus, DSC/FTIR can easily be utilized to obtain information that should provide the chemist with additional insight into polymer behavior in various thermal environments.

By coupling FTIR to a differential scanning calorimeter we were able to gain some insight into the final molecular structure and curing steps of cycloaliphatic polyamine crosslinked DGEBA polymers. Our results suggest that the system under study reacts in steps, much the same way as most epoxy/aromatic amine polymers. In such systems, it is thought [10–13] that steric hindrance effects, due to an aromatic substituent adjacent to the amine nitrogen, make the secondary and primary amines react at different rates. Most systems using aliphatic primary and secondary amines seem to have reaction rates that are indistinguishable [10,12]. We in no way dispute that most aromatic and aliphatic amine-cured epoxies show these differences. However, by theorizing a distinct two-step reaction in our study, we suggest that steric hindrance factors influence epoxy/cycloaliphatic polyamines in much the same manner as epoxy/aromatic polyamine reactions.

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