

Spectroscopic Evidence for Mechanochemical Effects of Moisture in Epoxy Resins*

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Synopsis

Internal reflectance Fourier transform infrared (FT-IR) spectra of tetraglycidyl diaminodiphenylmethane (TGDDM) cured with diaminodiphenyl sulfone (DDS) obtained before and after exposure to the combined effect of stress, elevated temperature, and moisture (STM), elevated temperature and moisture (TM), or stress and elevated temperature (ST) environments were used to search for evidence of irreversible chemical changes in epoxy resins. These changes were compared with the infrared changes observed during the late stages of curing. The infrared intensities of the bands attributed to the sulfone group are sensitive to chemical changes and moisture content, which suggests their potential use as molecular monitors within the epoxy network. The results of eight experimental series provide spectroscopic evidence indicating that exposure of epoxy specimens to STM and TM environments that greatly exceed anticipated service conditions results in detectable rupture of chemical bonds in the polymer network. The extent of bond rupture is independent of the applied stress in the 0–90 kg/cm² range. Internal swelling stresses are therefore believed responsible for the observed bond cleavages. Spectral evidence indicates that postcure reactions are the most prominent chemical changes induced by exposure of epoxy specimens to the ST, SM, M, and T environments.

INTRODUCTION

Resin matrix composites (RMC) based on epoxy resins and graphite fibers appear to offer the greatest potential in composite materials technology. It has been shown, however, that the high-temperature properties of epoxy-based RMCs are adversely affected by sorbed moisture.^{1–4} This observation has prompted studies devoted to the physical aspects of epoxy moisture effects.^{2–4} The deleterious effect of moisture on the properties of RMCs is attributed mainly to plasticization of the epoxy resin. A comprehensive review of epoxy moisture effects was given by Browning.⁴

Two workshops,^{2,3} encompassing a broad range of disciplines, considered various aspects of RMC durability moisture/temperature problems. Distinct areas of study included the matrix–fiber interface, fiber surface characteristics, resin matrix properties, rate of water diffusion, and dimensional stability. Browning⁴ stressed the need to study the neat resin matrix materials in order to differentiate between composite structure problems and matrix-related problems. The plasticization mechanism^{2–5} explains the reversible and short-term aspects of the observed moisture effects. The possibility of other mechanisms being concurrently operative and possibly enhanced by the plasticization

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phenomena is of special interest. It has been postulated³ that stress-induced, irreversible chemical changes could cause a small but cumulative loss of properties. Mechanochemical considerations^{5,6} suggest that two stages can be distinguished for considering the effect of stress at the molecular level: (1) stress activation of chemical bonds without causing bond rupture, and (2) stress-induced bond cleavage leading to formation of free radicals or other chemical species capable of further reaction.

Stress-induced bond activation can accelerate the degradative effects of the environment and must therefore be considered in estimating service life. Other processes which could lead to irreversible chemical changes in epoxy resins exposed to stress, elevated temperature, and moisture are as follows: (1) Continued polymerization or crosslinking of the polymer network can occur; (2) internal stresses induced by swelling can cause bond rupture with the resulting network degradation effect.

The study described here is directed toward the detection of irreversible chemical changes in epoxy resins induced by stress, elevated temperature, and moisture environments.

Experimental

The general experimental approach for detection of minor mechanochemical changes in polymers is based primarily on the application of difference Fourier transform infrared spectroscopy (FT-IR). This approach consists in exposing stressed polymer specimens in an environmental chamber and recording their internal reflectance FT-IR spectra before and after environmental exposure, as schematically illustrated in Figure 1.

Sample Fabrication. The epoxy samples used to perform the experiments for this study were produced by a casting procedure developed by Fanter.⁷ Silicone rubber molds (General Electric RTV-664) were made from stainless steel

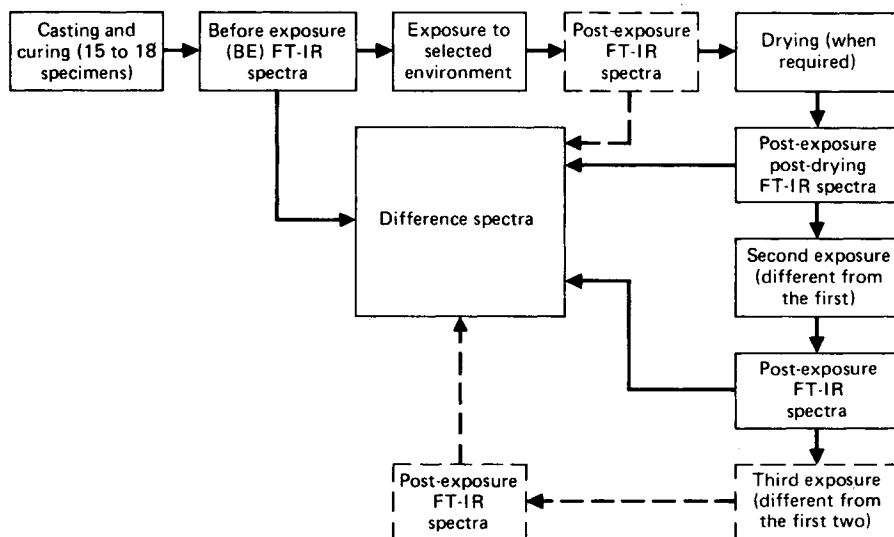


Fig. 1. Overall experimental sequence for the detection of moisture and stress-induced chemical changes in epoxy resins.

tensile coupon patterns which had been polished to facilitate internal reflectance infrared analysis. A tetraglycidyl epoxy resin (Ciba-Geigy MY720) and diamindiphenyl sulfone (DDS) curing agent (Ciba-Geigy Eporal) were heated at 150°C until the DDS was completely dissolved; then the hot solution was vacuum degassed and poured into the preheated molds. The resin was cured within the molds at 150°C for 1 hr followed by 177°C for 5 hr; then the cured samples were removed after cooling to room temperature. A special set of specimens containing 17, 23, 27, and 35 parts per hundred (phr) DDS was cast for the experiments designed to determine the effects of DDS concentration on the susceptibility of the epoxy resin to the various environments.

Environmental Exposure. Exposure of samples to the stress, temperature, and moisture (STM) environment was conducted by clamping the sample in a spring-loaded stress rig, setting it to the desired stress level, and placing it in an autoclave at 135°C. Stress and temperature (ST) exposure was conducted by stress loading the samples within a nitrogen-purged oven at 135°C. Samples exposed to temperature and moisture (TM) were placed, unstressed, in the autoclave. Exposure to stress and moisture (SM) and moisture (M) environments at room temperature was conducted by placing stressed and unstressed specimens in a 100% relative humidity environment. To minimize the effects of rapid cooling of moisture-saturated samples and prevent the formation of liquid inclusions, the samples were removed from the autoclave and placed immediately in a nitrogen-purged oven where they were maintained at 135°C for 5 min and then cooled slowly to room temperature in nitrogen. The environmental exposure experiments described in this study were conducted in six different series which are summarized in Table I.

Difference FT-IR Spectroscopy of Various Curing Stages. A small quantity of uncured resin mix was placed on an internal reflection KRS-5 plate, and the FT-IR internal reflection spectrum was immediately recorded. The plate and the plate holder were placed in a preheated oven; the specimens were kept at the curing temperature for a predetermined period of time, i.e., 15–45 min, and then were removed from the oven and the spectrum recorded again. This procedure was repeated 12 times during the total curing time of 315 min. The chemical changes occurring either during consecutive stages of curing or between any two stages were observed by difference spectra representing stage n minus stage $n - x$, where x is the difference in the stage numbers.

Conditions of the Thermal Spiking Experiment. Thermal spiking refers to rapid heating for a short duration of a specimen exposed to ambient temperature environments such as stress and moisture (SM) or moisture only (M). The schedules for two specimens exposed to SM combined with three thermal spikes at 135° and 100°C, respectively, and two control specimens exposed to SM and M without thermal spikes are shown in Figure 2.

Acid/Base Immersion. Five aqueous solutions, pH 3, 5, 7, 9, and 12, were prepared from hydrochloric acid, distilled water, and potassium hydroxide. The spectra of five epoxy specimens were recorded before exposure, and then one sample was immersed in each solution for 40 hr. The samples were dried 3 hr at 110°C in nitrogen, and their FT-IR spectra were recorded. The five samples plus one control were then exposed to STM. Other control specimens were exposed to ST, TM, and T.

Spectrometric Conditions. Infrared spectra were recorded on a Fourier

TABLE I
Environmental Exposures for the Experimental Series

Series	Exposure 1	Exposure 2
*Acid/base immersion and STM	pH3, 40 h, D ₁	STM
	pH5, 40 h, D ₁	STM
	pH7, 40 h, D ₁	STM
	pH9, 40 h, D ₁	STM
	pH12, 40 h, D ₁	STM
	Control, not immersed	STM
	Control, not immersed	ST
	Control, not immersed	TM
	Control, not immersed	T
*Thermal spiking and SM	SM, 100°C spikes	D ₂
	SM, 135°C spikes	D ₂
	SM, Control	D ₂
	M, 135°C spikes	D ₂
	M, Control	D ₂
*Post-cure heating and STM	185°C, 2 h	STM, D ₃
	200°C, 2 h	STM, D ₃
	Control	
	S (90 kg/cm ²)	
	177°C, 10 h	STM, D ₃
	177°C, 10 h	ST, D ₃
*Stress effects- in STM	STM, 16 kg/cm ²	
	STM, 30 kg/cm ²	
	STM, 60 kg/cm ²	
	STM, 90 kg/cm ²	
	Control	
*Effects of curing agent ratio	STM (17 pph DDS)	
	ST (17 pph DDS)	
	STM (23 pph DDS)	
	ST (23 pph DDS)	
	STM (27 pph DDS)	
	ST (27 pph DDS)	
	STM (35 pph DDS)	
	ST (35 pph DDS)	
Transmission spectra of STM and ST exposed coupons	STM (17 pph DDS)	
	ST (17 pph DDS)	
	STM (23 pph DDS)	
	ST (23 pph DDS)	
	STM (27 pph DDS)	
	ST (27 pph DDS)	
	STM (35 pph DDS)	
	ST (35 pph DDS)	

*Internal reflection spectra recorded before and after each exposure

Note: Unless indicated otherwise, STM exposure consists of S = 30 kg/cm²,
T = 135°C, M = 100% RH for 10 h. Specimens were produced from
one mix of MY720 + 23 pph DDS.

D₁ = Dried at 110°C, N₂ atmosphere for 10 h

D₂ = Dried at 90°C, N₂ atmosphere for 3 h

D₃ = Stored in vacuum dessicator for 96 h

transform infrared spectrometer (Digilab Model FTS-20). Interferometric data from 200 repetitive scans were summed, transformed, and recorded on magnetic tape. Internal reflectance data were obtained with an internal reflectance at-

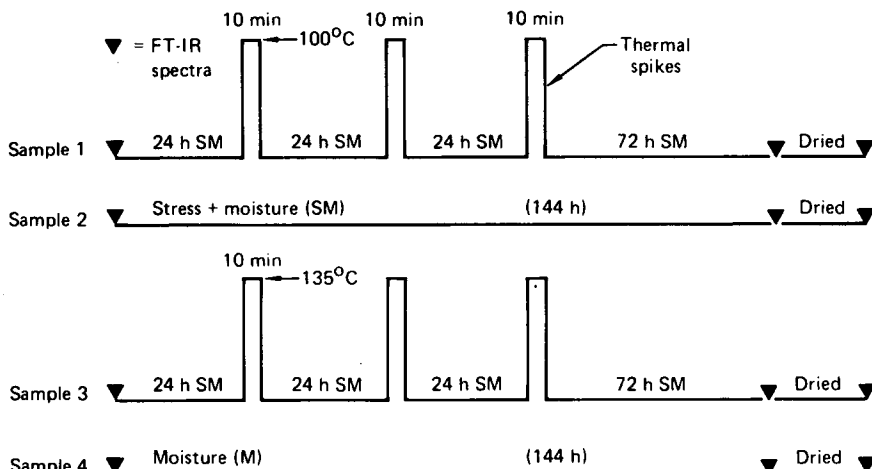


Fig. 2. Schematic record of sample exposure to SM, M, and thermal spiking environments.

tachment (Harrick Model 4XTBCVA) using a KRS-5 plate. Specimens were clamped against the plate using a torque wrench set at 0.45 N·m (0.33 ft·lb) to ensure repeatable spectra. Backgrounds on the KRS-5 plate were recorded immediately prior to obtaining spectra of each specimen.

Infrared spectra were recorded on a digital tape recorder (Kennedy Model 9700) at 315 bits/cm. The data were transferred to a 630 bits/cm tape and were processed by a time-shared computer (Sigma-9) via an interactive CRT computer terminal (Tektronix 4010).

RESULTS AND DISCUSSION

Spectroscopic evidence for occurrence of minor mechanochemical changes in epoxy resins can be obtained by the difference between FT-IR spectra recorded before and after exposure of epoxy specimens to a particular environment. In principle, any mechanochemical change that occurs to an extent exceeding the limits of detectability of the FT-IR spectrometer should be manifest in the difference spectrum. Changes of intensity observed in the difference spectrum at a particular frequency represent the sum of the individual changes occurring in the different bands absorbing at that frequency. The limits of detectability are therefore dependent on the detailed knowledge of spectral contributions of each chemical group and the intermolecular interactions in the network. Obtaining such detailed knowledge for a complex tetraglycidyl epoxy network is beyond the scope of this work.

Despite the above limitations, information on the mechanochemical changes in epoxies can be obtained by comparing the spectral changes occurring during curing with spectral changes induced by different environments. The spectral changes occurring during the late stages of cure reflect the incorporation of new molecules into the polymer network or additional reactions of molecules already partly reacted. Using these spectral changes as a basis for comparison, we can determine which environmental factors lead to further polymerization of the network or, conversely, lead to degradation of the network through mechanochemical bond cleavages.

Absorption Bands in Internal Reflectance Infrared Spectra

In comparison to spectra obtained by infrared transmission, the internal reflection spectra exhibit certain differences in the relative intensities of the bands. These differences in relative intensities arise mainly because of the change in the depth of penetration of the beam into the sample as a function of the frequency.⁸ The internal reflectance spectra of the individual components of the epoxy resin are shown in Figure 3 together with a spectrum of the uncured mixture and a spectrum of the cured specimen. The relative contributions of the DDS and the MY-720 components of the polymer network to the infrared spectrum of uncured and cured resin can be easily observed. The assignments of the molecular origins for the major bands appearing in the infrared spectra of the MY-720, DDS, and the cured resin⁹⁻¹² are summarized in Table II, which also includes remarks on the diagnostic value of individual bands and the direction of changes observed in the curing sequence or the exposure to STM.

Acid/Base Immersion and STM Series

The catalytic effect of acids and bases in hydrolytic reactions is a well-known phenomenon. Therefore, the possible effect of acidic or basic impurities present on the surface of the graphite fibers or in the starting materials was investigated. The acid/base immersion and STM exposure series was performed to determine if contact with acidic or basic impurities affects the susceptibility of the epoxy resin to the STM environment. The experiments performed as part of this series are summarized in Table I and include a total of nine specimens: five immersed in solutions of pH 3-12 and four controls exposed to STM, ST, TM, and T without any contact with acidic or basic solutions.

The difference FT-IR spectra representing after-minus-before immersion of five epoxy specimens to aqueous solutions of pH 3, 5, 7, 9, and 12 showed negligible features. It can be concluded from these experiments that, in general, immersion to acidic and basic solutions (followed by drying) does not induce major infrared spectral changes. The superimposed difference spectra representing after-minus-before exposure of the acid/base-immersed specimens to the STM environment are shown in Figure 4. The features observed in these spectra are remarkably reproducible. All spectra show the small positive doublet at 691 and 717 cm^{-1} . These spectra indicate that immersion of the specimens in acidic or basic solutions does not alter their susceptibility to the STM.

Exposure to SM Combined with Thermal Spiking (TS)

The long-term ambient environment of aircraft with RMC composite components includes stress and moisture, while the short-term extreme conditions occurring during supersonic flight include rapid aerodynamic heating. Therefore, to simulate the long-term ambient and the short-term extreme environments of supersonic fighter aircraft, epoxy specimens were exposed to the SM environment at room temperature and thermally spiked as schematically shown in Figure 2. The difference FT-IR spectra representing after-minus-before exposure of two specimens to the SM plus ST along with difference spectra of the two control specimens exposed to the SM and M environments are shown in Figure 5. These spectra indicate that the main changes induced by SM plus

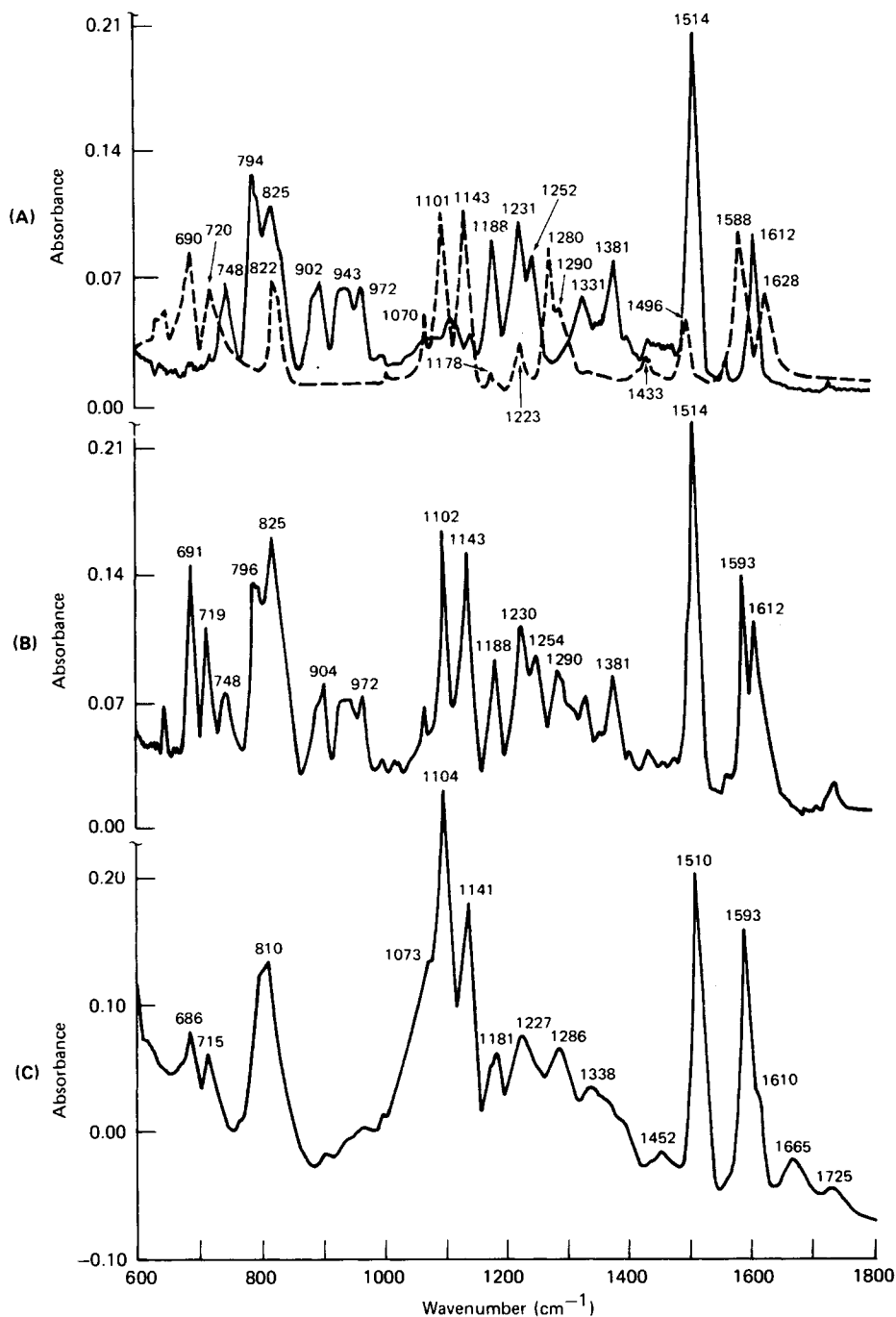


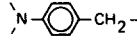
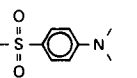
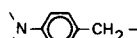
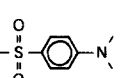
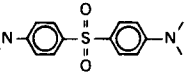
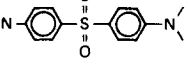
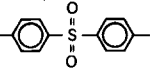

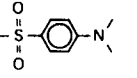
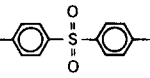


Fig. 3. Internal reflection FT-IR of cured and uncured epoxy resin and its components: (A) (—) MY720 resin, (---) DDS curing agent; (B) MY720 + 23 pph DDS (uncured); (C) MY720 + 23 pph DDS (cured).

TS resemble the changes induced by exposure to ST which are characterized mainly by occurrence of postcure reactions. The spectral features that indicate this effect are the appearance of the negative sulfone doublet at 1104 and

TABLE II
Assignment of Bands Appearing in the Internal Reflectance Infrared Spectra of MY720, DDS,
and a Cured Epoxy Specimen

Frequency ν (cm^{-1})	Assignment	Position in the Network	Origin	Remarks
1725	$\text{C}=\text{O}$	Unknown	.	Product of thermoxidative reaction; decreases as result of STM exposure
1665-75	Conjugated $\text{C}=\text{O}$	Unknown	.	Absorption at this frequency is characteristic for benzophenones and quinones
1640-56		Absorbed, free and H-bonded	.	
1622-8		Not present in the cured resin	DDS	Observed as negative band in curing sequence and in the pure DDS
1612	Benzene ring quadrant stretching		TGDDM	Less sensitive to mass of the substituents than the semicircle stretching band
1588	Benzene ring quadrant stretching		DDS	Less sensitive to mass of the substituents than the semicircle stretching band
1514	Benzene ring semicircle stretching (para subst)		TGDDM	Shifts to lower frequencies during curing and post-curing. This shift reverses as a result of exposure to STM
1496	Benzene ring semicircle stretching (para subst)		DDS	Not intense as the 1514 cm^{-1} band
1280	ν asym $-\text{S}-$ stretch		DDS	Heavily overlapped and considerably less intense than the ν sym band at 1141 cm^{-1}
1135-46	ν sym $-\text{S}-$ stretch		DDS	Unobscured, valuable for diagnosis of changes, strong, appearing in most difference spectra, decreases upon absorption of water
1101-6	ν C-S		DDS	Strong, appearing in most difference spectra, decreases upon absorption of water
904	Oxirane ring	Not present in the cured resin	** TGDDM	
822-5 798	Two adjacent H wag (p-disubstituted benzene)		DDS TGDDM	Frequently appearing in difference spectra, valuable for establishing direction of the curing changes
715-20	Suspected to originate in benzene in-plane quadrant bending		DDS	Increases as a result of STM decreases in curing, valuable for direction of changes
686-91	ν sym C-S-C or quadrant in-plane bending of benzene		DDS	In both cases of assignment this band would be mass sensitive. STM causes an increase and curing causes a decrease

*Band not present in the spectra of DDS and MY-720

**Not present in the spectra of the cured resin

$1141\text{--}1143 \text{ cm}^{-1}$, the weak but noticeable negative doublet at 691 and 717 cm^{-1} , and the unique pattern of the $1498\text{--}1512 \text{ cm}^{-1}$ benzene semicircle stretching band.

The positive $1660\text{--}1664 \text{ cm}^{-1}$ band which also appears in all ST minus before-exposure difference spectra, tentatively assigned to an unknown conjugated

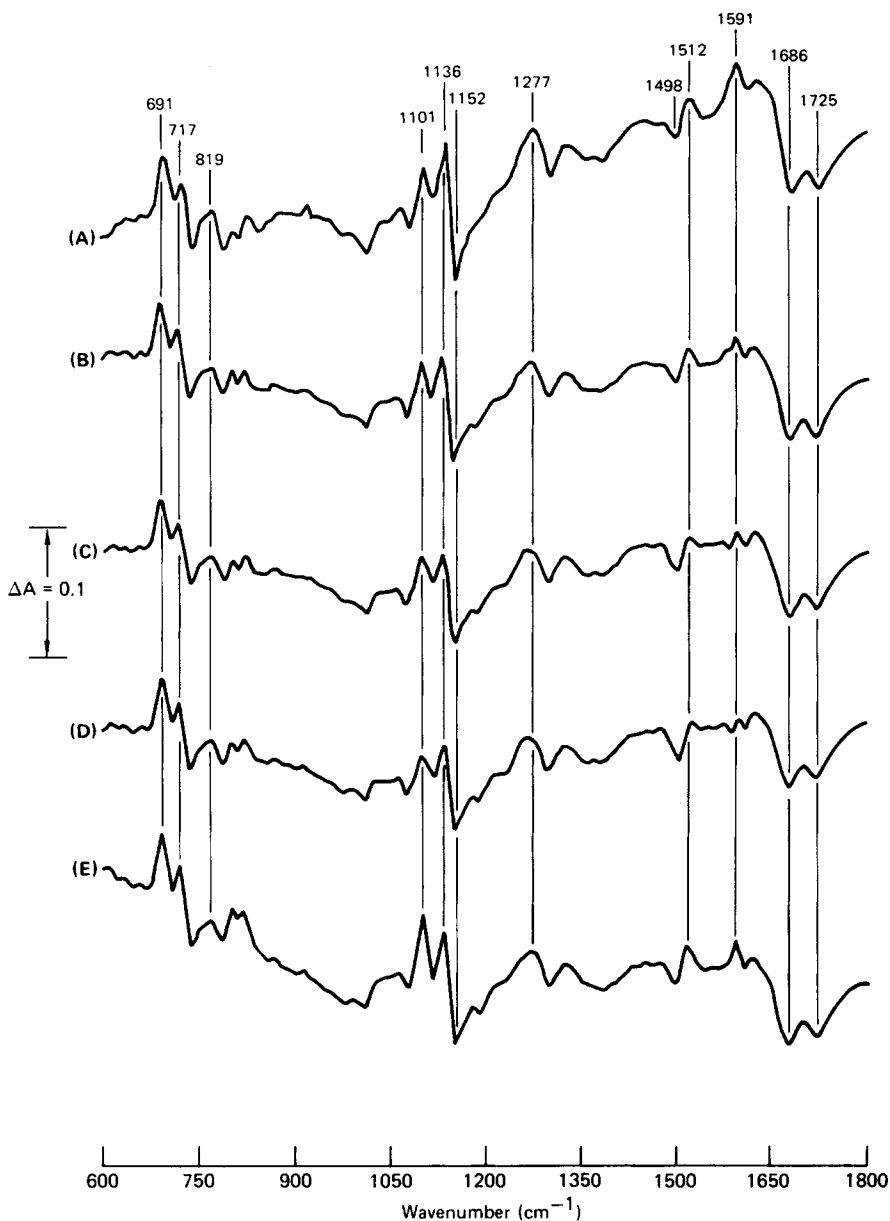


Fig. 4. Difference FT-IR spectra of samples exposed to STM following immersion in aqueous solutions: (A) pH 3; (B) pH 5; (C) pH 7; (D) pH 9; (E) pH 12.

carbonyl (Table II), is undoubtedly a product of a thermo-oxidative reaction which occurs to approximately the same extent in both the thermally spiked and unspiked specimens. The overall similarity of the thermally spiked and unspiked samples can be attributed to drying at 90°C (Table I) which follows exposure to all three environments (SM plus STM, SM, and M). The only spectral differences between the spiked and unspiked specimens appear in the $780\text{--}850\text{ cm}^{-1}$

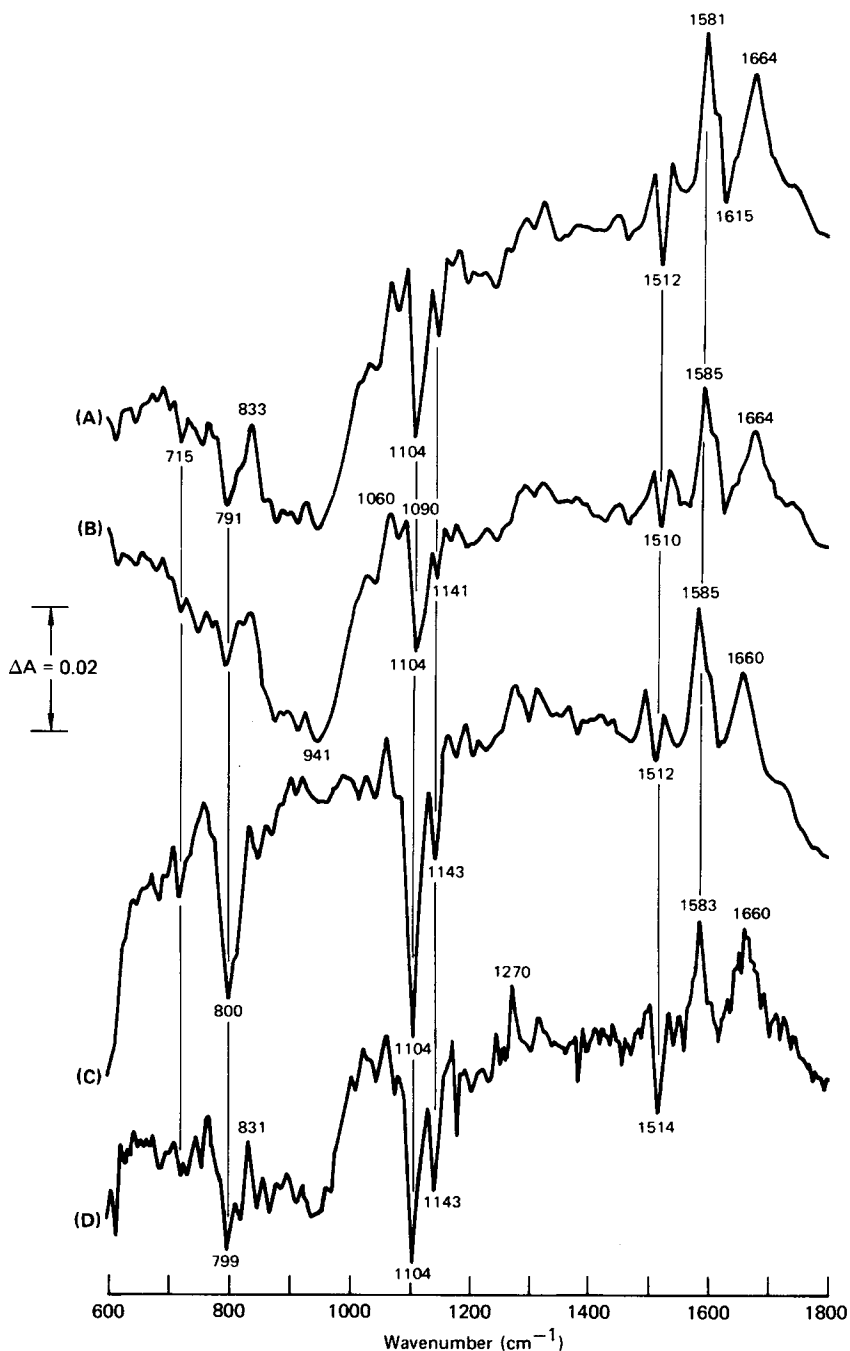


Fig. 5. Difference FT-IR spectra representing after-minus-before exposure to SM combined with thermal spiking (SM + TS), to the SM and M environments: (A) SM + TS at 100°C; (B) SM + TS at 135°C; (C) SM, (D) M.

region. In conclusion, thermal spiking of moisture-containing specimens at 100° and 135°C does not induce any major changes relative to moisture-containing specimens exposed to the same stress but thermally unspiked.

Establishment of an Infrared Direction of Chemical Changes in Late Stages of Curing

During late stages of curing, the epoxy network resembles closely the network of a completed cured resin. Therefore, the chemical changes occurring during postcuring reactions can be recognized and distinguished from changes induced by bond cleavages. The difference spectrum representing the FT-IR spectrum obtained after curing for 60 min at 150°C and 135 min at 177°C minus the spectrum obtained after curing for 60 min at 150°C and 60 min at 177°C is shown in Figure 6(a). This internal reflectance difference spectrum is unique because the specimen remained in the same degree of contact throughout the curing sequence and thus its spectra could be directly subtracted without use of scaling factors.⁵ The observed changes therefore have both quantitative and qualitative significance. Starting with the higher frequency bands, the important spectral features that indicate the direction of change characteristic of late curing are: (1) the frequency shift of the benzene semicircle stretching band from 1514 to 1493 cm^{-1} , (2) decrease of the sulfone band intensities at 1101 and 1141 cm^{-1} , (3) decrease of the 823-5 cm^{-1} band originating from adjacent aromatic H wagging, and (4) decrease of the 690, 717-9 cm^{-1} doublet.

The usefulness of change concept can be illustrated by comparing the spectral changes observed in Figure 6(a) with those observed in difference spectra of specimens exposed to the STM environment. Such comparison is provided in Figure 6 where the difference spectrum shown in Figure 6(a) is superimposed with two difference spectra representing after-minus-before exposure of two postcured specimens to the STM environment. The two spectra that illustrate qualitative reproducibility, Figure 6(b) and 6(c), exhibit spectral changes in the opposite direction of the curing spectrum in all four of the characteristic regions of the spectrum outlined earlier. The shift of the benzene semicircle stretching band in the opposite direction is visually detected even in weak difference spectra. The increase of the sulfone bands is also highly visible. The 1135-1145 cm^{-1} symmetric stretch band of the sulfone group exhibits a frequency shift, and the absorbance increases upon exposure to STM.

Although less dramatic, the 823-825 cm^{-1} band appears strong enough to corroborate the absorbance increase observed by the other bands. Finally, the positive doublet at 690 and 717 cm^{-1} , which at times is too weak to be observed, exhibits remarkable consistency in all STM spectra.

Postcure Heating Followed by Exposure of STM

Since enhancement of postcure reactions is postulated to be one of the important chemical effects of moisture,^{4,5} it was assumed that the degree of postcure can affect the susceptibility of the resin to the STM environment. Epoxy specimens were therefore postcured at 177°, 185°, and 200°C (Table I), and FT-IR spectra were recorded before and after postcuring. The difference spectra representing after-minus-before postcuring at these temperatures shown in Figure 7 indicate occurrence of curing reactions by the direction of the frequency shift of the benzene semicircle stretch vibration at 1496-1512 cm^{-1} and by the negative 800 cm^{-1} band.

The negative sulfone doublet which accompanies the late stages of curing is not observed here, the 1144 cm^{-1} sulfone symmetric stretch vibration appears positive in all three spectra, and the 1102-4 cm^{-1} band appears partially obscured

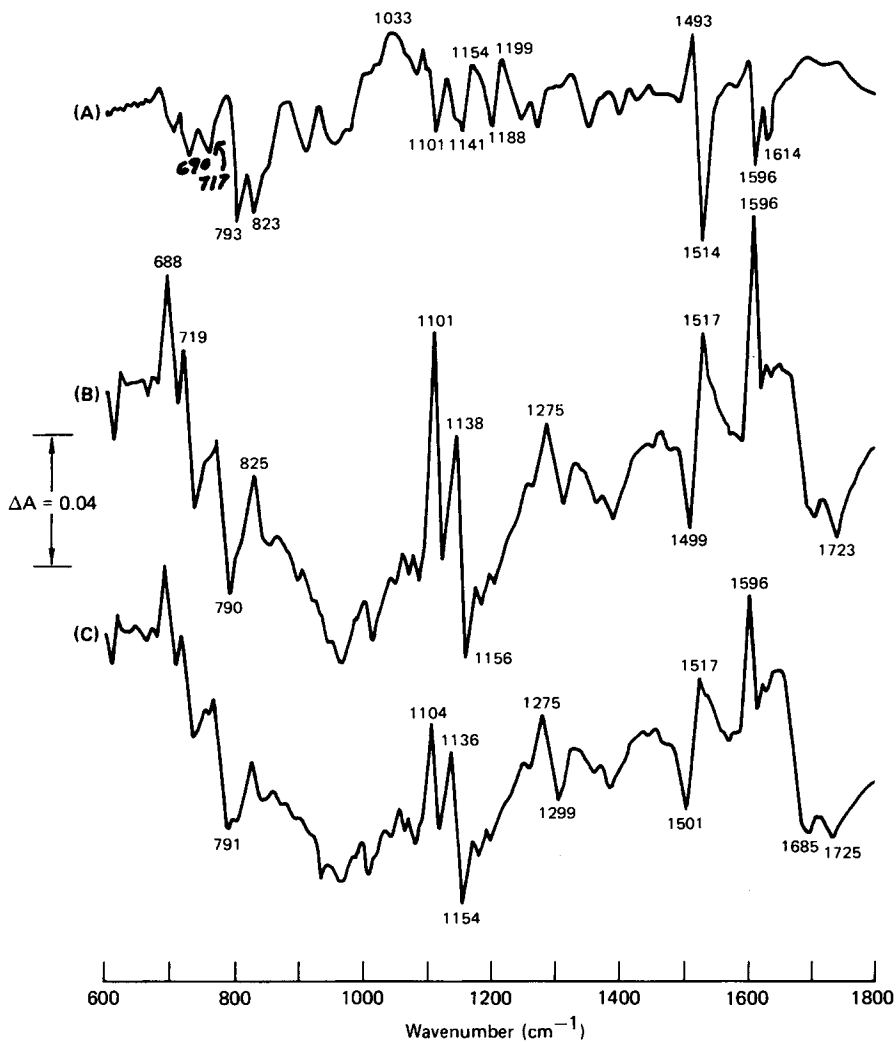


Fig. 6. Difference spectrum of late curing stage superimposed on two spectra representing after-minus-before exposure of two postcured specimens to STM: (A) 195 min cure minus 120 min cure; (B) STM minus postcure (sample 1); (C) STM minus postcure (sample 2).

by the unusual broad negative band at 1060 cm^{-1} . One possible explanation for this reversal of the 1144 cm^{-1} sulfone band is the removal of residual water from the network, thus freeing sulfone groups that are hydrogen bonded to water. An alternative explanation is to attribute the broad negative band as H_2O elimination through loss of a hydroxyl group by a mechanism known to occur in epoxy resins as the first stage of thermal degradation.¹³ This hypothesis agrees with the presence of a broad negative band at 1060 cm^{-1} . (Secondary alcohols generally present in epoxies do not absorb at frequencies as low as 1060 cm^{-1} .) The true position of the broad negative band maxima is probably 1100 cm^{-1} but is obscured by the development of the positive sulfone band. A dotted line shown in Figure 7 illustrates the possible true shape of this broad negative band.

Following postcure heating, the specimens were exposed to the STM environment. The difference spectra representing after-STM minus after postcure

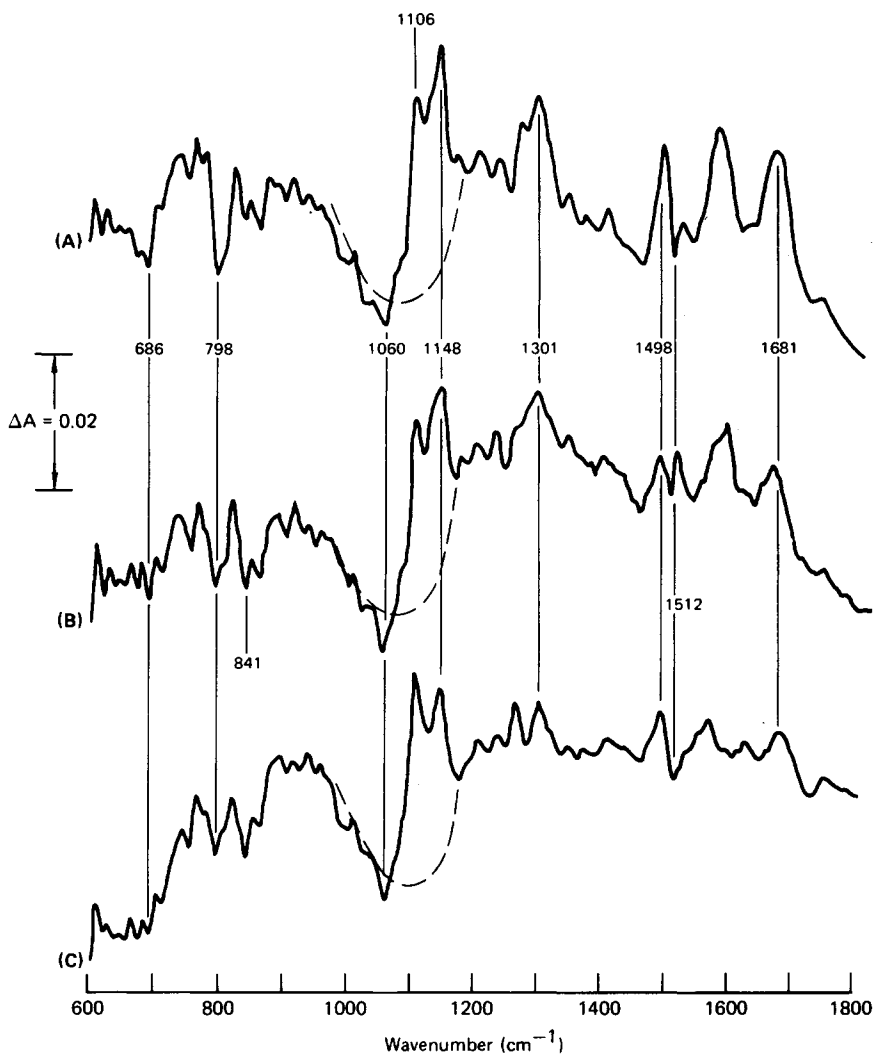


Fig. 7. Difference FT-IR spectra representing after-minus-before postcure heating: (A) 177°C, 10 h; (B) 185°C, 2 h; (C) 200°C, 2 hr.

are shown in Figure 8. Two of these difference spectra are also shown in Figure 6, and their features were discussed earlier. All three difference spectra exhibit absorbance deviations associated with changes characteristic of network degradation.

Spectral Effects of Absorbed Atmospheric Moisture

The ability of the sulfone group to participate in hydrogen bonding is recognized.¹⁰ On the molecular level, the plasticizing effect of water in epoxy resins is attributed to disruption of interchain hydrogen bonding by sorbed water. In addition, the absorbance of the sulfone was believed to be related to hydrogen bonding effects. It was therefore essential to investigate the spectral effects of

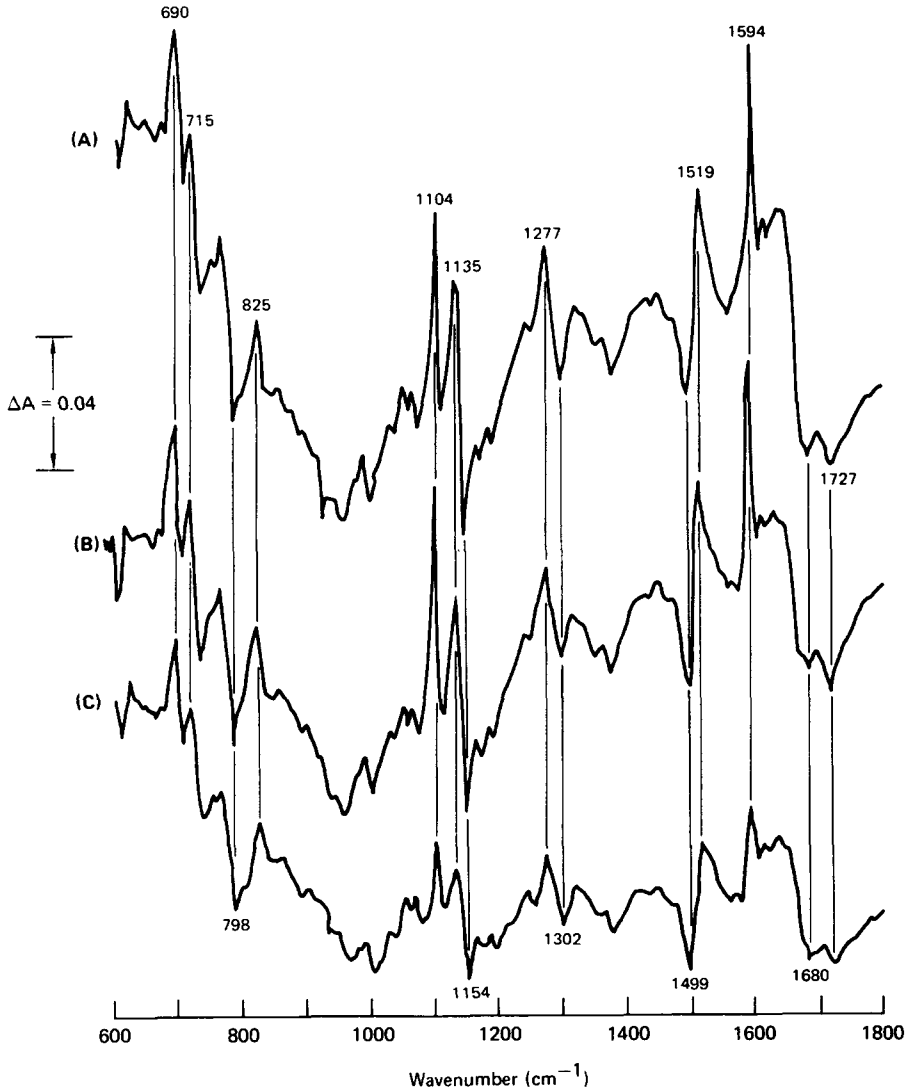


Fig. 8. Difference FT-IR spectra representing after-STM minus after-posture for specimens postcured at (A) 177°C (10 h); (B) 185°C (2 hr); and (C) 200°C (2 hr).

absorbed atmospheric moisture on the various spectral bands and on the sulfone bands in particular.

Epoxy specimens were allowed to sorb different weight percentages of moisture by exposure to 100% R.H. at room temperature. Spectra were recorded before and after the water sorption. The difference spectra representing after-minus-before sorption of 1.3, 1.5, 2.6, and 3.0 wt-% water are shown in Figure 9. The positive 1650 cm^{-1} band is attributed directly to the increase of water content. The highly diagnostic shift of the benzene ring semicircle band at $1496\text{--}1512 \text{ cm}^{-1}$ indicates a small change in the direction of further curing.

If this small change reflects a slight water-induced postcure reaction occurring in the plasticized resin at room temperature, then the effect of water as a plas-

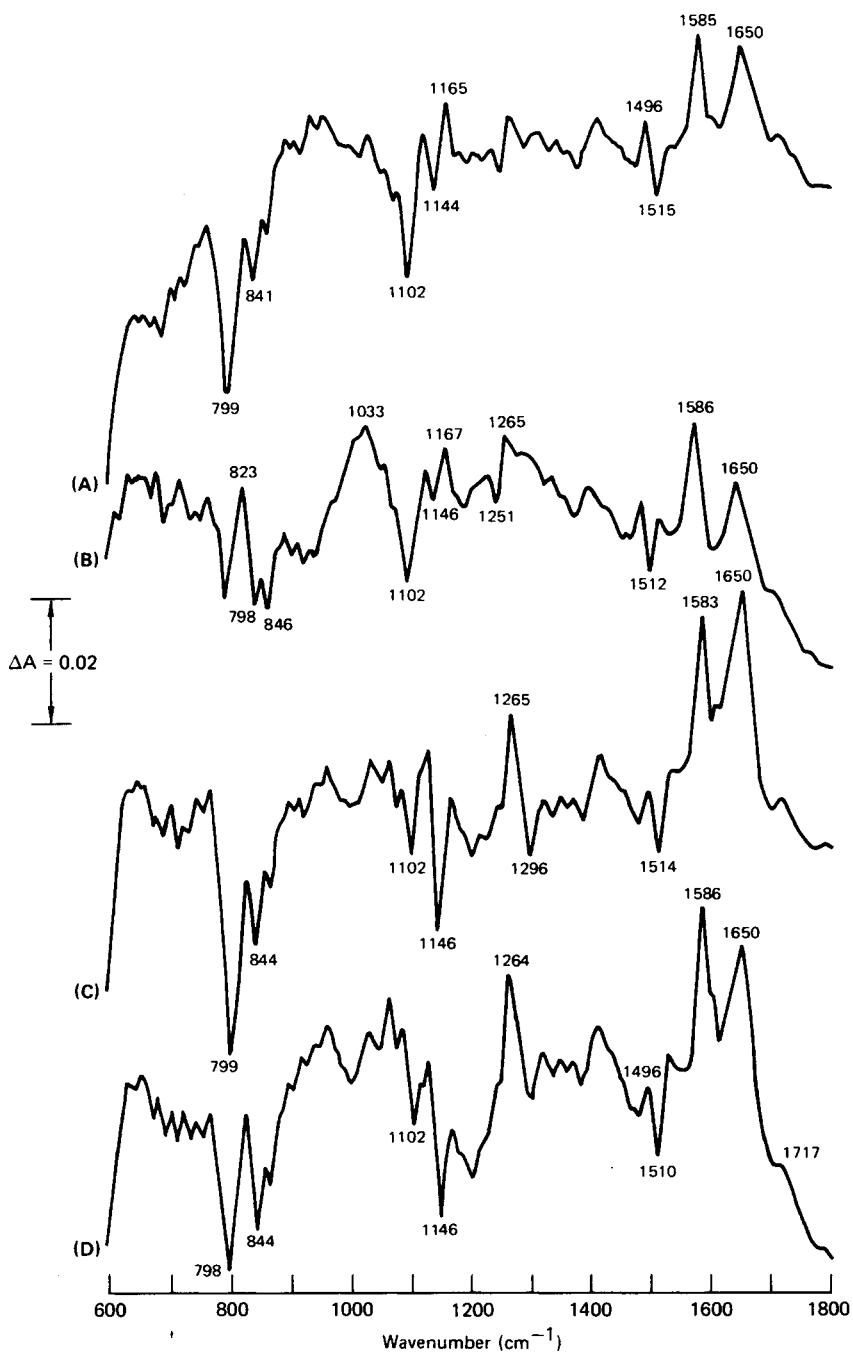


Fig. 9. Difference FT-IR spectra representing after-minus-before absorption of water: (A) 1.3 wt % water; (B) 1.5 wt % water; (C) 2.6 wt % water; (D) 3 wt % water.

ticizing catalyst for the postcure reaction at elevated temperature⁴ also occurs at lower temperatures. Such a room-temperature effect would probably be limited to those postcure reactions that can be facilitated by relaxation of internal stresses induced by the plasticizing effect of water. Absorbed moisture at room

temperatures induces changes in the sulfone bands at 1102 and 1135–1146 cm^{-1} . The changes induced in these bands by sorption of 1.3 wt-% water (Fig. 9) along with the negative 800 cm^{-1} band and the diagnostic shift mentioned earlier strongly resemble the difference spectrum representing ST minus before-exposure for $T = 150^\circ\text{C}$ shown in Figure 10. In both cases, the negative sulfone band at 1102 cm^{-1} is larger than the companion band at 1145 cm^{-1} . Since it has been established earlier⁵ that the main effect of exposure to ST is the postcure reaction, this similarity offers additional proof for the suspected room-temperature, postcure effect of water. As the water content increases to 2.6 wt-%, the changes in the sulfone bands exhibit a reversal of their relative intensity. The 1146 cm^{-1} band assigned to the symmetric stretch vibration is reduced more than the 1102 cm^{-1} stretch vibration. Hydrogen bonding of water to the oxygen atoms of the sulfone group is offered as an unconfirmed explanation for this observation.

Exposure of Epoxy Specimens to Elevated-Temperature ST Environments

In principle, all ST experiments were conducted to provide the control needed to obtain the STM-minus-ST difference spectra which were expected to yield the net effect of moisture on the chemical changes. Therefore, exposures to the ST environment were always performed at 135°C (which is the temperature for all STM experiments) and at the same stress levels used for the STM experiments. However, as a consequence of the plasticizing effect of water, the molecular mobility in a moisture-saturated resin is greater than that of a dry resin. Therefore, chemical changes that depend on molecular mobility progress further in an STM environment than in an ST environment. A series of experiments based on exposure of epoxy specimens to ST and T environments at temperatures higher than 135°C was conducted to determine the effect of stress on the chemical changes occurring in a dry resin at molecular mobilities comparable to those of a plasticized resin at 135°C. The difference FT-IR spectra representing after-minus-before exposure to the ST environment at 165°C are shown in Figure 10. All three spectra exhibit features associated with postcure reactions. The diagnostic 1512 to 1496 cm^{-1} shift appears in all three spectra; the negative sulfone doublets at 1102 and 1141 cm^{-1} (with the 1102 cm^{-1} band larger than the 1141 cm^{-1} band) also appear in all three spectra. The difference spectrum representing ST-minus-T does not exhibit spectral features of sufficient intensity to permit measurement of a net stress effect. It can be concluded that exposure of specimens to the ST environment at temperatures up to 30°C higher than the standard 135°C does not cause detectable stress effects.

Stress Effects in Exposure to the STM Environment

To determine the extent stress affects the observed chemical changes induced by the STM environment, a series of specimens was exposed to the STM environment at stress levels ranging from 0 to 90 kg/cm^2 . Difference FT-IR spectra representing after-minus-before exposure to the STM environment at stress levels of 0, 16, 30, 60, and 90 kg/cm^2 are shown in Figure 11. All spectra exhibit remarkably similar spectral features with similar relative intensities; because

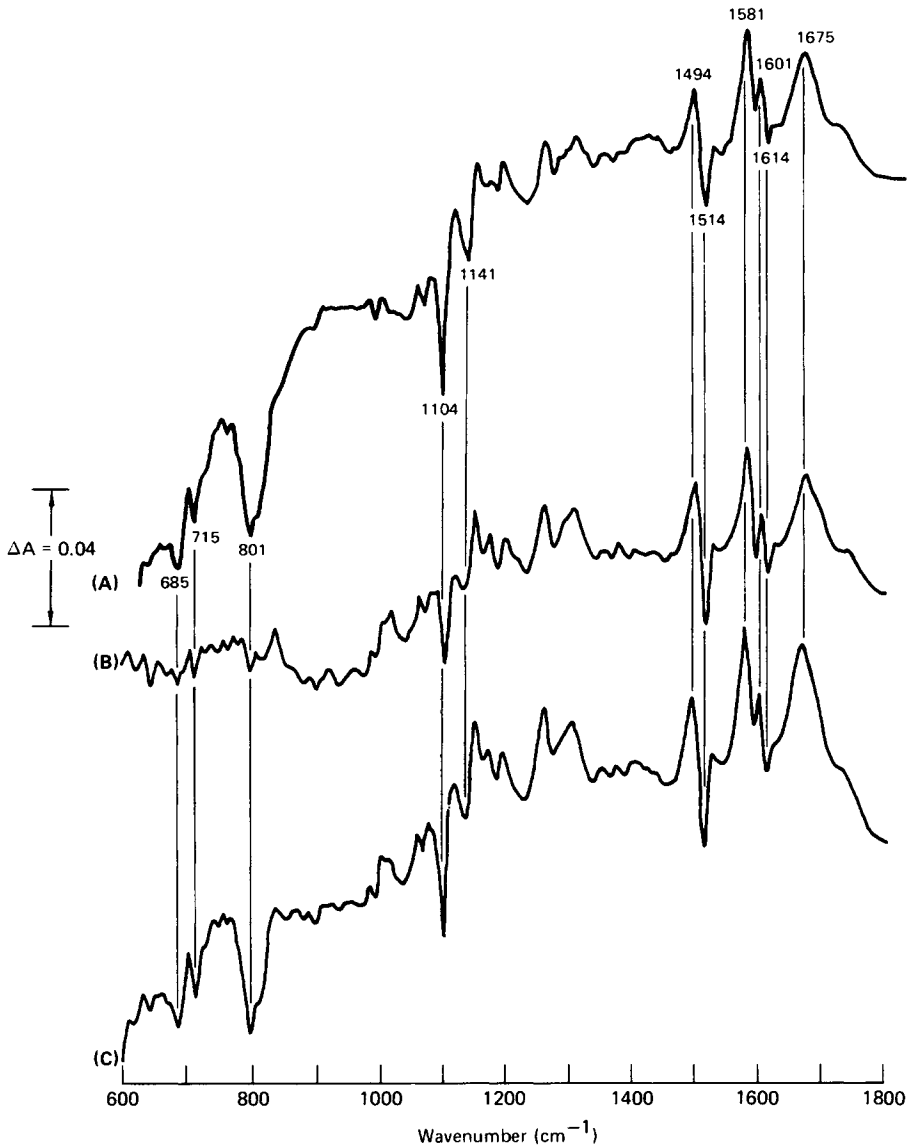


Fig. 10. Difference FT-IR spectra representing after-minus-before exposure to the ST and T environments: (A) $T = 150^{\circ}\text{C}$, $S = 30 \text{ kg/cm}^2$; (B) $T = 165^{\circ}\text{C}$, $S = 30 \text{ kg/cm}^2$; (C) $T = 165^{\circ}\text{C}$, $S = 0$.

of these features we conclude that tensile stress is not the factor responsible for the observed changes.

Effect of DDS Concentration on the Susceptibility to the STM Environment

The possibility that the DDS concentration could alter the response of the epoxy resin to the STM environment through its effect on the network structure was investigated by exposing a series of specimens containing different per-

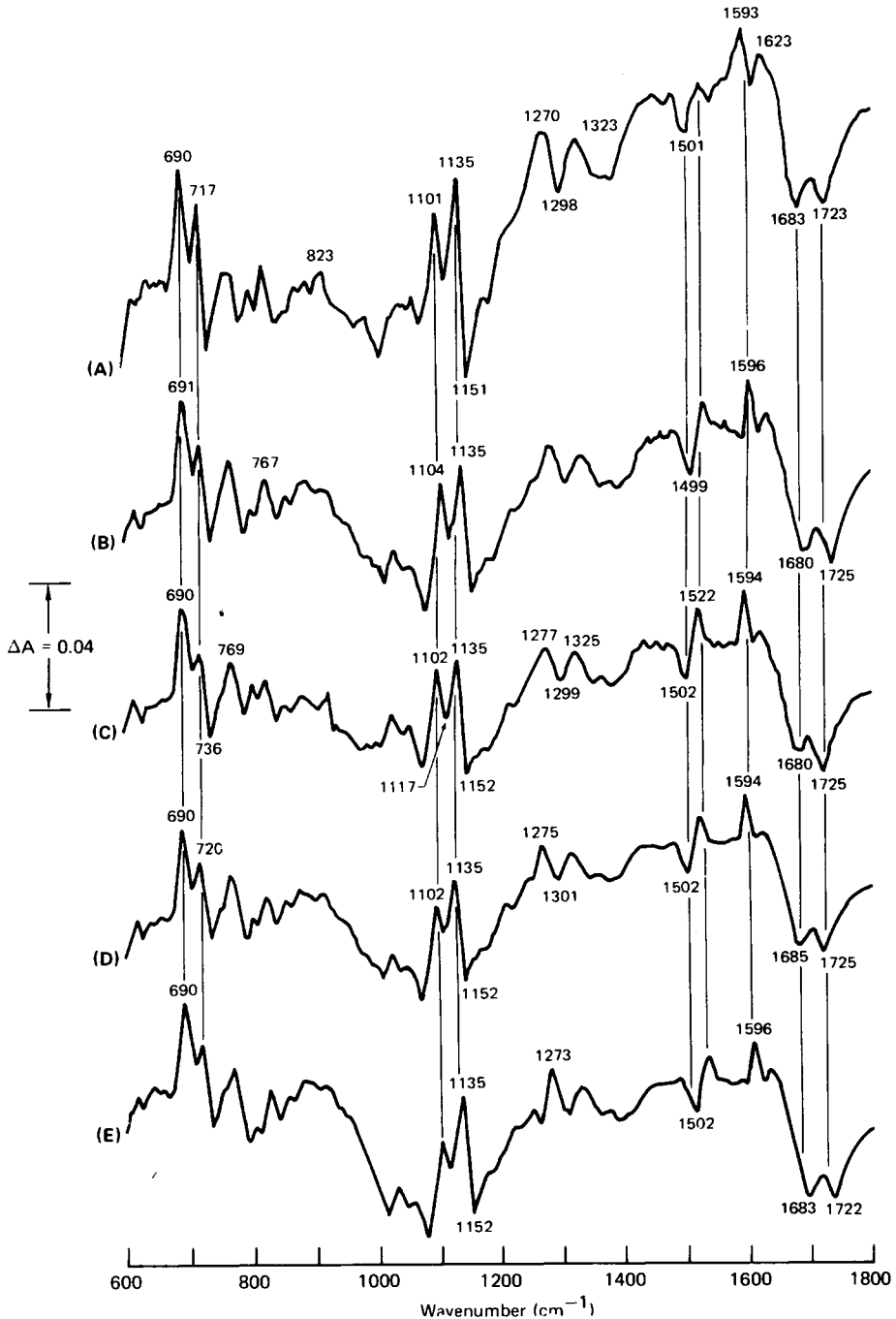


Fig. 11. Difference FT-IR spectra representing after-minus-before exposure to STM at different stress levels: (A) $S = 0$, (B) $S = 16 \text{ kg/cm}^2$, (C) $S = 30 \text{ kg/cm}^2$, (D) $S = 60 \text{ kg/cm}^2$, (E) $S = 90 \text{ kg/cm}^2$.

centages of DDS to the STM environment. The difference FT-IR spectra representing after-minus-before exposure to the STM environment of specimens containing 23, 27, and 35 parts per hundred (phr) DDS were recorded. All three spectra exhibited spectral features which were qualitatively identical to the

spectral features observed in Figure 11. It can therefore be concluded that the general changes induced by the STM environment remain relatively independent of the DDS concentration for the range of concentrations studied.

Transmission Near-Infrared Measurements for Specimens Exposed to the STM and ST Environments

The successful near-infrared experiments conducted by Browning⁴ with a dispersive infrared spectrometer indicated that FT-IR spectroscopy might provide additional information on the processes occurring during exposure to STM because of the greater sensitivity of difference spectroscopy.⁵ Difference spectra representing after-minus-before exposure to the STM environments for specimens containing 17, 23, 27, and 35 phr DDS are shown in Figure 12. The negative 4508 cm^{-1} band attributed to the epoxy group^{4,8} appears in all four spectra shown in Figure 12, as well as a positive band at $5200\text{--}5212\text{ cm}^{-1}$ which can be assigned to OH in water.^{4,9} These data clearly indicate that for all four DDS concentrations, exposure to the STM environment induces a decrease in the number of residual epoxy groups.

A decrease in this band as a function of cure was observed by Browning⁴ for different stages of cure ranging from 1–3 hr at 121°C followed by 1 hr at 150°C and 0.5 hr at 177°C , and also for a specimen immersed in 150°C water for 1 hr (pressurized vessel). Browning also found that the decrease of the residual epoxy for the specimen immersed in 150°C water is accompanied by an increase of the rubbery modulus, thus proving that the disappearance of the residual epoxy group is caused by additional cure and not merely a result of epoxy hydrolysis producing a diol.

Of course, the possibility of such hydrolytic conversion of epoxy groups to diol cannot be excluded. Transmission FT near-infrared spectra of epoxy specimens exposed to STM at two different stress levels (16 and 90 kg/cm^2) and to ST (16 kg/cm^2) along with the spectrum of a control specimen were recorded to explore the possibility that the effect of stress might be detectable in the near-infrared. The difference spectra representing STM-minus-control for the two different stress levels and ST-minus-control are shown in Figure 13. The two STM difference spectra appear almost identical, indicating no detectable stress effect at near-infrared wavelengths. The ST-minus-control spectrum shows only a negligible reduction of the residual epoxy groups, indicating that most of the observed changes in difference spectra ST minus before-exposure (Fig. 10), which we attributed to postcure reactions, represent mainly reactions which do not involve residual epoxy groups.

POSTULATED MECHANISMS RESPONSIBLE FOR THE OBSERVED SPECTRAL CHANGES

Based on these observations and the limitations of internal reflectance spectroscopy, the following qualitative mechanism for the irreversible chemical changes induced by the specific environments is proposed:

1. Exposure of epoxy specimens to the autoclave STM and TM environments leads to bond cleavage in the aliphatic portions of the epoxy network. These observed bond cleavages are induced by swelling stresses and are independent

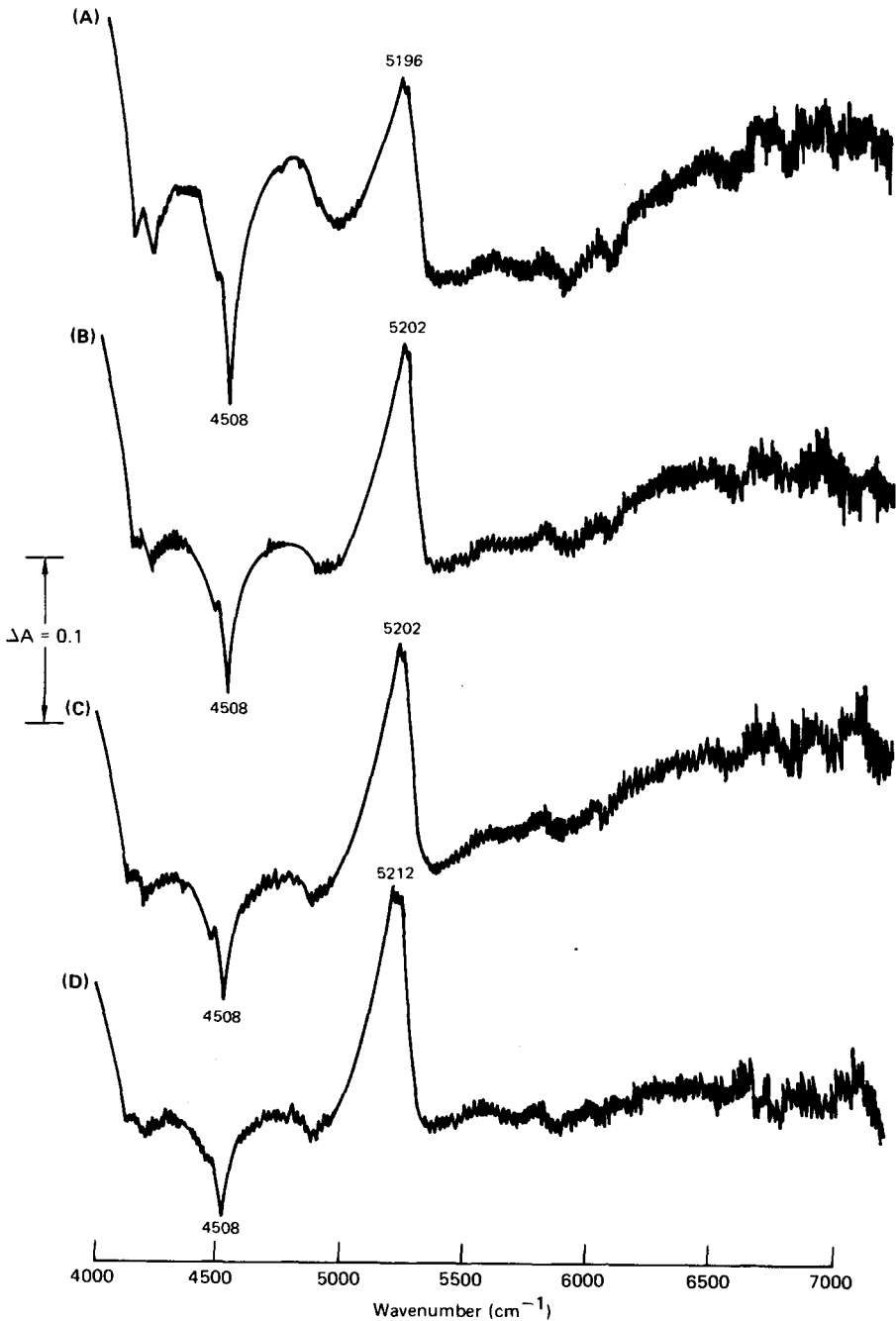


Fig. 12. Near-IR difference transmission spectra representing after-minus-before exposure to STM for specimens containing different amounts of curing agent: (A) 17 pph DDS; (B) 23 pph DDS; (C) 27 pph DDS, (D) 35 pph DDS.

of the external tensile stress, at least for the surface layer examined by internal reflection spectroscopy.

2. Exposure to the autoclave STM also leads to enhancement of the postcure reaction of residual epoxy groups by increasing the molecular mobility.

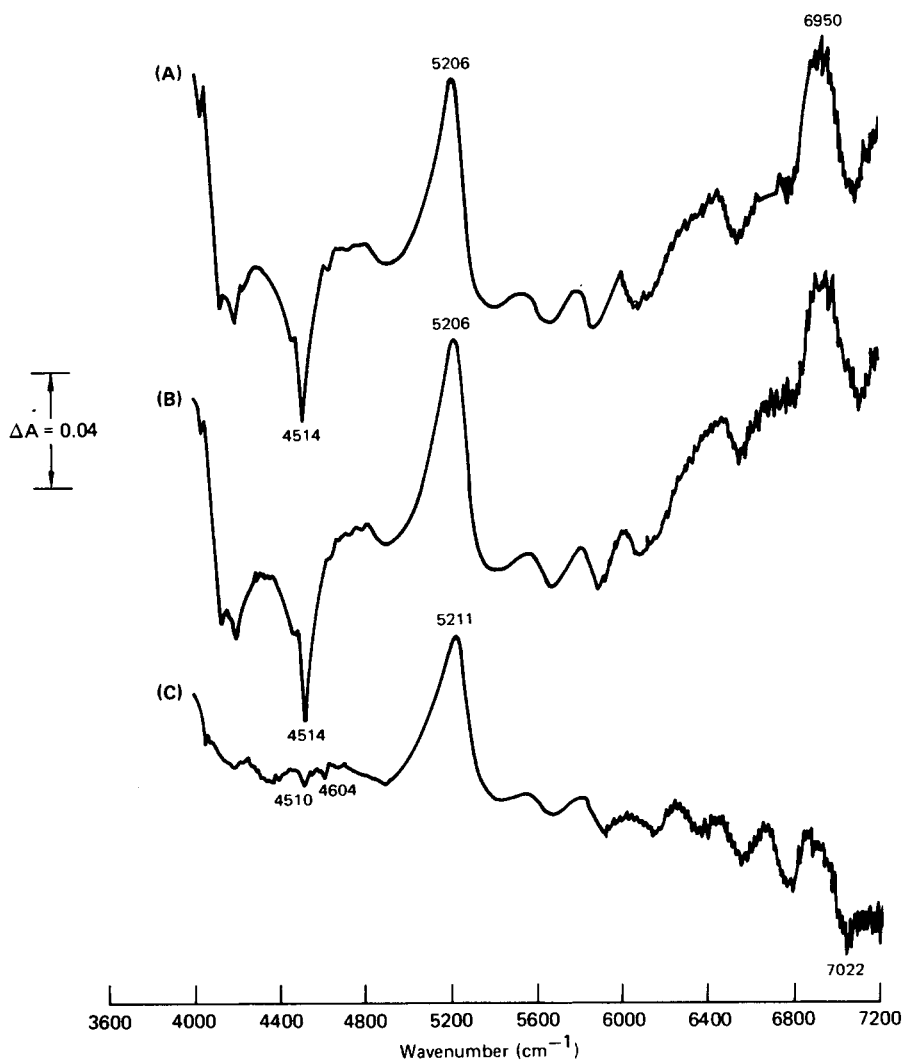


Fig. 13. Near-IR difference spectra representing STM-minus control and ST-minus control: (A) STM-minus control, $S = 16 \text{ kg/cm}^2$; (B) STM-minus control, $S = 90 \text{ kg/cm}^2$ (C) ST-minus control, $S = 16 \text{ kg/cm}^2$.

3. The extent of postcure reactions induced by the STM and TM environments appears to be less than the bond cleavage induced in the network by these environments.

4. Infrared spectral evidence suggests that sorption and desorption of water by epoxy specimens at room temperatures induces limited postcure reactions through relaxation of internal stresses, thus bringing reactive groups closer.

5. No significant spectral evidence could be directly linked to the effect of internal tensile stress on the observed changes.

6. The mechanism responsible for the decrease of the intensities during curing probably reflects an alignment of part of the DDS molecules participating in the curing so that they form hydrogen bonds which interchain neighboring OH groups.¹⁴ Part of the reacted DDS sulfone groups do not enter into such hy-

drogen bonding interactions and are the first to form hydrogen bonds with sorbed water.

7. The bond rupture induced by STM and TM releases certain segments of the network which vibrate (i.e., absorb infrared radiation) at frequencies and with intensities characteristic of their unreacted or monomeric state. Thus observed band-intensity increases and frequency shifts characteristic of bond cleavage exceeded the changes characteristic of the postcure process.

8. The rupture of the carbon-sulfur bond suggested⁵ as one possible explanation for the observed changes in the sulfone bands appears incompatible with the experimental evidence presented herein. The changes of the sulfone bands at room temperature clearly indicate a hydrogen bonding mechanism, thus eliminating the need to invoke the thermal degradation model proposed by Levantovskaya¹⁵ for polysulfone.

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