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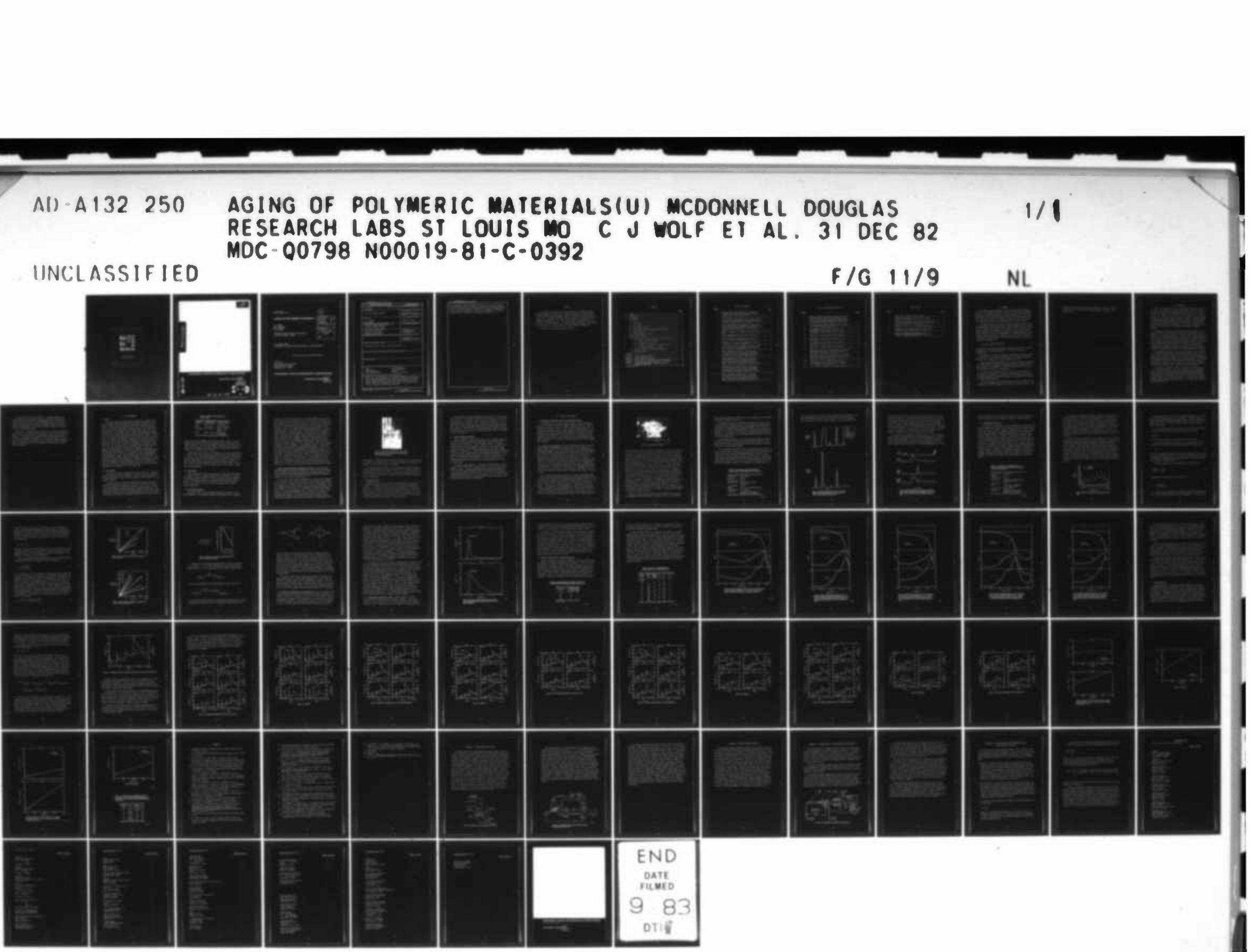

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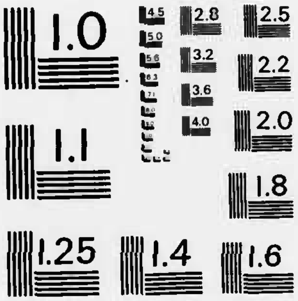
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Report MDC Q0798
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AGING OF POLYMERIC MATERIALS

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McDonnell Douglas Research Laboratories
St. Louis, Missouri 63166

31 December 1982
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Changes in the microchemistry of the MY720/diaminodiphenyl sulfone epoxy resin system were investigated as a function of simulated environmental aging. Chemiluminescence (CL) was used to monitor changes in the resin system, samples of which were aged at 35° and 65°C at 0% RH (relative humidity), 100% RH, or immersed in liquid water. The reciprocal of the CL is a linear function of the aging interval.

The low-temperature thermal decomposition of the cured resin was investigated from 125° to 215°C. The primary decomposition product was propenal. Several other aldehydes were observed; however, they are formed during cure and are not thermal decomposition products. The apparent activation energy for the production of propenal is 67 kJ/mole (16 kcal/mole). Possible mechanisms for the source of this compound are discussed.

PREFACE

This report is an account of the work performed by the McDonnell Douglas Research Laboratories on the Aging of Polymeric Materials for the Department of the Navy, Naval Air Systems Command, Contract No. N00019-81-C-0392, from 30 September 1981 - 31 December 1982. The work was performed in the Chemical Physics Department, managed by Dr. D. P. Ames. The principal investigator was Dr. C. J. Wolf; Mr. M. A. Grayson and Mr. D. L. Fanter were co-investigators. The technical monitor was Mr. M. A. Stander, Naval Air Systems Command, Washington, DC.

This report has been reviewed and is approved.

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I. SUMMARY

The objective of this program was to relate the microchemical changes produced in the MY720/DDS (Ciba Geigy) epoxy resin system during environmental aging with the corresponding changes in mechanical properties and investigate the potential of using chemiluminescence (CL) to monitor these changes. This resin was chosen because it is the primary constituent in many high-performance carbon/epoxy-resin matrix prepregs used in the aerospace industry.

Microchemical changes in the resin system were monitored by vaporization gas chromatography and mass spectrometry. Several aldehydes, such as ethanal, propanal, propenal, and 2-methyl-2-pentenal were positively identified as compounds desorbed from the cured resin. Propenal is not produced during the curing process but results from decomposition of a compound (possibly a cyclic morpholine-like moiety) which is formed during cure. The rate of production of propenal can be described by a first-order reaction whose rate constant as a function of temperature is:

$$k = 1.65 \times 10^3 \exp\left[\frac{-8.13 \times 10^3}{T}\right] \qquad (1)$$

The diffusion coefficient and solubility of propenal in the cured resin were measured and, at room temperature, are 2×10^{-14} m^2/s and 0.04 wt%, respectively.

The production of 2-methyl-2-pentenal is associated with moisture sorbed in the resin; it is observed only from resins aged in a humid environment. The role of this compound in the aging process is not known.

Dynamic mechanical analysis (DMA) of the aged resin revealed the presence of a secondary peak associated with the glass transition temperature (T_g). This peak occurs at temperatures 30-35°C lower than T_g and is observed only when the resin is aged in a dry environment.

The origin of SO_2 observed in the brittle fracture of the resin was investigated. SO_2 probably is produced by cleavage of a main-chain bond in the resin followed by an elimination reaction. It represents direct evidence of a stress-induced reaction.

The chemiluminescence (CL) of samples aged at 35° and 65°C while in a dry atmosphere, in a 100% RH atmosphere, and immersed in water was measured. The

reciprocal of CL is a linear function of the aging time; the rate of change of CL during aging is a function of environmental exposure, temperature, and sorbed moisture.

II. INTRODUCTION

The use of resin matrix composites has dramatically increased in the last 8-10 years; the F-4 Phantom II contained essentially no composite material, while the F-18 Hornet and AV8B-Advanced Harrier contain more than 9 and 26%, respectively. Because of the attractive strength-to-weight ratio of these materials, their use will continue to increase. However, as their application in load-bearing structural systems expands, it becomes increasingly important to determine the long-term properties of these materials. New methods are required which will enable the designer to fully utilize the physical properties of these materials as well as predict their long-term mechanical behavior.

Although some long-term, real-time aging studies are needed, it is not feasible to test all new and potential materials in actual service environments for the anticipated lifetime of the system. What is needed, however, is a short-term testing technique that can reliably predict long-term properties. If we assume that the overall structure and mechanical properties of the composite system are related to its chemistry, changes in mechanical properties can be monitored by measuring changes in the chemistry of the material. Furthermore, if a sensitive technique can be found to monitor the chemical changes, an effective method to monitor environmental aging can be developed.

The engineering materials used in aerospace applications are considered quite stable and generally inert. Therefore any changes that occur during aging are slow and reaction rates are low. Techniques must be evaluated that measure these microchemical changes, and these changes must be correlated with micromechanical properties that are related to the macroscopic properties of the materials in question. Last, a sensitive method which can both monitor these changes and predict their long-term effect must be developed.

One material of particular interest is the epoxy resin system used in most of the high-performance carbon epoxy composites: MY720 (a Ciba-Geigy product which is primarily N,N,N',N'-tetraglycidyldiaminodiphenylmethane) cured with Eporal (a Ciba-Geigy product which is greater than 90% diaminodiphenyl sulfone). This system is the basis of the resins in the commercial prepregs widely used in the aerospace industry, i.e., Narmco 5208, Hercules 3501, and Fiberite 934.

Our initial objectives were threefold: 1) determine changes in the microchemistry of the cured resin system during controlled environmental aging, 2) determine the utility of chemiluminescence (CL), a new ultrasensitive analytical technique, to monitor environmental aging, and 3) begin preliminary measurements on the mechanical response of the resin system as a function of environmental aging.

Since CL is an extremely sensitive analytical tool (which is described in depth in Appendix A), slow reactions with rates as low as 10^{-14} moles/s can be measured. If a correlation can be found between the aging-induced chemical reactions and the mechanical properties of the epoxy resin systems, and if CL can be used to monitor these reactions, then a potentially powerful technique exists for extrapolating short-term environmental exposure data to predict long-term properties.

III. EXPERIMENTAL

3.1 Resin

All samples used for this program were produced from a single blend of resin and hardener, thereby ensuring sample-to-sample repeatability of the mixture. MY720 epoxy resin and Eporal curing agent were obtained directly from the manufacturer, Ciba-Geigy Corporation, and mixed in our laboratory in the ratio 27 parts by weight Eporal to 100 parts MY720. This ratio is not stoichiometric, but was chosen because it closely approximates the hardener/resin ratio used to blend commercially available pre-preg yardgoods. Approximately 1 kg of MY720 was heated to 70°C, and the Eporal was stirred into the resin. The temperature was gradually increased to 100°C while the mixture was continually stirred. After the Eporal had dissolved, the mixture was separated into 20 mL aliquots, cooled to room temperature, and stored at -20°C until used. The starting materials were characterized by liquid chromatography in a manner similar to that described by Hagnauer.[1] MY720 was dissolved in dichloromethane, injected into the liquid chromatograph (Spectra Physics 8000), and separated on a 9.4 mm diameter x 50 cm column (Whitman Partisil Magnum-9). The principal constituent in MY720, tetraglycidyldiaminodiphenylmethane (TGDDM), comprises approximately 72% of the resin. The remainder is composed of epichlorohydrins, triglycidyl derivatives, and other reaction intermediates with concentrations of 1.5 to 14%. The Eporal was approximately 90% pure diaminodiphenylsulfone (DDS) and contained four major impurities with concentrations of < 1% to almost 4%.

3.2 Test Coupons

Four different sample configurations were used in this work. Coupons of specific shapes and sizes were necessary to optimize results from different analytical procedures. Table 1 lists the coupon type and dimensions for each method of analysis.

All samples except the powder were fabricated by casting in silicone rubber molds according to the method of Fanter.[2] Patterns for each type of coupon were designed and machined from stainless steel, polished to the desired surface finish, and positioned inside a demountable Teflon form. Room-temperature vulcanizing silicone rubber (General Electric RTV-664) was mixed according to the manufacturer's suggestions and poured into the form until the

TABLE 1. SAMPLE TYPES PREPARED FOR AGING STUDIES.

Sample type	Dimensions (mm)	Analytical procedure
Coupon	0.80 × 13.0 × 25.0	Chemilumescence
Blocks	3.0 × 10.0 × 20.0	Precision abrasion MS
DMA coupon	0.75 × 13.0 × 64.0	Dynamic mechanical analysis
Powder	particles, 10 μm thick	Vaporization gas chromatography

pattern was completely immersed in the liquid silicone. After a 24 h room-temperature cure, the Teflon form was dismantled, and the mold was slit to remove the pattern. The coupons were highly reproducible because all molds of each type were produced from a single pattern. The molds were post-cured at 177°C for 5 h to prepare them for casting.

During sample casting, molds were arranged on a flat sheet and preheated to 150°C for 1 h. Vials containing frozen pre-mixed resin were withdrawn from the freezer to thaw. The resin was placed in a circulating-air oven with the preheated molds, heated to 150°C, and periodically stirred to dissolve the DDS. The heated resin was carefully poured into the molds, cured for 1 h at 150°C, and 5 h at 177°C. The oven was then turned off and allowed to slowly cool to room temperature.

3.3 Resin Powder

Finely divided resin was used to qualitatively and quantitatively measure the amounts of volatile compounds indigenous to the cured resin. The powder was produced by grinding a block of cured resin using the precision abrasion device.[3] The particles produced in this manner had a thickness of approximately 10 μm, a surface area of 2.4 m^2/g,[4], and rapidly sorb and desorb volatile substances.

3.4 Environmental Exposure

Cured epoxy coupons were environmentally aged at 35° and 65°C in one of three conditions: a dry atmosphere, 100% relative humidity (RH), or immersed in water. The coupons were placed in a test tube suspended in a water bath whose temperature was controlled to ± $1^{o}C$. The test tube was partially filled with distilled water, the coupon was immersed in the water, and a stainless-steel screen was wedged above the water level. A second coupon was placed on the screen so that it was exposed to exactly the same temperature as the immersed coupon. The top of the tube was sealed with paraffin to isolate the sample and ensure a 100% RH atmosphere. A dry environment was obtained by partially filling a test tube with a layer of dessicant above and below the coupon. This particular arrangement was chosen so that the temperature of samples immersed in water, exposed to 100% RH, or completely dry could be maintained exactly the same throughout the experiment. A special test was conducted to determine whether or not a temperature difference existed between the immersed and the 100% RH (i.e., the suspended) samples. A small iron-constantan microthermocouple was imbedded in test coupons by curing in situ. The thermocouples from the immersed and 100% RH samples were connected to a potentiometer (Honeywell model 2745) and, after equilibration of 30-40 min, no difference in temperature was observed. Therefore, the temperatures of the liquid and vapor water in a given experiment are the same within ± $0.1^{o}C$. Figure 1 is a photograph of the water bath containing several test tubes. Samples were periodically withdrawn from the environmental aging baths and analyzed by one or more of the analytical techniques discussed in this report.

3.5 Vaporization Gas-Chromatography/Mass-Spectrometry Vaporization gas-chromatography/mass-spectrometry (VapGC/MS) is a technique developed specifically to analyze for trace organic compounds in intractable matrices.[5] The technique has been utilized successfully to characterize the trace organic compounds in lunar samples and meteorites.[6-9]

In this study, thin shavings, approximately 10 μm thick, were milled from the resin coupons. The fine dust was placed in a tared quartz tube, weighed, and connected to the desorption heater inlet of the gas chromatograph. Volatile compounds desorb from the sample shavings when they are inserted into the heated regions of the VapGC oven. The compounds are transferred by flowing helium to an in-line low-temperature trap. The sample can be heated to any temperature from ambient to $250^{o}C$ for periods as long as several hours. Chromatographic analysis is accomplished by removing the sample from the heated zone, heating the column trap, and starting the chromatographic temper-

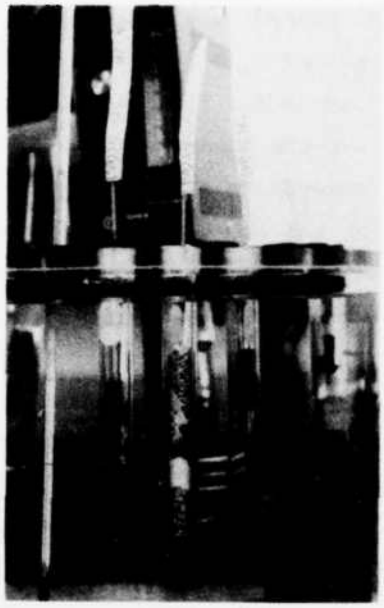

Figure 1. Samples in test tubes immersed in a heated bath: (a) sample in a dry air environment and (b) sample immersed (lower) and 100% RH (upper).

ature program. In many experiments the mass spectrometer was not used because the identity of all products had been determined previously. Experiments conducted in this manner are referred to as VapGC.

The procedure can be repeated at a given temperature thereby generating a series of chromatograms which represents the total of the products released at that temperature as a function of time. The detector was quantitatively calibrated by injecting known amounts of hydrocarbons and oxygenated hydrocarbons into the chromatograph.

3.6 Chemiluminescence

Chemiluminescence (CL) is a relatively common phenomenon in which part of the energy of an exoergic chemical reaction is released as electromagnetic radiation, i.e., light.[10,11] Many reactions such as oxidation and hydration exhibit CL. In general, there are only two requirements for a reaction to be chemiluminescent: 1) the reaction must be sufficiently energetic to raise one of the reaction products to an excited state, and 2) the excited state must be sufficiently long-lived to deexcite by a radiative process.

Resin samples were analyzed immediately after removal from the environmental chamber. The coupons were inserted into the CL system at 50°C with an oxygen flow rate of 15 cm^3/min. The CL intensity was measured for 1 h, and the temperature was increased to 65°C. The process was repeated at 75° and 90°C. This series of measurements constitutes an intensity-temperature-time (ITt) profile. The profiles of all aged samples were measured in the manner described above. The CL system and technique developed at MDRL are described in detail in Appendix A.

3.7 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) has been used to determine mechanical properties such as glass transition temperature, Young's modulus, shear modulus, and tensile modulus. In DMA a polymeric material is subjected to a sinusoidal stress, and the deformation is analyzed to give the parameters controlling energy lost and energy stored per cycle. The dynamic storage modulus (G' for shear or E' for Young's modulus) defines the energy stored per cycle in a perfectly elastic manner, and the dynamic loss modulus (G'' or E'') defines the energy dissipated (as heat) in a perfectly viscous manner. The ratio of loss modulus to storage modulus is the loss tangent ($\tan \delta$), a dimensionless parameter defining the ratio of energy dissipated to energy stored per cycle.

The dynamic storage modulus, G', the dynamic loss modulus, G'', and the tangent of their ratio, $\tan \delta$, were measured for a series of specially prepared DMA coupons. A Dynamic Spectrometer (Rheometrics model RDS-7700) located in another McDonnell Douglas laboratory was used for these analyses. Instrumental problems (beyond our control) caused a lack of confidence in the experimental data obtained on the coupons aged for time periods greater than 2000 h, and these results are not reported.

IV. RESULTS AND DISCUSSION

4.1 Microchemical Characterization of the Aged Resin System

Determination of the chemical changes produced in the MY720/DDS resin system is an integral part of this program. Previous studies have shown two compounds of particular interest: sulfur dioxide (SO_2) and propenal.[12] We have positively identified both of these compounds and have shown that SO_2 is released at the instant of fracture while propenal is formed by the low-temperature thermal decomposition of the cured resin. The relation of these compounds to each other and to the production of CL is not completely known; however, experiments to elucidate the origin and connection of these compounds were conducted.

4.1.1 Search for Sulfur Dioxide Previous experiments have shown that SO_2 is released when cured MY720/DDS is fractured in the stress MS apparatus.[13] Dogbone-shaped samples of the resin were fractured in the time-of-flight mass spectrometer (TOFMS), and SO_2 was positively identified by its characteristic mass spectrum at ionizing potentials of 70 and 11.6 eV, respectively. The origin of SO_2 is of prime interest to this investigation: if it is an indigenous volatile compound trapped in the resin matrix and released from the fresh fracture surface, it has no value in characterizing the aging process; however, if it is actually produced during fracture, i.e., a mechanochemical reaction product, it may serve as evidence that stress-induced chemistry plays an important role in the failure of the epoxy resin. Furthermore, the weak links in the polymer chain may correspond to those reaction sites that produce the SO_2.

To elucidate the processes by which SO_2 is produced, the amounts formed in brittle fracture (stress MS) and mechanical abrasion (VapGC analysis of the fine powder) were compared. The resin was carefully ground with the mill head of the precision abrasion apparatus, and the fine powder was collected and used for VapGC analysis. A photomicrograph of a typical grain is shown in Figure 2 . The surface area is approximately 2.4 m^2/g,[4] and the thickness of a fine shaved particle is approximately 8-10 μm. During brittle fracture in stress MS experiments,[13-16] tensile coupons with cross-sectional areas of 0.5 cm^2 (0.4 x 1.2 cm) produced fresh exposed fracture surface areas of approxi-

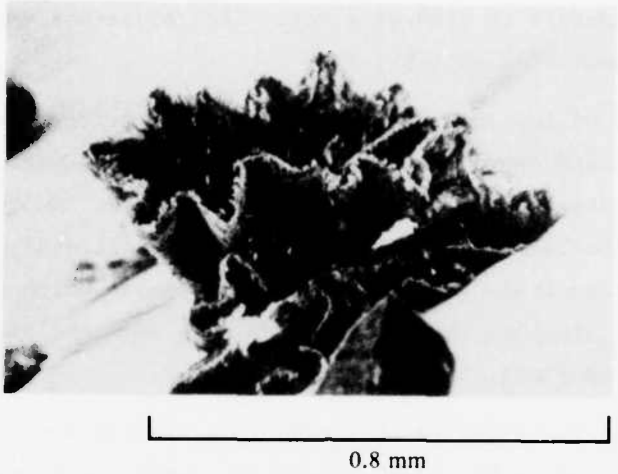

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Figure 2. Typical grain of resin powder.

mately 2.5 cm^2, while the 50 mg used in VapGC powder had a total surface area of 1.2×10^3 cm^2. The total exposed surface area of the resin in the VapGC experiments is approximately 10^3 greater than in the fracture experiments in which SO_2 is positively identified. If we assume that 1% of all the polymer chains normal to the surface are broken during the mechanical deformation processes, approximately 2×10^{12} and 10^{15} broken bonds would be produced in the stress MS and VapGC grinding process, respectively. If most of the broken bonds occurred at the phenyl sulfur bond, and if each of these radicals produced a molecule of SO_2, 3.3×10^{-12} and 1.6×10^{-9} moles of SO_2 would be released in the stress MS and mechanical grinding experiments, respectively. If the pressure increase in the ion source of the TOF from the expanding SO_2 was uniform and distributed over 0.5 L, the maximum pressure would be $1\text{-}3 \times 10^{-5}$ Pa ($1\text{-}2 \times 10^{-7}$ Torr); this value is consistent with the SO_2 spectra observed. The amount of SO_2 formed in the mechanical milling process would be approximately 10^{-7} g, a value which is slightly greater than the minimum detectable quantity of SO_2 in the VapGC system. Therefore, if SO_2 is not observed in the VapGC experiments, we can assume that it is probably produced at the moment of brittle fracture and is evidence of stress-induced chemistry occurring in the cured epoxy resin.

Because the flame ionization detector (FID) normally used with the gas chromatograph in the VapGC analysis is insensitive to SO_2, it was replaced with a thermal conductivity (TC) detector. The conditions used in these VapGC experiments are summarized in Table 2.

Chromatograms of the volatile compounds desorbed from consecutive heats at 125°C and 175°C are shown in Figure 3. The compounds were identified by combined gas-chromatography/mass-spectrometry analysis. Sulfur dioxide was not observed. To confirm these observations, two additional experiments were performed: a) the analysis was repeated with a sample which was deliberately spiked with sulfur dioxide, and b) the GC/MS data were analyzed with the aid of mass-chromatogram plots.

Sulfur dioxide was added to the resin dust through a special septum injection port installed at the inlet end of the quartz sampling tube. Thus, SO_2 was injected during the thermal desorption period and trapped along with the volatiles released from the sample.

In this fashion, sulfur dioxide elutes in the spiked sample exactly as it does in a normal sample. However, SO_2 elutes during the same time interval as that of water; thus, a single chromatogram using the TC detector is not sufficient to positively confirm or deny the presence of SO_2. Consequently, the TC detector was replaced with the MS-30 mass spectrometer, and the entire mass spectrum (from m/z 250 to 12) of the eluates was recorded every second. Characteristic masses of interest, for example, m/z 64 (the parent ion of

TABLE 2. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF SULFUR DIOXIDE IN RESIN POWDER.

Helium flow rate:	5 $cm^3 \cdot atm/min$
Sample size:	40-60 mg
Sample surface area:	2.4 m^2/g
Oven heating rate:	20 min at 125°C followed by 20 min at 175°C
Trap temperature:	– 196°C
Column:	2 m × 1.5 m i.d. 80-100 mesh Porapak Q
Column flow rate:	18 $cm^3 \cdot atm/min$
Column oven:	Program at 10°C/min from room temperature to 170°C and hold

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SO_2), were plotted as a function of time to generate mass chromatograms. The mass chromatograms of water (m/z 18) and SO_2 (m/z 64) from the resin dust heated for 20 min at 175°C are shown in Figure 4a. The ion currents of the

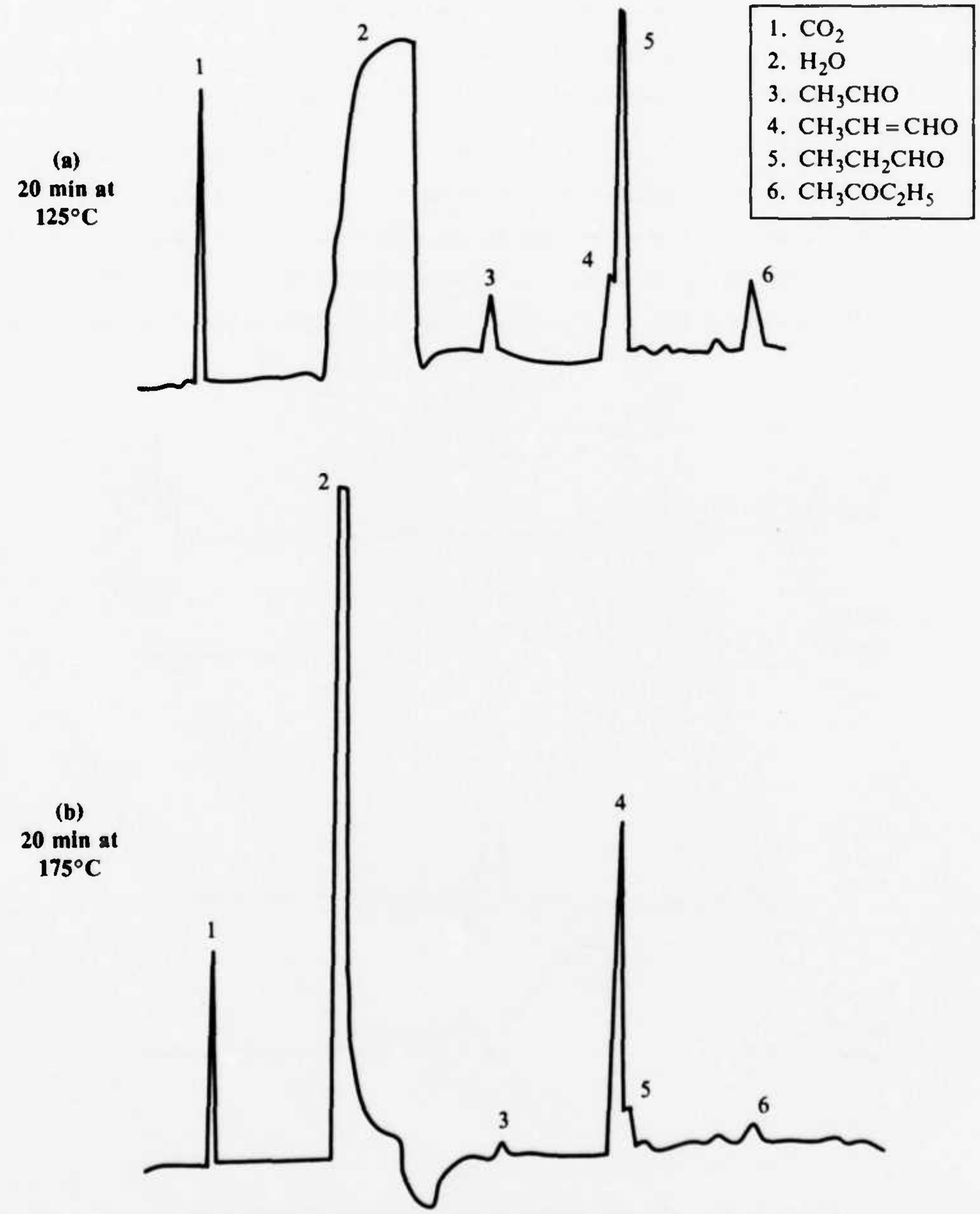

Figure 3. Vaporization gas chromatogram of the compounds released from the fresh powder resin: (a) heated for 20 min at 125°C and (b) heated for 20 min at 175°C.

same masses are plotted for the epoxy sample spiked with sulfur dioxide and are shown in Figure 4b. The sensitivity of the sulfur dioxide trace in the epoxy sample is 1000 times greater than that shown for the spiked sample. We conclude that SO_2 is neither released nor present in the cured MY720/DDS resin. In addition, similar VapGC/MS experiments were repeated on both of the resin starting materials, i.e., the MY720 and the Eporal hardener. In neither case was SO_2 observed. [The detection limit for sulfur dioxide in this experiment is approximately 5 parts per million (ppm) by weight.]

Since SO_2 is not an indigenous compound in either of the starting materials or in the cured resin system but is observed during fracture of the epoxy resin, SO_2 must be produced as the result of a stress-induced reaction in which the activation energy is supplied by the fracture process. This conclusion suggests that the SO_2 moiety in the diaminodiphenylsulfone is a weak

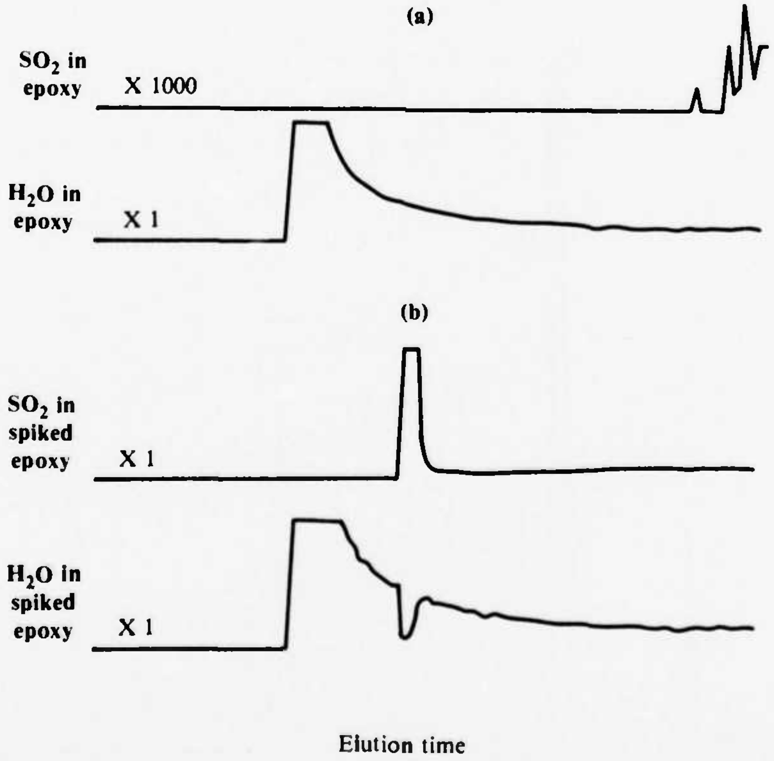

Figure 4. Mass chromatograms of the desorption of water and sulfur dioxide from resin powder: (a) heated for 20 min at 175°C and (b) repeat analysis of resin powder deliberately spiked with SO_2.

link in the polymer chain and represents the chemical bond in the chain which is most susceptible to failure under the influence of a mechanical load.

4.1.2 Low-Temperature Pyrolysis

We have previously reported that several compounds were observed when the resin was heated at the relatively low temperatures of 100° to 150°C for times as short as 20 min.[12] Ethanal, propanal, isobutyraldehyde, propenal, butenal, methyl ethyl ketone (MEK), and methyl pentenal were positively identified. With the exception of MEK, all compounds identified were aldehydes. Small amounts of MEK are known to be present in the MY720 and remain even after cure. The aldehydes, however, are not impurities in either the MY720 or DDS and represent compounds that are either formed during the curing reactions or produced by the subsequent thermal decomposition of some compound formed during cure. The evolution of two similar compounds, propanal and propenal, was studied in depth. The amount of propenal evolved relative to that of the propanal increased as the desorption temperature increased. The kinetics for propenal formation were determined. The VapGC conditions used in these experiments to quantitatively separate these two compounds are summarized in Table 3.

TABLE 3. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF PROPANAL AND PROPENAL DESORBED FROM THE EPOXY RESIN.

Sample flow rate:	15 $cm^3 \cdot atm/min$
Sample mass:	35 mg
Sample surface area:	2.4 m^2/g
Sample heating:	Multiple 20 min heating intervals every 10°C from 125° to 215°C
Trap temperature:	−196°C
Column	50 m × 0.5 mm i.d. Carbowax 1540 support coated open tubular
Column flow rate:	2.5 $cm^3 \cdot atm/min$
Column oven:	Program at 4°C/min from room temperature to 140°C and hold

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The production of propanal and propenal was measured at a series of temperatures between 125^o and 215^{o}C by VapGC (Appendix C). A 35 mg charge of resin powder was held at the desired temperatures for 20 min while the volatile compounds were collected; the sample was removed from the desorption heater inlet, and the products were analyzed. The sample was reinserted into the desorption heater inlet, and the process was repeated. A total of 123 individual analyses were performed in this manner from 125 to 215^{o}C. The results are summarized in Figure 5 where the amounts of propanal and propenal released from consecutive 20 min heating intervals are shown as a function of temperature.

During the initial measurements at 125^{o}C, propanal was the major compound desorbed; four times more propanal was released than propenal. However as the volatilization/pyrolysis temperature increased, propenal was released in greater quantities. The total amounts of propanal and propenal observed in the 123 individual VapGC analyses were 1.06 and 3.72 μmoles, respectively. It is important to note that 57% of the propanal from all heats was released at 125^{o}C (and 75% of that or 43% of the total was released in the first three analyses). However, less than 4% of the propenal from all heats was released at 125^{o}C. The distinction between the rate of release of these two similar compounds is quite marked and suggests entirely different mechanisms for their origin.

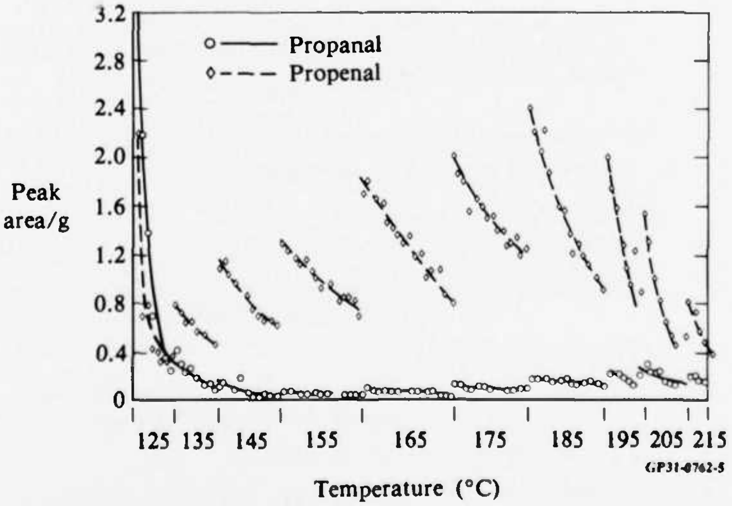

Figure 5. Release of propanal and propenal from heated epoxy resin.

Separate experiments have shown that propanal and propenal are not impurities in either starting material, i.e., the MY720 or the DDS. Propanal is probably formed during the cure and remains trapped in the matrix of the cured resin. Thus, its rate of release is similar to that of a known indigenous impurity such as MEK.

If we assume that propenal, P, is produced via a unimolecular decomposition from some compound, M, formed during the curing process, then

$$\frac{dP}{dt} = kM \ , \tag{1}$$

where k is the rate constant for the reaction and t is the time.

If we further assume that the amount of M in the epoxy resin is finite and decreases on a one-to-one basis with the production of propenal, then

$$M = M_o - P \ , \tag{2}$$

where M is the molar concentration of the precursor compound at time t during the thermal decompositon process, M_o is the molar concentration of the precursor compound at the beginning of the experiment, and P is the molar concentration of propenal produced at time t.

By substituting (2) into (1) and expressing it in integral form:

$$\int \frac{dP}{M_o - P} = k \int dt \ . \tag{3}$$

Integrating (3) over the limits from 0 to a time t,

$$kt = \ln \left[\frac{M_o}{M_o - P} \right] \ . \tag{4}$$

To apply the above expressions to analyze the thermal decomposition data from a sample repeatedly heated at various temperatures, it is necessary to compute the amount of precursor at the first heat at each new temperature. Since a one-to-one molar correspondence is assumed between the production of propenal and the precursor compound, the moles of propenal produced during the experiment equal the moles of M_o. At the first heat of each new temperature, a new M_{oi} is computed by subtracting the amount of propenal produced up to that time from M_o:

$$M_{oi} = M_o - P_{i-1} , \tag{5}$$

where M_{oi} is the molar concentration of precursor at the beginning of the i-th decomposition study, M_o is the concentration of precursor at the start of the experiment, and P_{i-1} is the concentration of propenal produced prior to the decomposition studies at the i-th temperature.

Thus, in the sequential-heating VapGC experiments, the following relation describes the production of propenal at any given temperature:

$$kt = \ln\left[\frac{M_{oi}}{M_{oi} - P}\right] . \tag{6}$$

A plot of $\ln[M_{oi}/(M_{oi} - P)]$ as a function of time should yield a straight line of slope k, the first-order rate constant at the temperature in question. The appropriate plots are shown in Figure 6 for temperatures of 135°, 145°, and 155°C and in Figure 7 for temperatures of 165°, 175°, 185°, 195°, 205°, and 215°C. All plots are linear indicating that the mechanism for propenal production does not change from 135° to 215°C. A typical Arrhenius plot of the logarithm of the rate constant as a function of the reciprocal of the temperature is shown in Figure 8. The solid line corresponds to at least-squares fit to the experimental data. The slope of the line yields an activation energy of 67.4 kJ/mole (16.1 kcal/mole) for the production of propenal. The rate constant, k is given by

$$k = 1.65 \times 10^3 \exp\left[\frac{- 8.13 \times 10^3}{T}\right]. \tag{7}$$

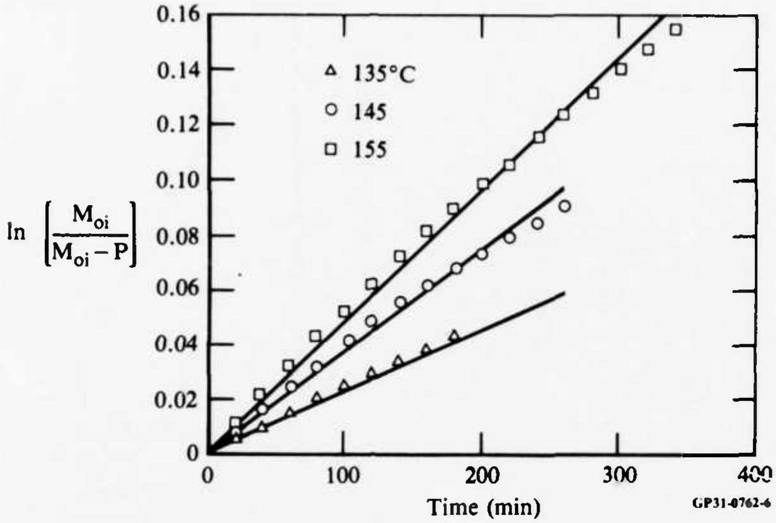

Figure 6. Rate of formation of propenal from cured resin at 135, 145 and 155°C.

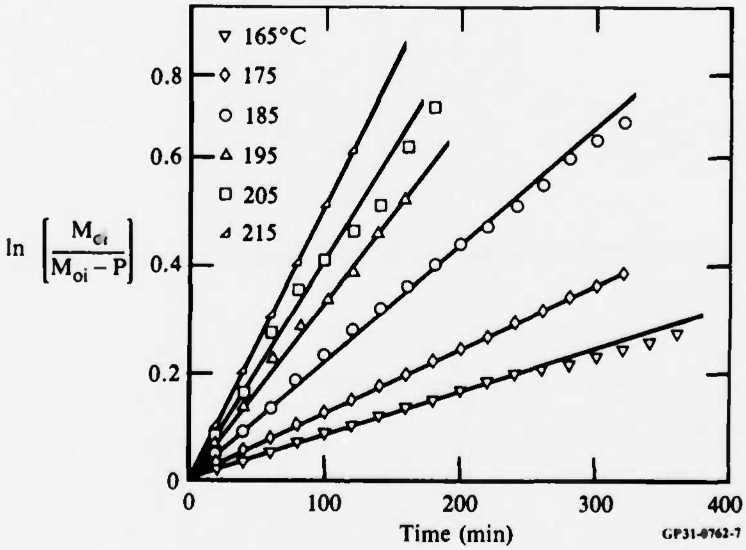

Figure 7. Rate of formation of propenal from cured resin at 165, 175, 185, 195, 205, and 215°C.

$\Delta E = 16.1$ kcal/mole

$\Delta E = 67.4$ kJ/mole

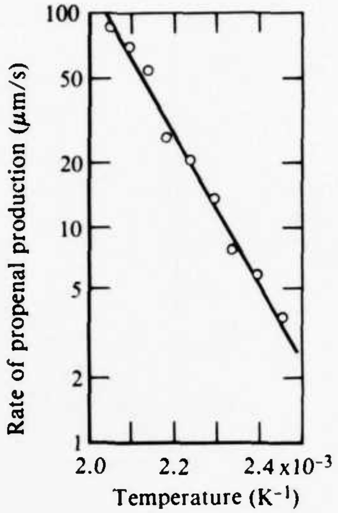

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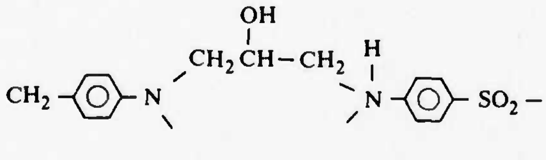
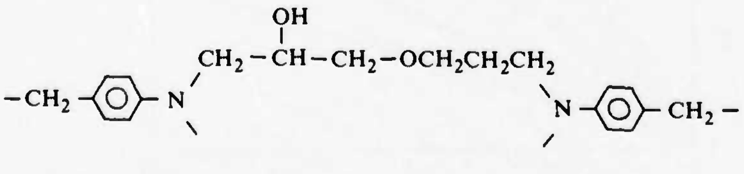
Figure 8. Arrhenius plot of the rate of propenal production as a function of reciprocal temperature.

Polymerization of MY720 epoxy and DDS amine can proceed via three distinct reactions: 1) an epoxy amine addition reaction yielding a hydroxy-secondary amine (I) (or a tertiary amine if the secondary hydrogen reacts),



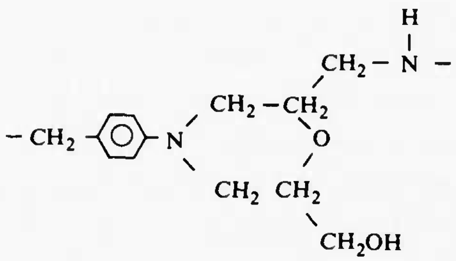
I

2) an epoxy homopolymerization reaction yielding a hydroxy ether, (II),

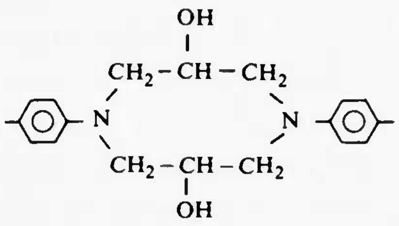


II

or 3) an intracyclization reaction of the glycidyl and hydroxy groups to yield a morpholine-type structure (III) or an eight-membered dihydroxy ring (IV),



III



IV

The resin mixture used in this study, as well as the commercial prepreg resins, is epoxy rich. [The stoichiometric ratio is 50 phr DDS while the commercial mixtures vary from 23 to 29 phr.] Therefore, formation of the homopolymerized alcohol-ether bond (II) or the cyclized ring structures (III and/or IV) may be expected. In fact, Morgan et al.[17] recently reported that as much as 75% of the hydroxy groups formed in the initial reaction between the epoxide and the primary amine may undergo further reaction to form ring-like structures, III and/or IV. Other investigators[18-20] have also speculated on the existence of morpholine-type ring structures formed during cure of the MY720/DDS system.

The evidence suggests that relatively small amounts of a thermally unstable compound (either a hydroxy-ether homopolymer or a intracyclized ring compound) is produced during cure of the MY720/DDS resin system. This compound decomposes to propenal with an apparent activation energy of 67 kJ/mole. The role of propenal or its precursor on the production of chemiluminescence from the resin and its change during environmental aging will be investigated.

4.1.3 Diffusion of Propenal into the Epoxy Resin The role of propenal in the low-temperature aging of the resin was further investigated by measuring the transport properties of propenal in the cured resin. Resin coupons 3-mm thick were immersed in propenal at room temperature for various times and analyzed by PAMS (see Appendix D). The distribution profiles of both water (measured at m/z 17 to decrease sensitivity) and propenal (measured at m/z 56) were measured after 27 and 207 h immersion in liquid propenal (that contained 5-10 wt% water). The propenal distribution profile after 27 h immersion was not sufficiently developed to permit diffusion coefficient analysis (see Appendix D); however, after 207 h immersion, the profile was capable of mathematical analysis (see Figure 9a). According to these data, the diffusion coefficient of propenal in the resin at 22°C is 2×10^{-14} m^2/s. Despite immersion of the sample in propenal, the water present in the propenal was readily sorbed by the epoxy resin and well-developed water distribution profiles were obtained (see Figure 9b). According to the profile, the diffusion coefficient for water in the resin is approximately 2×10^{-13} m^2/s, in excellent agreement with the value of 2.8×10^{-13} m^2/s reported previously for samples immersed in liquid water or in 100% RH environments.[21] Furthermore, the diffusion coefficient for propenal at this temperature is one-order-of-magnitude less than that of water. The maximum concentration of propenal in the resin is approximately 0.04 wt%, i.e., the solubility of propenal in the epoxy is nearly 100 times less than that of water.

If we assume that the rates of sorption and desorption of propenal in the resin are essentially the same and that the activation energy for diffusion in the resin is the same as that of water (i.e., 40 kJ/mole), the rate of desorption of propenal from the resin at the various temperatures used in the VapGC analysis can be calculated with the aid of the Arrhenius equation. For example, at 125°C, the lowest temperature used in the VapGC studies, the diffusion coefficient is approximately 10^{-12} m^2/s. For the typical resin powder used in the VapGC experiments, i.e., 10 μm thick, a compound with a diffusion coefficient of 10^{-12} m^2/s would completely (99.9%) desorb from the 10 μm thick sample in approximately 15 s. Even if the resin powder averaged five times thicker, i.e., 50 μm, at 125°C propenal would be completely desorbed in approximately 6 min. Propenal is observed to evolve from the heated resin for times more than an order of magnitude longer and at considerably higher temperatures. It is evident that propenal is produced during the heating period and is not an indigenous volatile compound.

4.1.4 Hygrothermal Degradation of Epoxy Another compound of interest observed during the VapGC analysis is 2-methyl-2-pentenal. Of particular importance is the observation that the release of this particular compound is sensitive to water. Resins aged in a dry environment are essentially free of

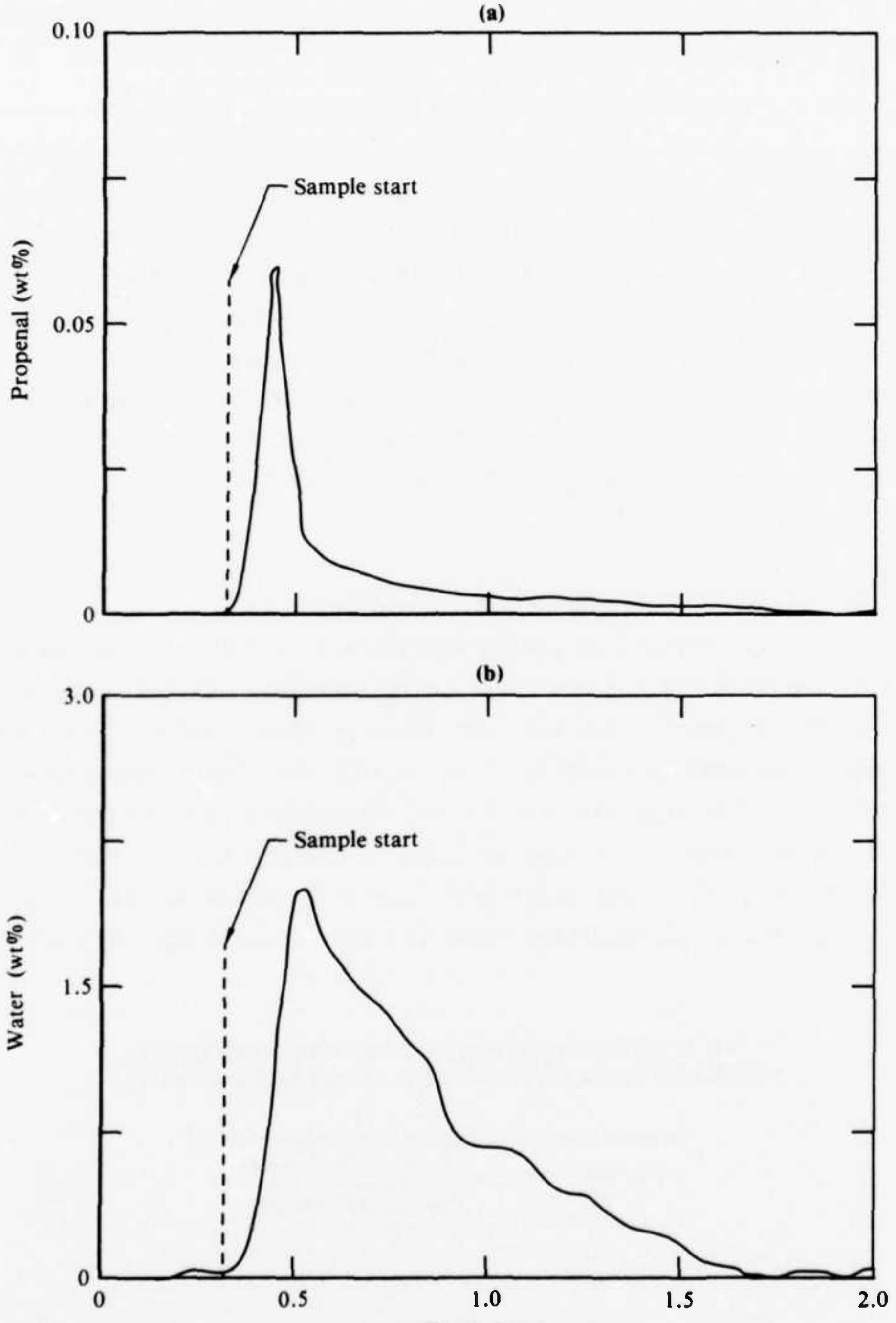


Figure 9. Distribution profiles of propenal and water in cured resin immersed in liquid propenal (5-10% water) for 207 h in (a) and (b), respectively.

2-methyl-2-pentenal while those aged in humid environments readily desorb it. A summary of the concentration of 2-methyl-2-pentenal desorbed from the resin aged at 65°C in dry and humid (100% RH) environments is given in Table 5.

The amount of 2-methyl-2-pentenal desorbed from the aged resin increases, although not linearly, as a function of aging time in the humid environment. Even after 7451 h, the amount released from samples in the dry environment is less than that from samples aged for 77 h at 100% RH. This result suggests that 2-methyl-2-pentenal is produced as the result of the combined effects of both moisture and temperature. It is not certain at this time what mechanism produces this compound from the cured epoxy matrix, although it is important to note that the two compounds which appear to be related to aging are 3 and 6 carbon aldehydes. These compounds may be thermally produced and/or formed from the reaction of water with partially reacted glycidyl groups or with intracyclized glycidyl groups of the TGDDM.

4.2 Mechanical Properties of the Aged Epoxy Resin

The use of polymeric and composite materials in structural applications is limited by the mechanical properties of the material. In fact, the ultimate failure of a polymeric material, particularly those used in structural applications, is mechanical fracture. The overall mechanical properties of these materials are strongly affected by the viscoelastic properties of the resin. The viscous response is time dependent while the elastic response is independent of time. If a continuous oscillatory stress is applied to a viscoelastic material, the resultant strain in the material will be oscilla-

TABLE 4. CONCENTRATION OF 2-METHYL-2-PENTENAL DESORBED FROM MY720/EPORAL RESIN AGED AT 65°C.

Exposure time (h)	Concentration (ppm)	
	100% RH	0% RH
77	26	*
450	44	*
1511	66	*
7451	78	16

*less than 5 ppm

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tory with the same frequency but out of phase with the stress by an amount that depends on the relative elastic and viscous responses. The properties of interest are conveniently measured by DMA.

The dynamic storage modulus, G′, the dynamic loss modulus, G", and the tangent of their ratio, tan δ, were measured for a series of cured resins environmentally aged at 35°C and 65°C. Typical mechanical spectra for samples fresh from the mold, aged for 195 h at 35°C and 0% RH, aged for 195 h at 35°C and 100% RH, aged for 200 h at 65°C and 0% RH, and aged for 200 h at 65°C and 100% RH, are shown in Figures 10-14, respectively. The results are summarized in Table 4 where the T_g (glass transition temperature) for two components, α_1 and α_2, are shown as a function of exposure temperature, time, and humidity. Additional spectra were obtained on coupons aged for times greater than 4000 h at 35°C and 65°C while at 0% RH and 100% RH. Long term exposure data (i.e., greater than 1200 h) and short-term 150°C exposure data were obtained; however, they are not useful, even for comparative purposes, because inadvertent experimental changes were made during operation of the dynamic mechanical analyzer.

TABLE 5. MECHANICAL PROPERTIES OF ENVIRONMENTALLY AGED EPOXY RESINS.

Aging temperature (°C)	Exposure time (h)	Exposure humidity (% RH)	$T_{g_{\alpha_1}}$ (°C)	$T_{g_{\alpha_2}}$ (°C)	$[T_{g_{\alpha_2}} - T_{g_{\alpha_1}}]$ (°C)
Fresh from mold	—	—	241	272	31
35	195	100	—	261	—
35	195	0	234	261	27
35	1004	100	—	255	—
35	1004	0	226	259	33
35	2230	100	—	258	—
35	2230	0	225	260	35
65	200	100	—	257	—
65	200	0	230	259	29
65	1004	100	—	257	—
65	1004	0	226	259	33

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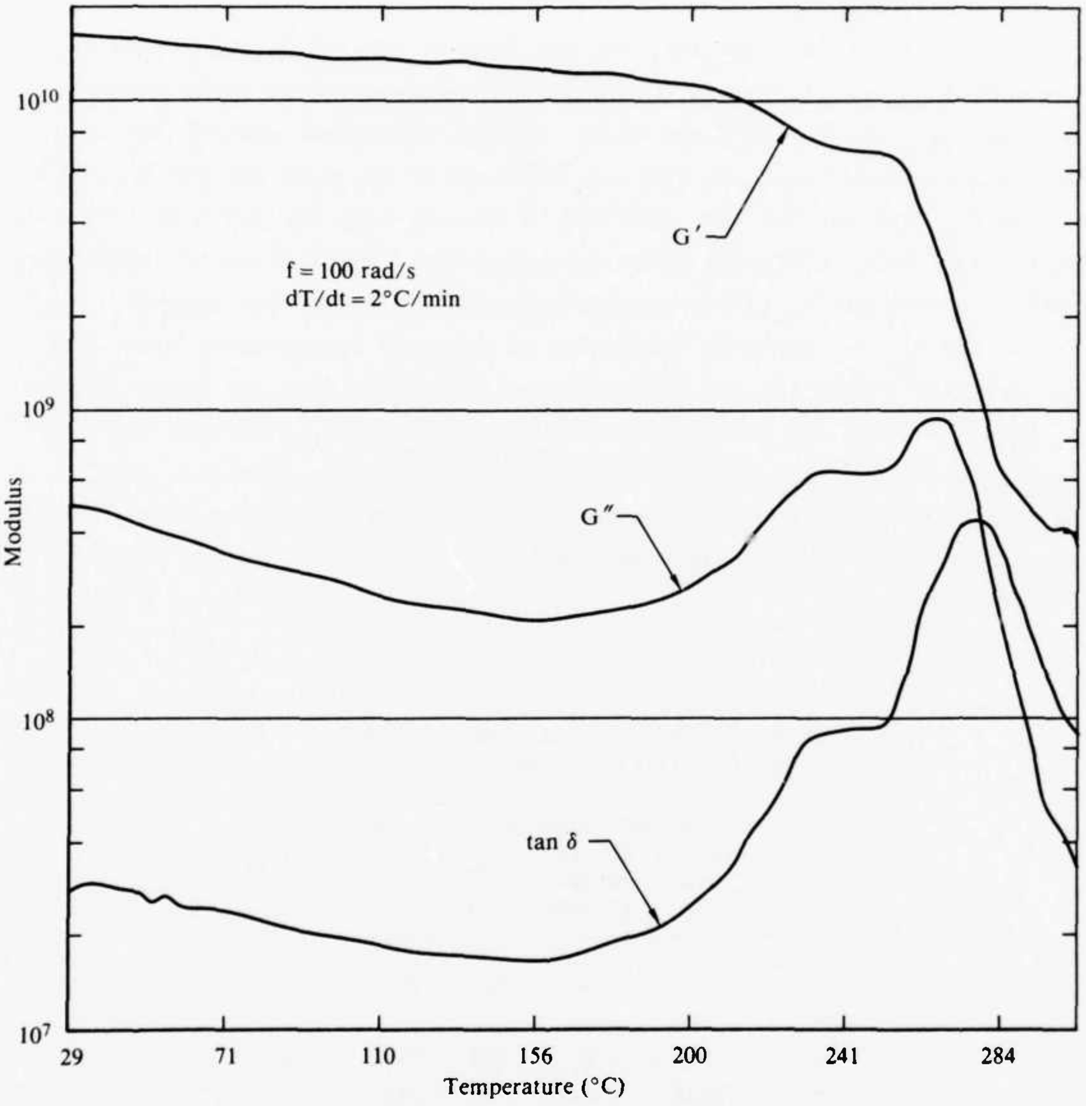

Figure 10. Dynamic mechanical response of the cured resin fresh from the mold as a function of temperature. G', G'', and tan δ are the storage modulus, the dynamic loss modulus, and their ratio, respectively.

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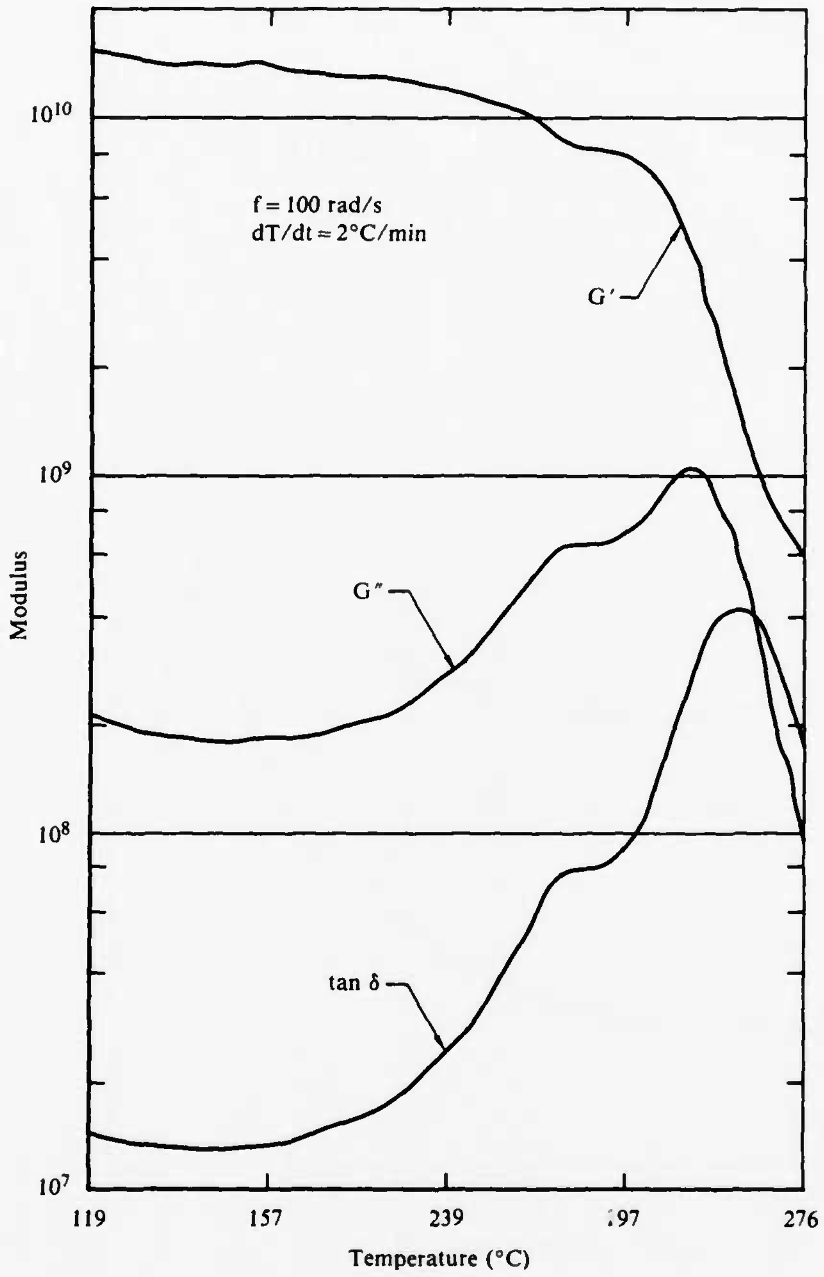

Figure 11. Dynamic mechanical response of the cured resin fresh from the mold as a function of temperature. G', G'', and tan δ are the storage modulus, the dynamic loss modulus, and their ratio, respectively, aged at 35°C in a dry atmosphere for 195 h.

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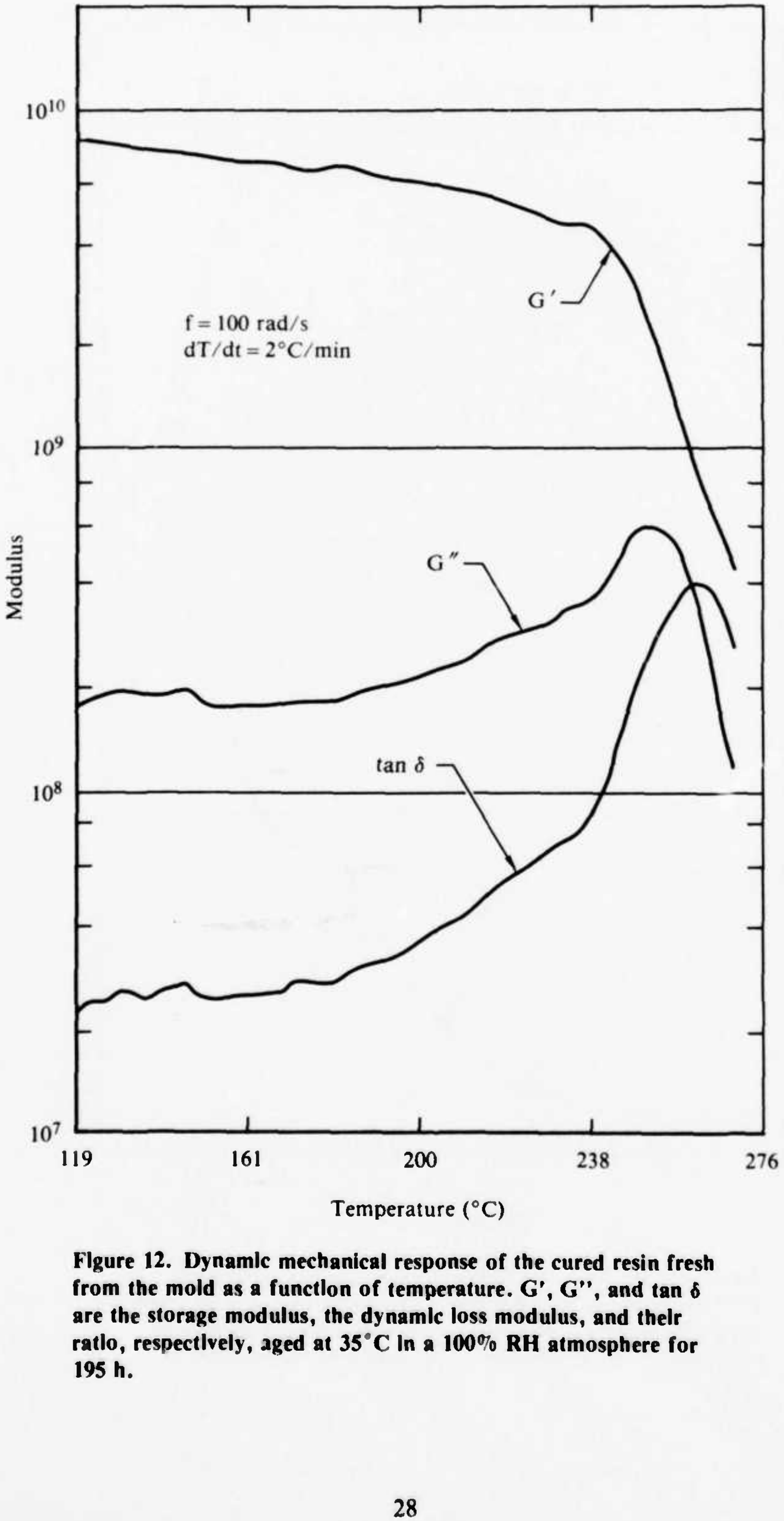

Figure 12. Dynamic mechanical response of the cured resin fresh from the mold as a function of temperature. G', G", and tan δ are the storage modulus, the dynamic loss modulus, and their ratio, respectively, aged at 35°C in a 100% RH atmosphere for 195 h.

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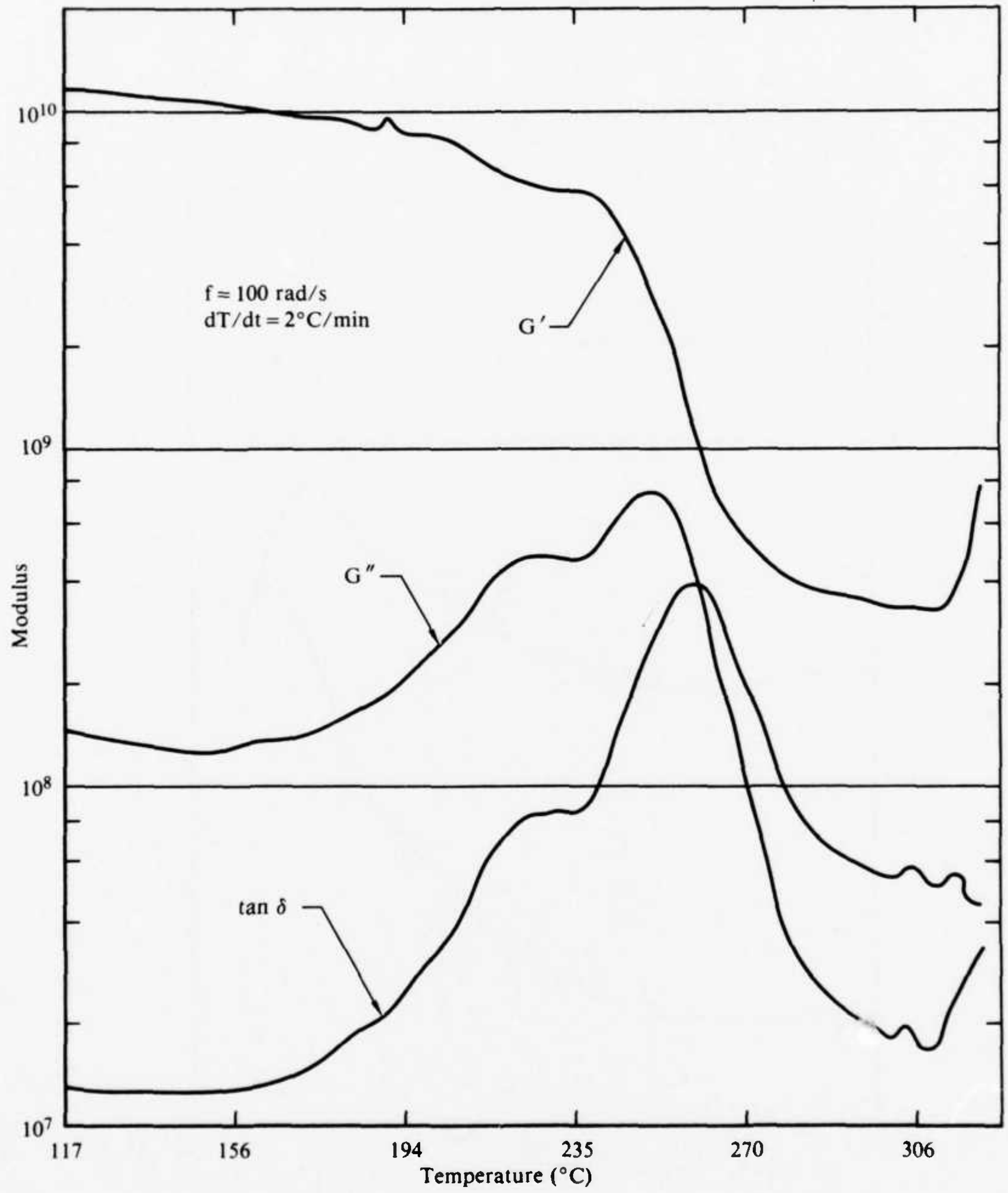

Figure 13. Dynamic mechanical response of the cured resin fresh from the mold as a function of temperature. G', G'', and tan δ are the storage modulus, the dynamic loss modulus, and their ratio, respectively, aged at 65°C in a dry atmosphere for 200 h.

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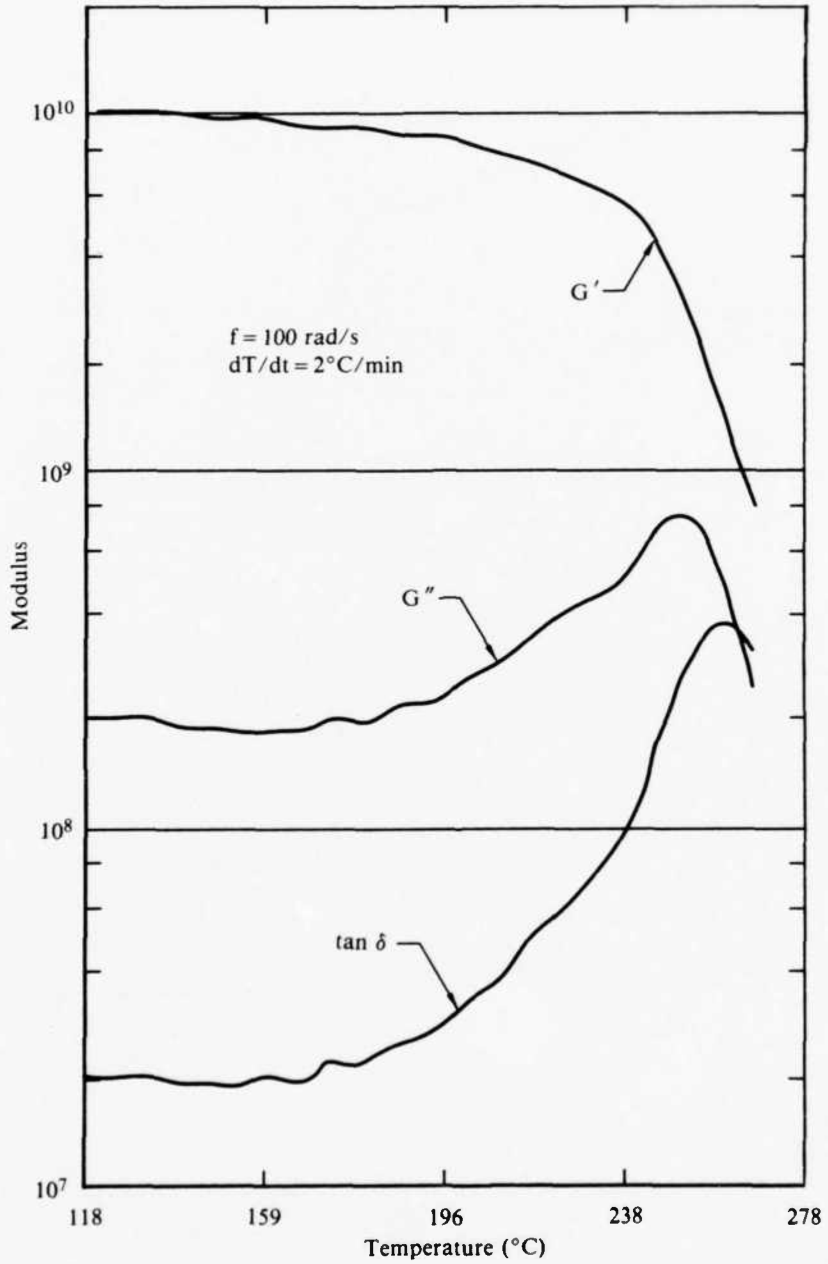

Figure 14. Dynamic mechanical response of the cured resin fresh from the mold as a function of temperature. G', G'', and tan δ are the storage modulus, the dynamic loss modulus, and their ratio, respectively, aged at 65°C in a 100% RH atmosphere for 200 h.

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Two major observations are noted: 1) T_g decreases during aging, and 2) the T_g is split into two peaks, $T_{g_{\alpha_1}}$ and $T_{g_{\alpha_2}}$, in the dry samples. Several authors have noted that T_g changes during aging; for example, water sorption has been reported to plasticize the resin leading to a lower T_g,[22] or an additional cure reaction may occur which normally leads to a higher T_g.[23] Neither of these hypotheses is consistent with our observations. The decrease in T_g is nearly the same in both wet and dry samples, and in no instance does T_g increase.

Danieley and Long[22] investigated the effects of curing on T_g and moisture sorption in the neat MY720/DDS resin system. They found an asymptotic increase in T_g toward a maximum value that was dependent both upon time and the cure temperature. They also found that the amount of moisture sorbed increased with the extent of cure. They concluded that the sorbed water interacts primarily with hydroxyl sites created during the curing reactions.

The most notable effect in this study, however, is that the T_g in dry resin is split into two peaks, approximately 30-35°C apart. This split occurs in the fresh resin as well as resin aged for several thousand hours. The reason for this split is not known, but Seferis et al.[23] have reported that additional curing in the resin after the processing is complete yields a similar effect. However, the analysis technique employed by Seferis et al. limited their studies to the dry resin. It is difficult to envision curing reactions occurring in the wet resin at 35°C which produce an 11°C decrease in T_g after aging only 195 h when the original resin was post-cured for 5 h at 177°C.

4.3 Chemiluminescence

Chemiluminescence is an extremely powerful technique for measuring the oxidation rates of very slow reactions. Several investigations reported on the use of this method to study the oxidation of hydrocarbons[10,11] and addition polymers. In addition, recently CL has been used to characterize the aging processes in nylon[24] and epoxy resin systems.[25,26] Previous work has shown that an oxidation reaction is responsible for the luminescence observed in these systems.[25,26] In a manner analogous to that observed in hydrocarbons, the rate of production of the chemiluminescence is proportional to the square of the peroxy radical concentration. The rate constant for the combination of peroxy radicals in the MY720/DDS resin system has been measured and is independent of the history of the resin[27]; this observation suggests that CL can serve as a useful monitor of the aging process in these resins.

We previously reported[12] that the reciprocal of the CL is a linear function of the aging period, τ, i.e.,

$$CL^{-1} = CL_o^{-1} + \gamma\tau ,$$

where CL_o^{-1} is the reciprocal of the CL from a freshly cured resin, i.e., at $t = 0$, and γ is the rate of change of CL during aging. γ is a function of aging temperature, humidity, and external mechanical stress. The ITt profile (intensity-temperature-time, see Section 3.6) of a fresh resin is shown in Figure 15. The data reported previously[12,27] used the height of the CL peak that occurred when the temperature was changed from 60 to 80° as a measure of intensity, although any of the ITt peaks could have been used to relate CL with aging period. However, to increase reliability and reduce statistical errors, the CL data reported here are the sum of three peaks, less the value of plateau just prior to the temperature change, i.e.,

$$\begin{aligned} CL_{\Sigma} = {} & CL_{\text{Peak}(60^{o})} - CL_{\text{Plateau }(50^{o})} + CL_{\text{Peak }(80^{o})} - CL_{\text{Plateau }(60^{o})} \\ & + CL_{\text{Peak }(100^{o})} - CL_{\text{Plateau }(80^{o})} \end{aligned}$$

The resin coupons were aged at three environmental conditions: in a dry atmosphere (0% RH), at 100% RH, and immersed in water. Previous studies have shown that the solubility of water in the resin depends upon the phase of the water in the environmental chamber, i.e., liquid or 100% RH.[28] The diffusion of water into the resin is not a function of phase, but the equilibrium concentration of water in the resin is 15-20% higher for coupons immersed in water compared to those exposed to 100% RH at the same temperature.

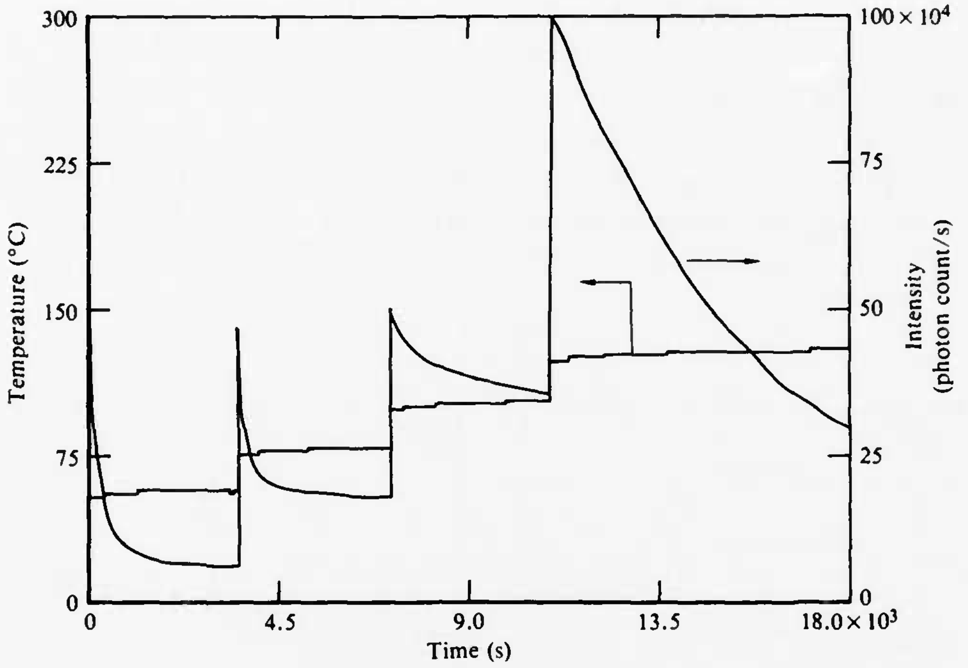

Figure 15. Chemiluminescence intensity-temperature-time profile of the resin fresh from the mold.

The ITt profiles of samples aged at 35°C in a dry atmosphere, in a 100% RH atmosphere, and immersed in water for times up to 2050 h are shown in Figures 16-18, respectively. Similar profiles for samples aged at 65°C in a dry atmosphere, 100% RH atmosphere, and immersed in water for times up to 1200 h are shown in Figures 19-21, respectively.

The linear relation between the reciprocal of the chemiluminescence, CL_Σ, and the aging period, τ, is illustrated in Figures 22 and 23. Experimental data are shown by the circles and the line represents the least-squares fit to the experimental data. The data are summarized in Table 6 where the intercept (CL_0^{-1}) and slope (γ) for aging the resin at the 35°C and 65°C in a dry atmosphere, 100% RH atmosphere, or immersed in water are shown.

As expected, the intercept (CL_0^{-1}) is essentially independent of the aging conditions and represents the value of a fresh sample; the slope (γ) is a strong function of the aging conditions and the parameter of interest when CL is used to monitor aging.

The CL is a strong function of both aging temperature and water in the sample. However, our previous studies have shown that the equilibrium concentration of water is higher in the samples immersed in water than in those maintained in a 100% RH atmosphere; these observations are not entirely consistent with the data reported in Table 6. Additional data are required before definitive conclusions regarding these two apparently contradictory observations can be reached.

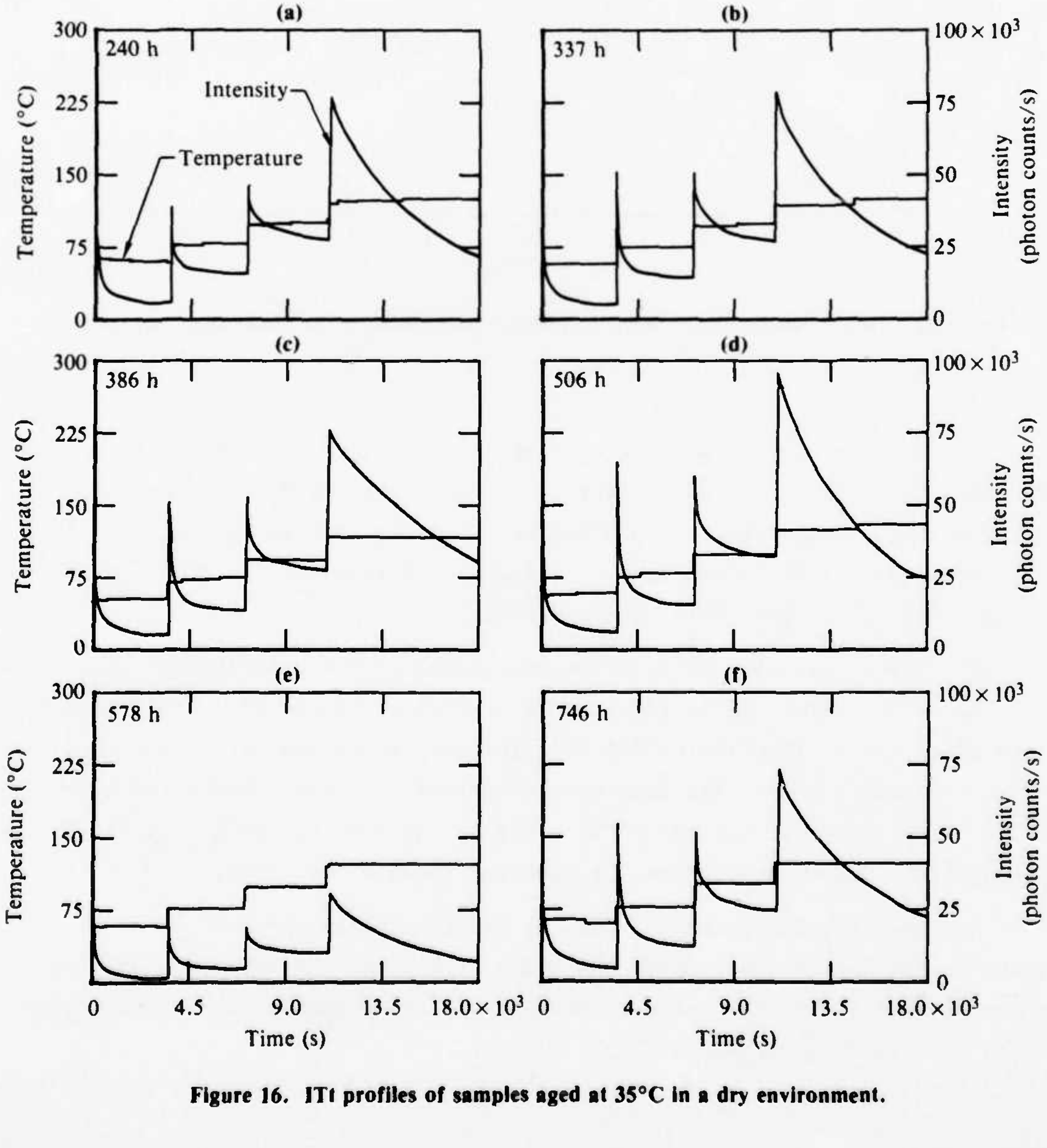

Figure 16. ITt profiles of samples aged at 35°C in a dry environment.

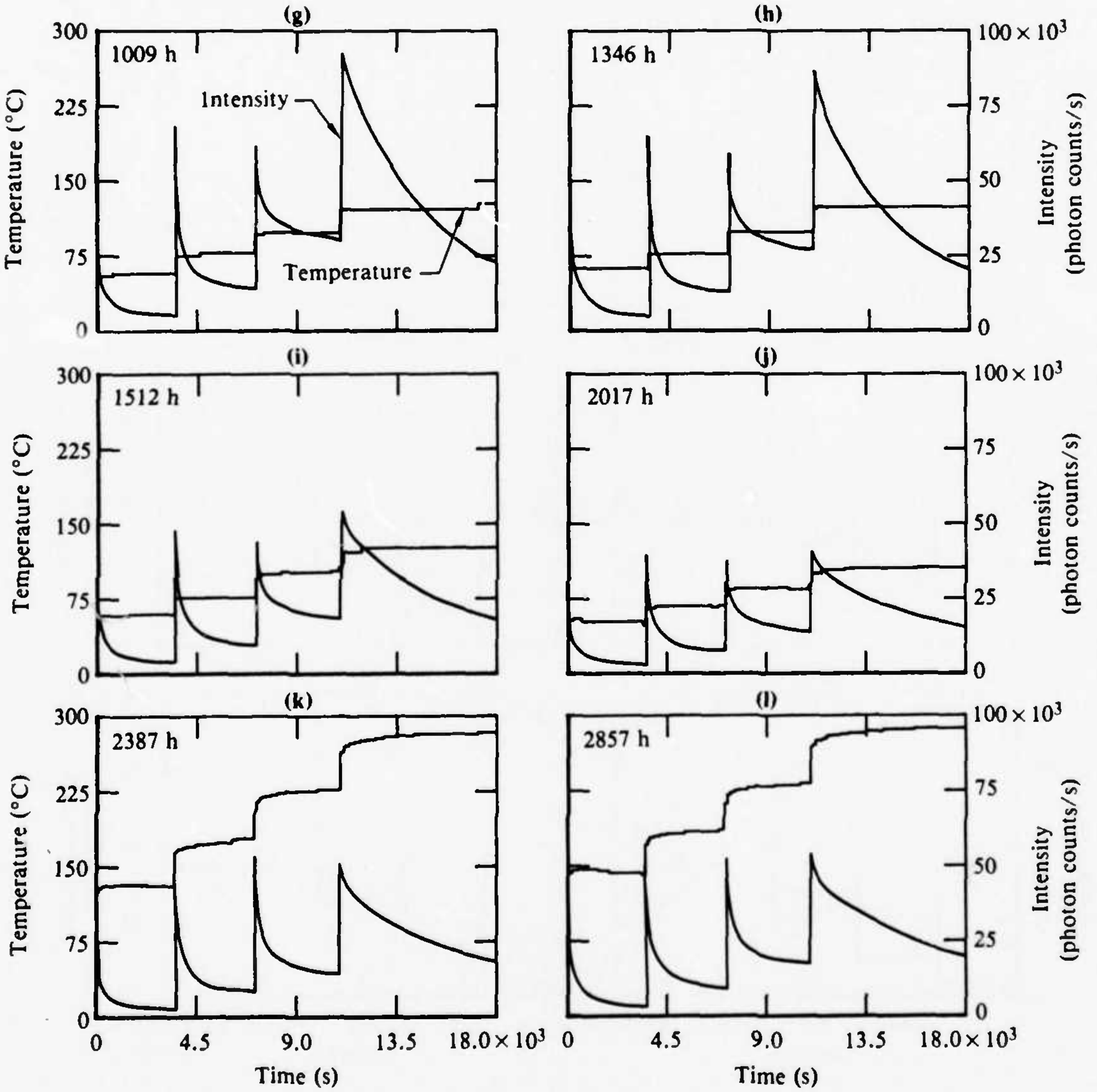

Figure 16. (Concluded).

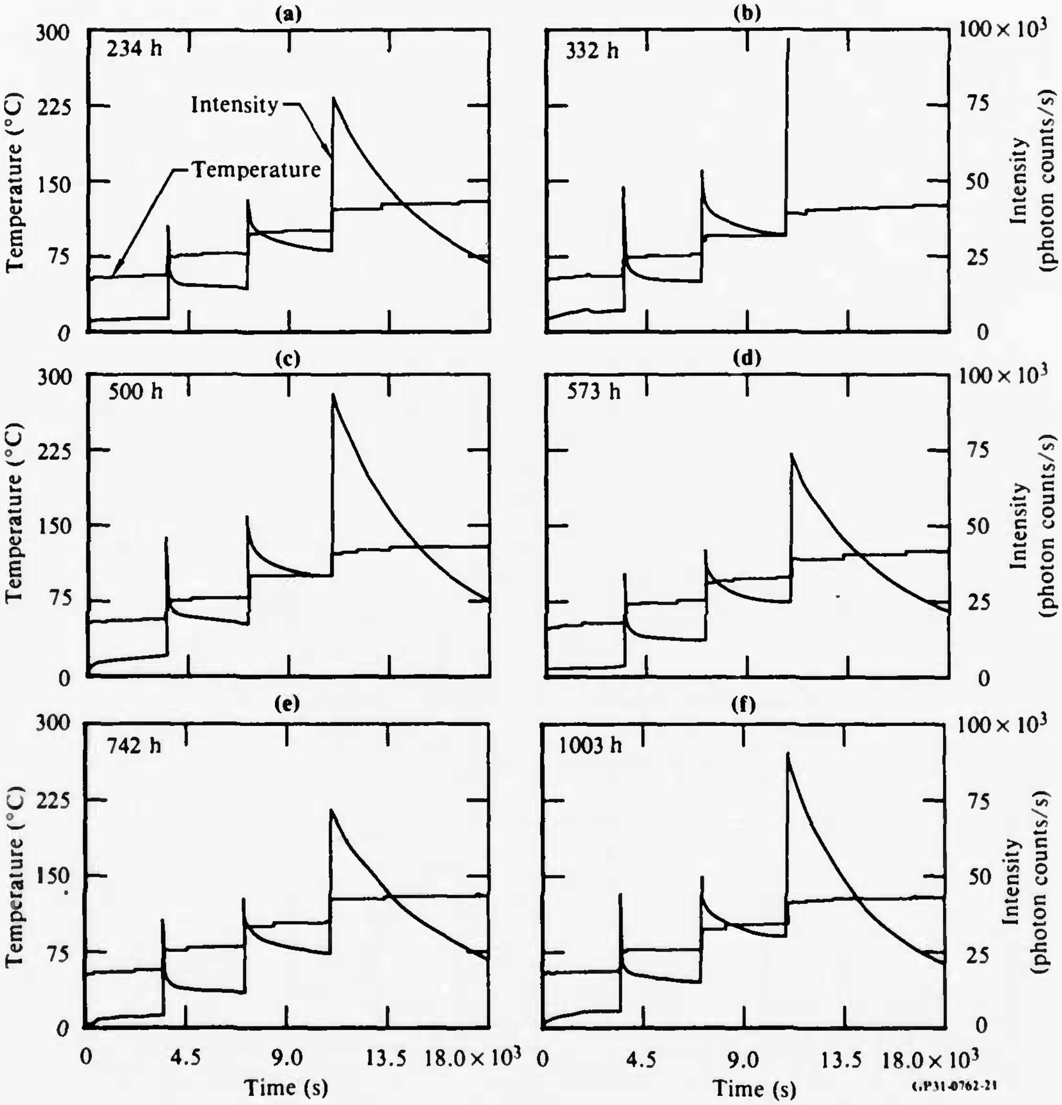

Figure 17. ITt profiles of samples aged at 35°C in 100% RH environment.

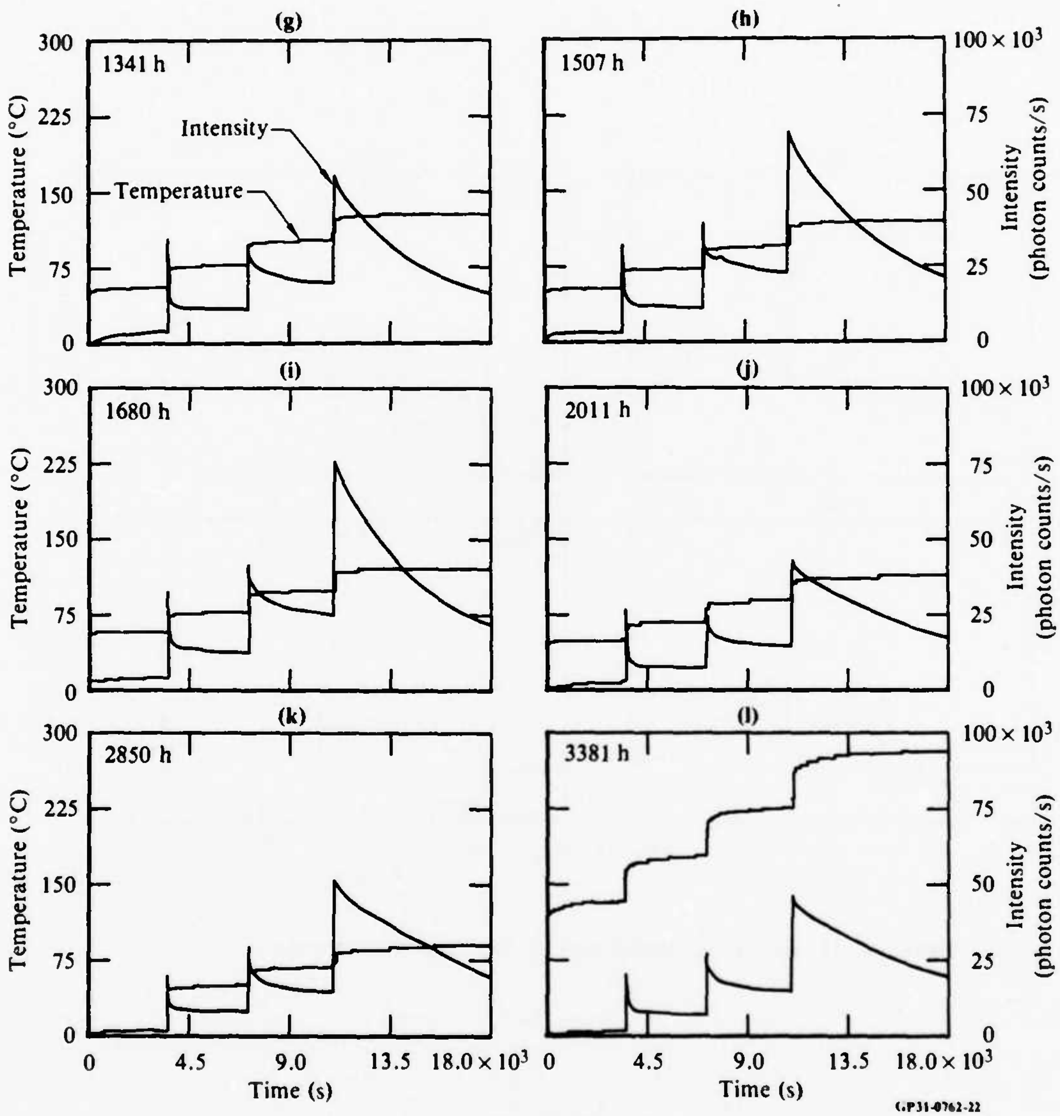

Figure 17. (Concluded).

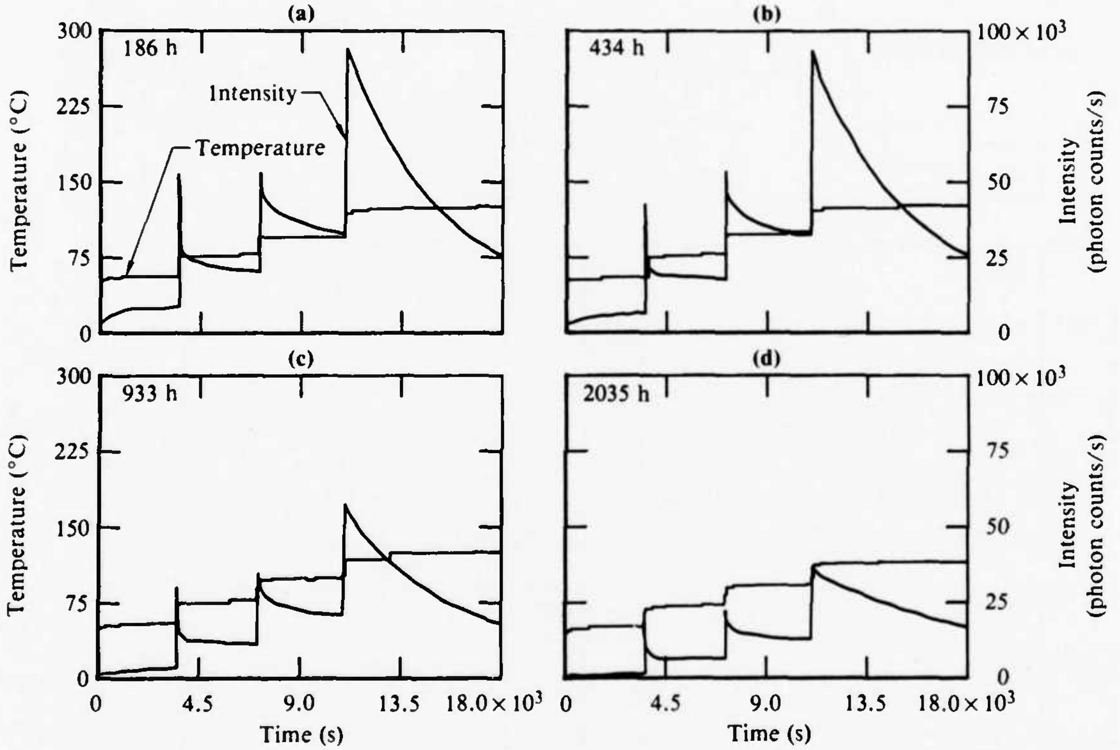

Figure 18. ITt profiles of samples aged at 35°C immersed in water.

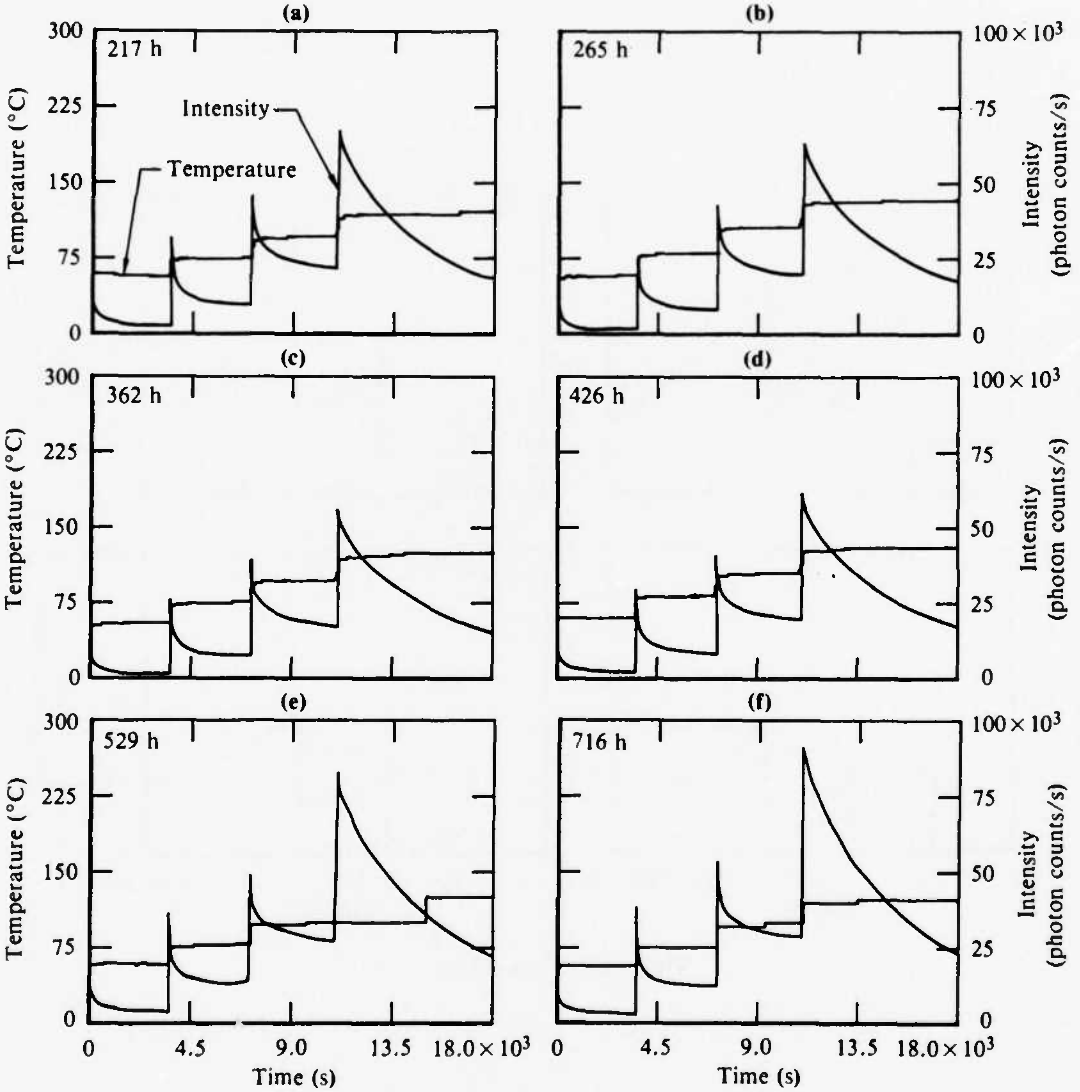

Figure 19. ITt profiles of samples aged at 65°C in a dry environment.

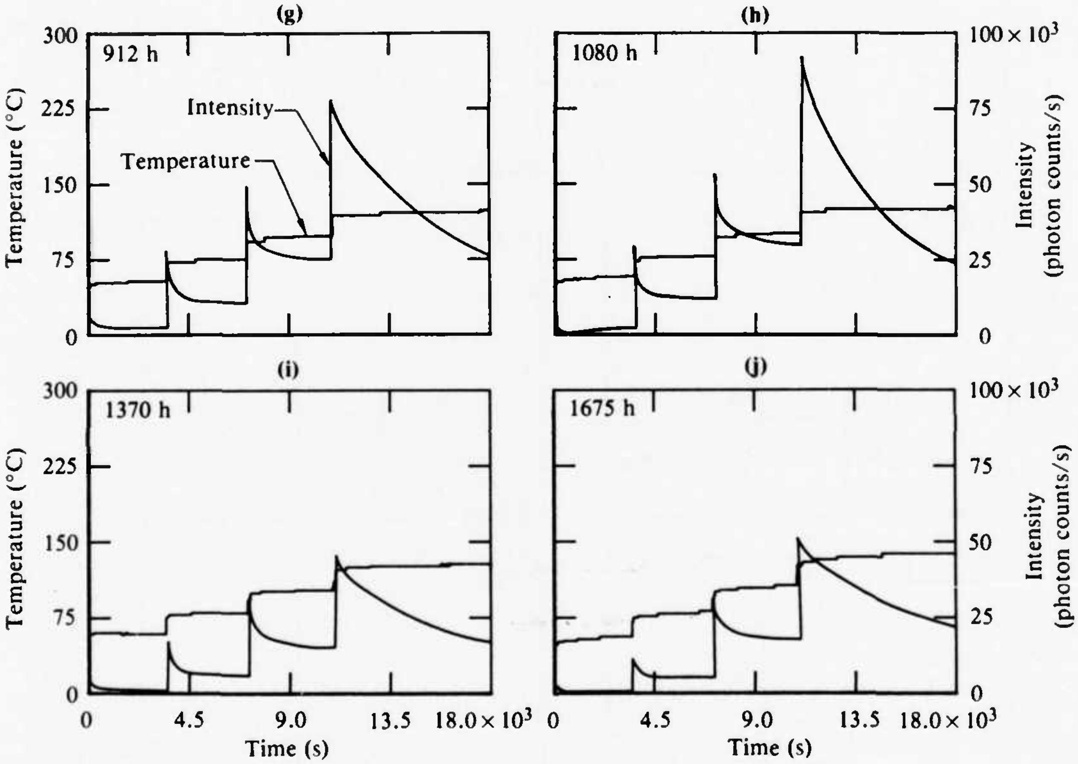

Figure 19. (Concluded).

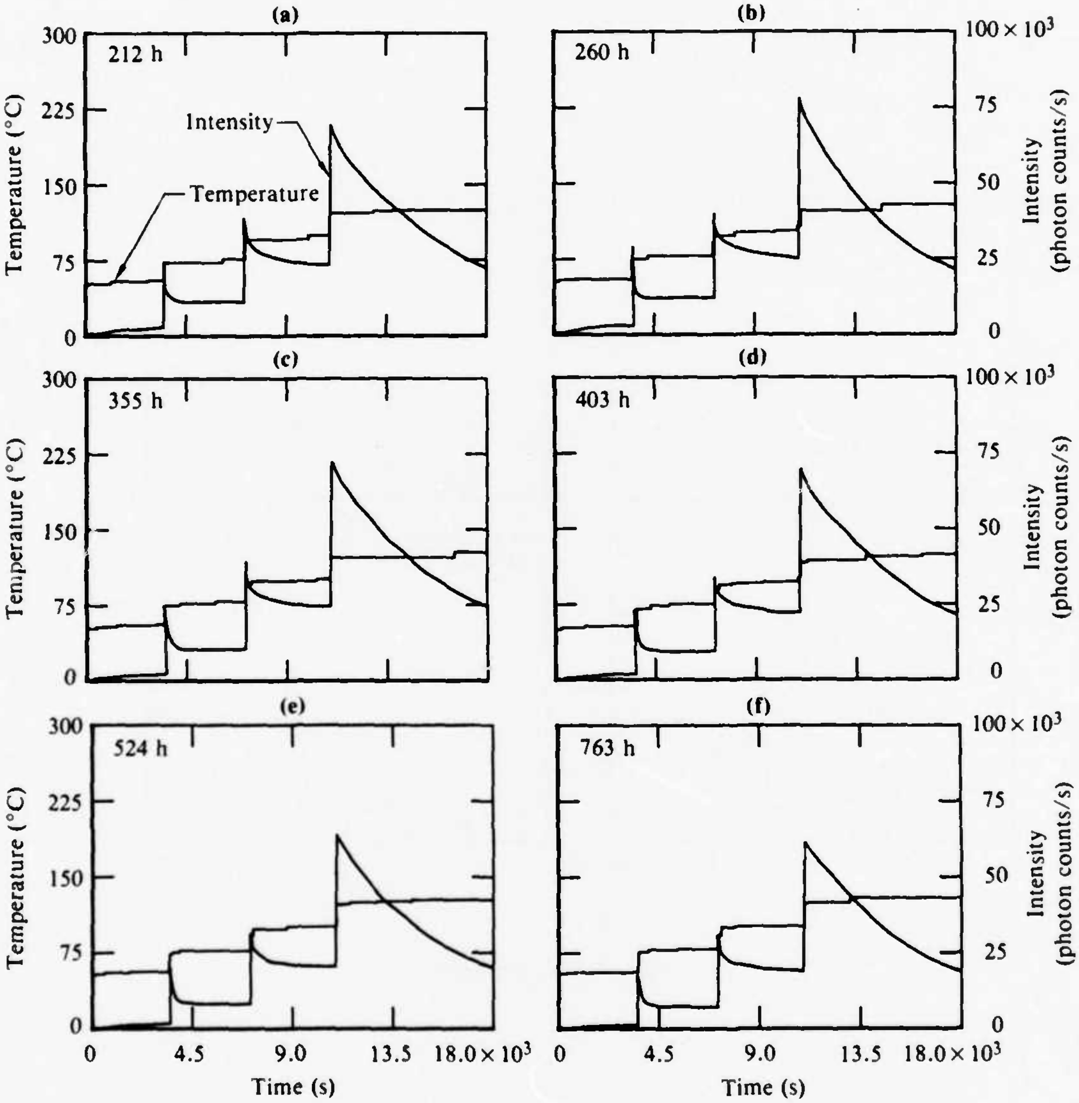

Figure 20. ITt profiles of samples aged at 65°C in 100% RH environment.

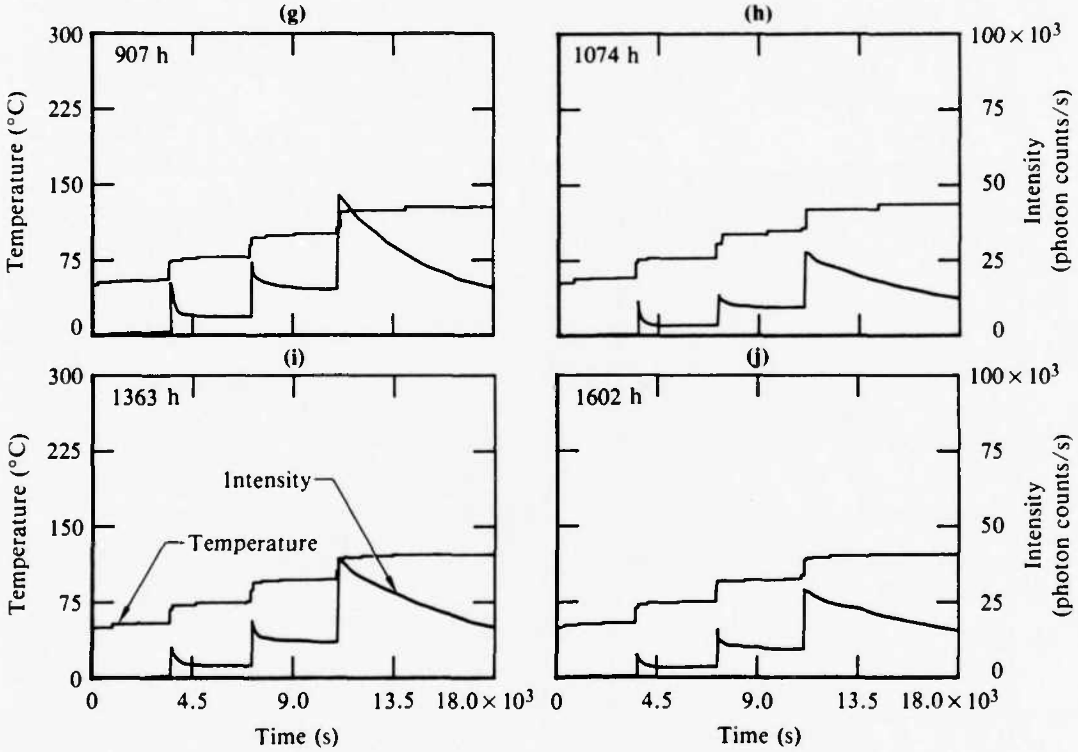

Figure 20. (Concluded).

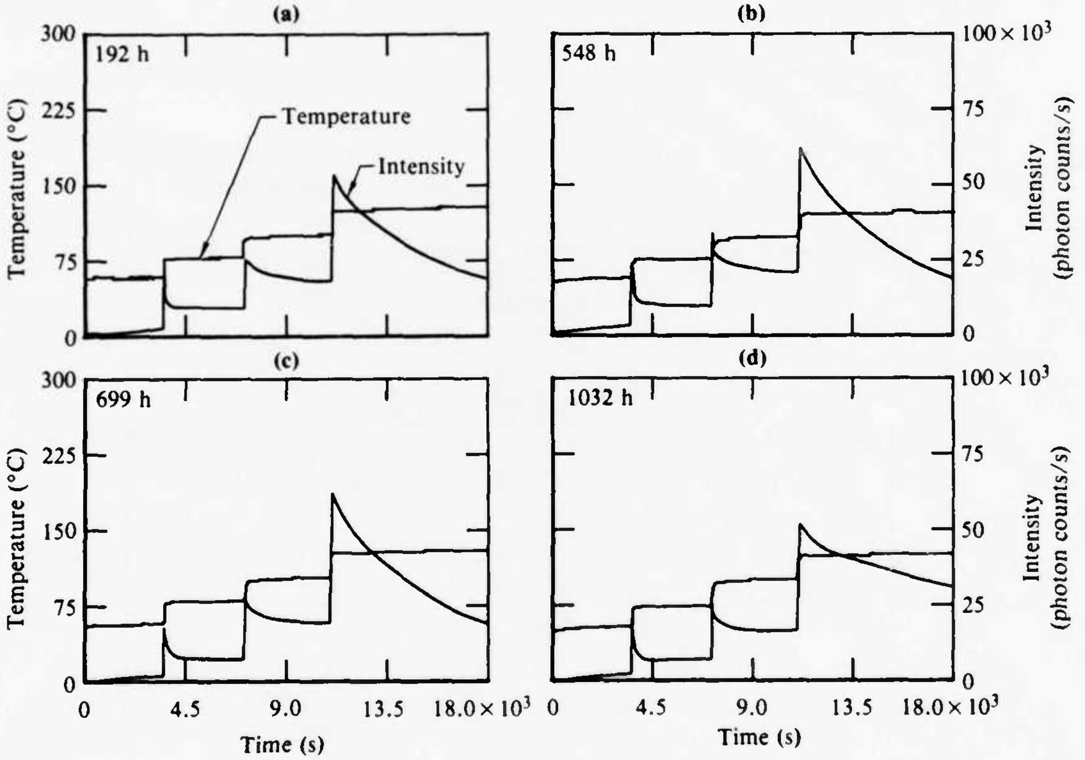

Figure 21. ITt profiles of samples aged at 65°C immersed in water.

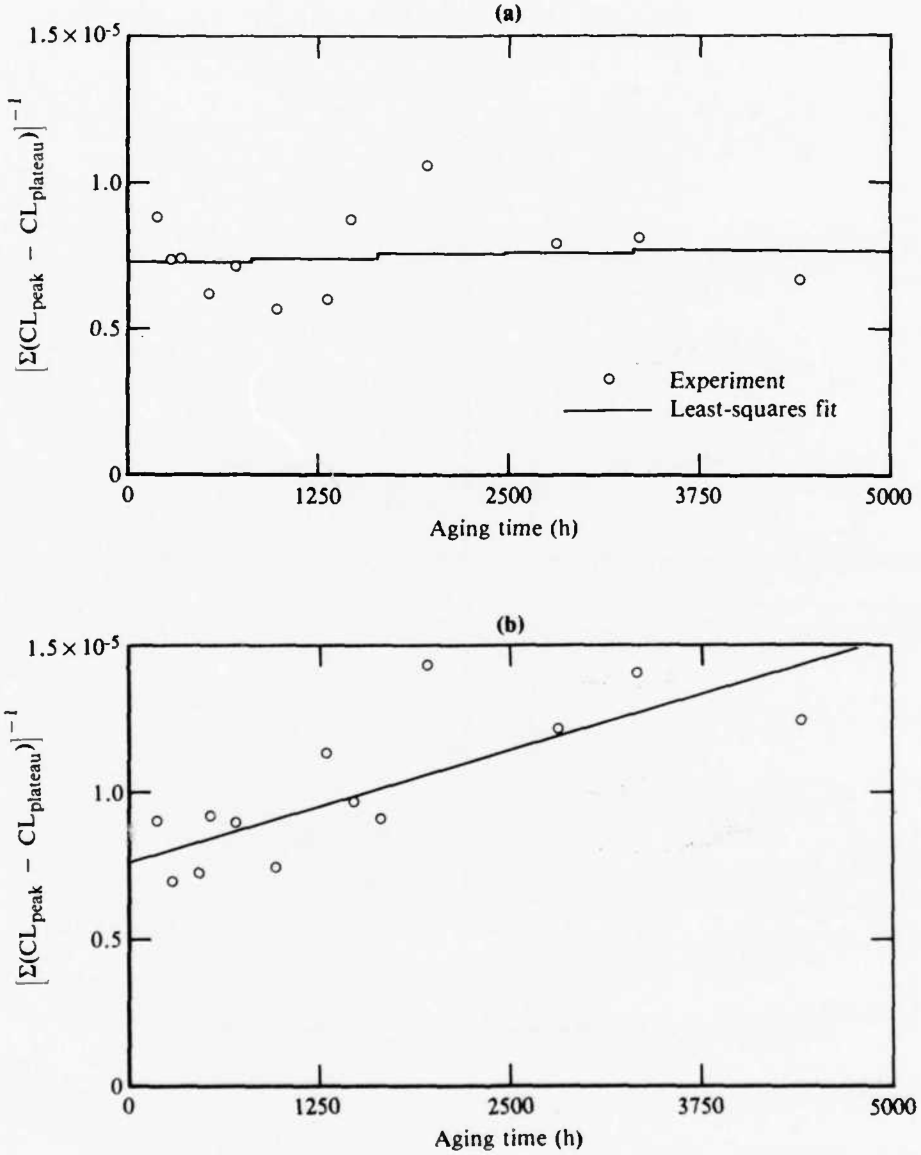

Figure 22. Reciprocal of the sum of the CL peaks as a function of aging time at 35°C (a) in a dry environment, (b) in 100% RH, and (c) immersed in water.

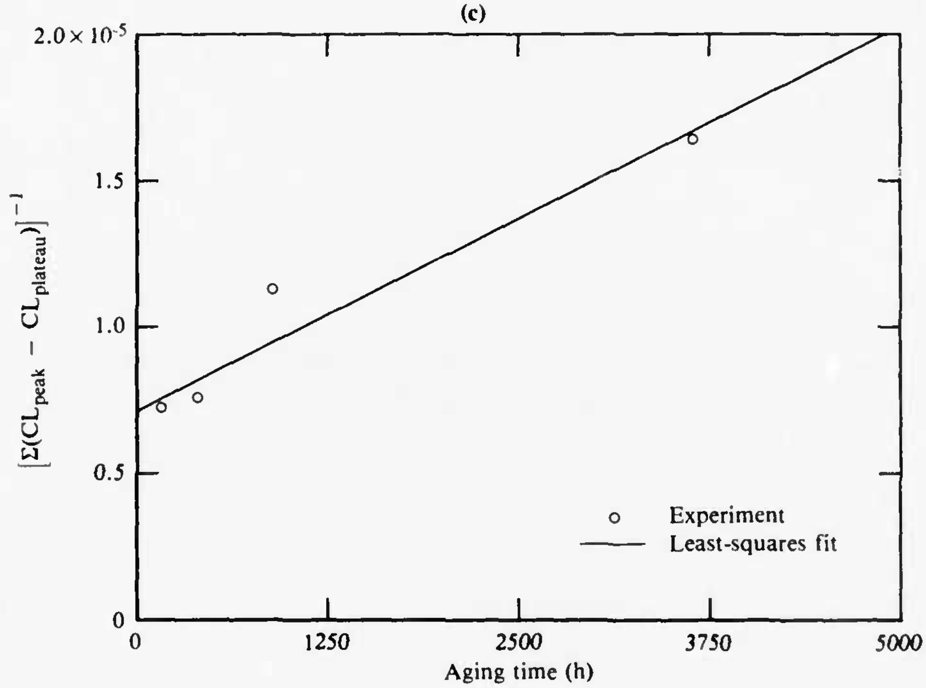

Figure 22. (Concluded).

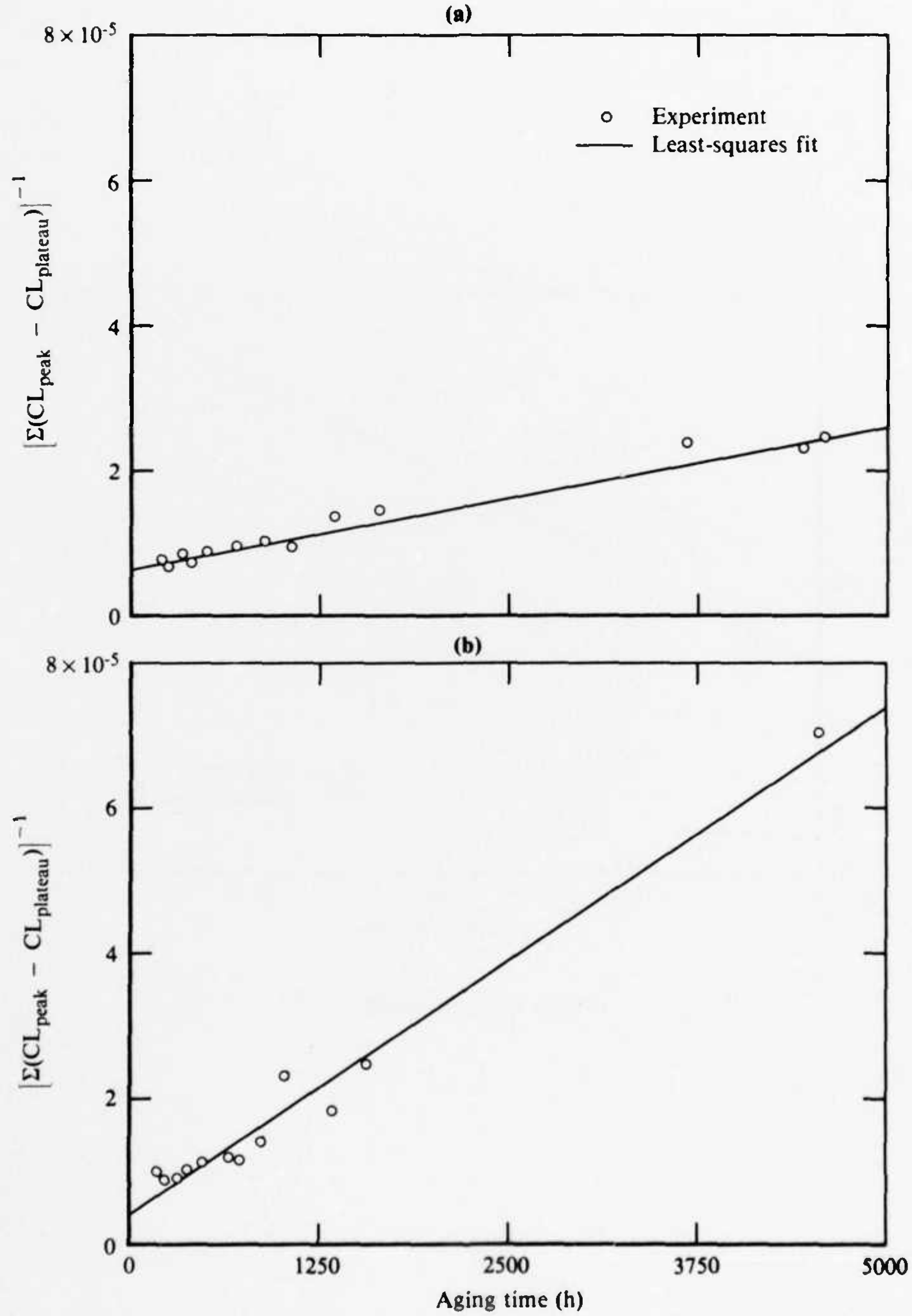

Figure 23 Reciprocal of the sum of the CL peaks as a function of aging time at 65°C (a) in a dry environment, (b) in 100% RH, and (c) immersed in water.

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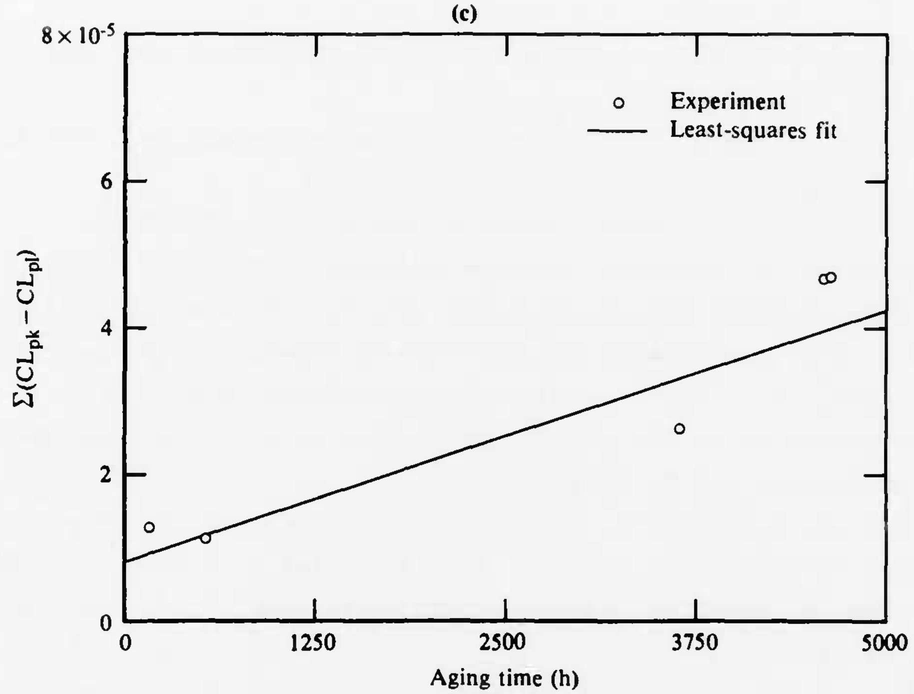

Figure 23. (Concluded).

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TABLE 6. SUMMARY OF PARAMETERS RELATING AGING TIME TO RECIPROCAL CHEMILUMINESCENCE INTENSITY ($1/CL_{\Sigma}$) AS A FUNCTION OF TEMPERATURE AND WATER.

Temperature (°C)	Water	Intercept $(CPS)^{-1}$	Slope
35	Dry	7.35×10^{-6}	0.11
35	100% RH	7.67	1.52
35	Immersed	7.14	2.59
65	Dry	6.90	3.93
65	100% RH	4.47	13.8
65	Immersed	8.17	6.95

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APPENDIX A: CHEMILUMINESCENCE FACILITY

The sample housing of the chemiluminescence system, shown in Figure A-1 is the third-generation luminescence-detection system designed and fabricated at MDRL. Samples are exposed to simulated service environments consisting of combinations of atmosphere, temperature, and tensile stress while the chemiluminescence emission from the sample is measured by highly sensitive photon counting instrumentation. Generally, the chamber is purged with oxygen during a chemiluminescence experiment to enhance the CL intensity; however, nitrogen can be used as a background. The chamber materials have been selected so that corrosive atmospheres can be used without damaging the chamber. The sample stage incorporates a small heater and two thermocouples, one to supply a feedback signal for the temperature controller and the second to monitor the temperature of the upper surface of the sample up to 200°C. A gearmotor and belt drive system can be used to apply tensile stress to samples inserted between the movable grip and a fixed grip attached to a load transducer. Tensile loads up to 500 N can be applied to samples and recorded by the load transducer. The cooled photomultiplier tube (PMT), located directly above the sample, is separated by a silica dewar containing a plano-convex condensing lens which increases the effective sensitivity of the PMT.

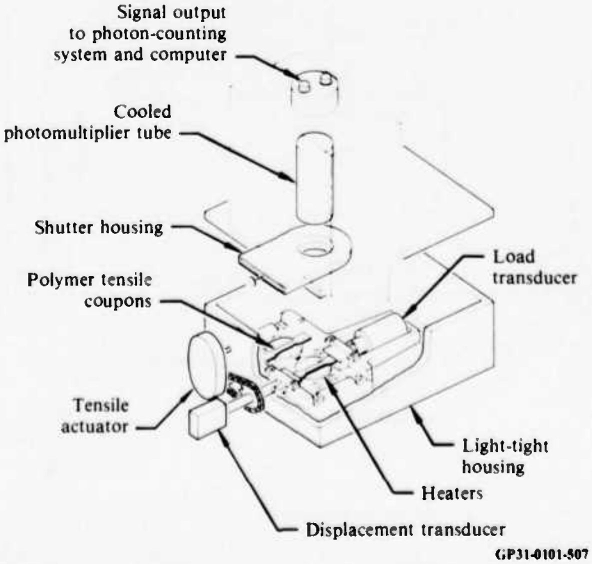

Figure A-1. Exploded view of the chemiluminescence system.

The relation between the CL sample chamber and the remainder of the computer-controlled system are shown in Figure A-2. Photons are detected by a photon counting system and are processed by an amplifier/discriminator (Princeton Applied Research models 1121 and 1112). Digital data consisting of photon counts per second and a time signal are input to the microcomputer (Digital Equipment Corporation MINC 11/23) which processes and stores the data. Other CL variables, analog stress and strain signals and a digitized temperature signal, are monitored continuously by the computer and updated at preselected intervals. Sample temperature is controlled by the microcomputer according to a preselected temperature/time program. The five channels of data, photon counts/second, time, temperature, stress, and strain, are stored in the computer's random access memory until completion of the experiment when a new data file is created on flexible disk for later processing and graphic presentation. The computer is programmed to operate unattended; thus experiments can be performed overnight, greatly increasing the data output of the CL system.

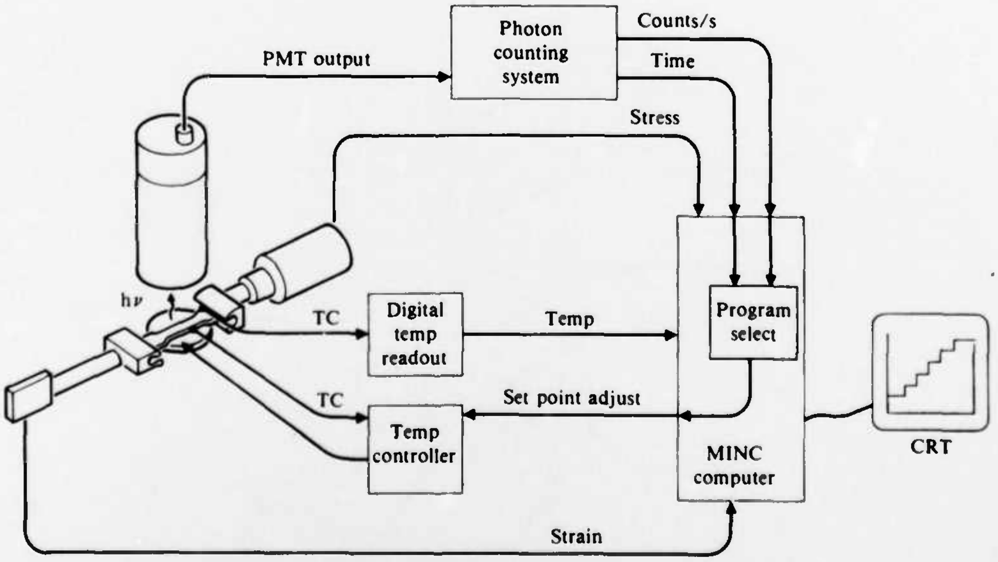

Figure A-2. Block diagram of the CL system with microcomputer data handling and control system.

The computer records the photon count every 50 s while controlling the experiment. Samples were initially heated to 50°C for 1 h. The initial peak occurring at this temperature was dependent upon the length of time the sample was exposed to room light and therefore was ignored. After 1 h, the temperature was increased to 65°C for another hour. This process was repeated at 75° and 90°C. The photon-count per second data recorded throughout the temperature program are called the ITt profile. The ITt profile of a typical epoxy sample (for example see Figure 15) shows a series of sharp increases in the photon-counts/second at each temperature increment, followed by a gradual decrease in intensity until the sample reached a higher temperature. The CL peak and decay curve differ at each succeeding temperature step. At temperatures below 100°C, the temperature increment produces a sharp spike in the CL intensity followed by a rapid decay to a plateau. At higher temperatures, the initial CL peak is less sharp and the decay curve slowly approaches a plateau. Analysis of the shape of the curves suggests that at least two mechanisms are responsible for the CL intensity: a rapid, intense reaction in response to sudden changes in temperature, and a steady-state level at each temperature. The processes responsible for these two types of CL decay curves are under investigation.

APPENDIX B: DYNAMIC MECHANICAL ANALYZER

The Rheometrics Dynamic Spectrometer, Model RDS-7700, characterizes the viscoelastic properties of polymers using dynamic oscillatory tests. The data described in this report were obtained in the sinusoidal strain mode, in which the sample is suspended between a dc torque motor and a fixed transducer. The torque motor, driven in a sinusoidal torsional mode by an analog servomechanism, applies shear stress to the sample. Sample strain is measured by a position transducer coupled directly to the motor shaft. Both torque and normal forces are determined by the transducer which connects one end of the sample to the frame of the instrument. The sample is housed in an oven with a controlled range of -150° to 400°C. During a typical experiment, the temperature is programmed from 120° to 250°C. Both lateral and torque signals are amplified and input to the central processor where they are used to compute the rheological properties using programs appropriate to the test mode and sample geometry. The processor separates the viscous and elastic components of the deformation force to calculate dynamic viscosity, dynamic modulus and loss angle. A data terminal is used to input operator-controlled parameters and print a tabular data output. User-selected data are graphed on the X-Y plotter as a function of temperature (for example, see Figures 10-14).

APPENDIX C: VAPORIZATION GAS CHROMATOGRAPHY MASS SPECTROMETRY

The characterization of indigenous volatile compounds is performed with the gas chromatographic inlet shown schematically in Figure C-1. The sample (typically 30-100 mg) is placed in a clean quartz tube (6 mm o.d. nominal), one end of which is attached to a source of helium (10 to 30 cm^3/min). A quartz wool plug is used to prevent the sample from being blown out the end of the tube. The tube is connected to the isolation valve by a Swagelok connection using Teflon ferrules.

For 2 min after the quartz sample tube is connected, the sample is purged at room temperature by opening both the sample gas valve and the vent valve. During this time, the isolation valve is closed and the column trap U-tube is immersed in liquid nitrogen.

The indigenous volatile compounds in the sample vaporize when the quartz tube is inserted into the controlled heated zone; this procedure requires opening the isolation valve, closing the vent valve, loosening the Swagelok nut at the isolation valve, and pushing the sampling tube through the open isolation valve. The Swaglok nut at the isolation valve is tightened when the sampling tube is butted against the exit tube of the controlled-heat zone.

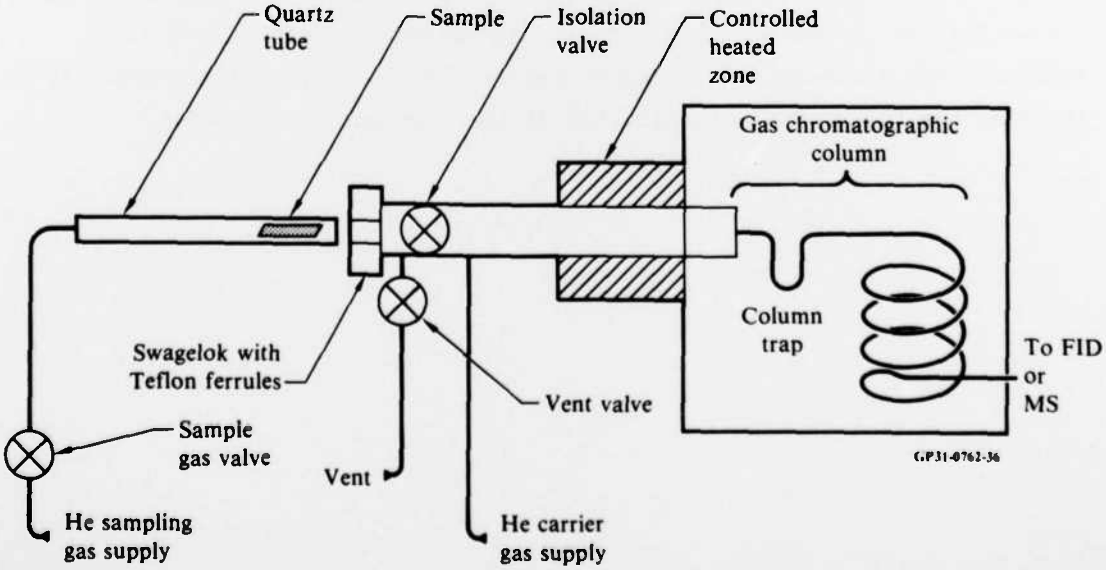

Figure C-1 .Block diagram of vaporization GC sampling system.

Volatile compounds desorbed from the sample are then carried by the helium stream into the U-tube. The quartz sample tube is left in the hot zone for the desired time, typically 10-20 min. While the sample is heated, the carrier gas flows around the outside of the sampling tube and into the column trap. This precaution is necessary to ensure that desorbed volatile compounds are not back-flushed into the space between the outer wall of the quartz sampling tube and the inner wall of the hot zone.

After the sample has been heated for the desired time, the Swagelok nut at the isolation valve is loosened, and the sample tube is removed from the hot zone. The isolation valve is then shut, and the vent valve is opened. This status is maintained for 2 min after heating to permit the flows in the system to equilibrate. The sampling gas supply is then shut off, and the vent is closed. Thus the quartz sample tube can be removed from the inlet, and a new sample can be loaded during the chromatographic analysis of the desorbed volatile compounds. If, on the other hand, it is desirable to heat the same sample again, the sampling tube is left in place while the sample remains under an atmosphere of helium.

During the entire desorption period, the U-trap is cooled to -196°C. After 2 min equilibrium following removal of the sample tube from the hot zone, the liquid nitrogen bath is removed from the trap, and the temperature program of the chromatographic analysis is initiated. Typical operating conditions for the chromatographic analysis are shown in Tables 2 and 3. A complete blank analysis with an empty sample tube is performed periodically to determine the background concentration of the compounds of interest.

APPENDIX D: PRECISION ABRASION MASS SPECTROMETRY (PAMS) AND DIFFUSION COEFFICIENTS

Precision abrasion mass spectrometry (PAMS) is used to measure the distribution profiles of volatile compounds in the epoxy resin.[3] The data can be used to determine solubility and diffusion coefficients. The procedure for obtaining PAMS data and analyzing it for transport parameters is summarized below.

- Experimental procedures: After controlled environmental exposure, the samples are mounted on a special stage and inserted directly into the ion source housing of a time-of-flight mass spectrometer (TOFMS). Four holes are milled in a typical sample: one full hole and three partial holes. During machining, the ion currents at the mass-to-charge ratios of interest (m/e for 56 propenal and m/e for 17 water) are monitored to record the evolution of compounds from the sample. These data and the total ion sum current are acquired simultaneously by the data system.

- Data Processing: After abrasion, the data are processed as follows: the ion currents are converted to weight percent, the data from the four holes are averaged, the curve is smoothed by digital methods, the concentration profile is corrected for finite desorption from the abraded sample (deconvolution), and the profile is averaged about the geometrical center of the sample.[28] The distribution profiles thus obtained were analyzed to obtain transport parameters of compounds of interest.

- Solubility and Diffusion Coefficient Analysis: The solubility coefficient is defined as:

  $$C_o = S_o p ,$$

  where C_o is the equilibrium concentration in the solution, S_o is the solubility coefficient, and p is the partial pressure of the vapor above the sample. Since both C_o and p are measured quantities, the solubility can be calculated directly.

Concentration profiles are analyzed by assuming that Fick's second law of diffusion describes the transport of dissolved gases through the resin:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad ,$$

where C is the concentration of diffusant in the sample at point x, t is the time of exposure to the diffusant, and D is the diffusion coefficient. Crank[29] has shown that this partial-differential equation has a series solution which converges rapidly when $Dt/\ell^2 < 1$:

$$C(x,t) = C_o \left\{ 1 - \frac{4}{\pi} \int_{m=0}^{\infty} \frac{(-1)^m}{2m + 1} \cos \left[\frac{(2m + 1)\pi x}{2\ell} \right] \exp \left[-D \left\{ \frac{(2m + 1)\pi}{2\ell} \right\}^2 t \right] \right\},$$

where ℓ is the sample thickness and C_o is the equilibrium concentration of the diffusant at the surface.

A numerical algorithm was developed in which the values of C_o and D are varied to minimize the sum of the squares of the differences between the measured and computed concentration profiles. The values of C_o and D that give the minimum are the equilibrium concentration and diffusion coefficient, respectively. This variational procedure is used to determine the concentration of the diffusant at the surface of the sample since the measured data are least reliable at the surface. The algorithm does not use the data in the first 0.05 to 0.15 mm of the sample but uses the data in the remaining part of the half-profile to calculate a value of the concentration at the surface.

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Figure C-1 .Block diagram of vaporization GC sampling system.

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