

# Environmental Degradation of an Epoxy Resin Matrix

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## Synopsis

With the increased use of graphite-reinforced composites as replacements for metals has come concerns about durability under harsh environmental conditions. Degradation is expected to begin on the surface and progress toward the center of the resin as a function of time, and reflectance infrared techniques are ideal for monitoring structural changes on surfaces. The present paper describes the application of Fourier transform infrared spectroscopy using internal reflectance elements to the determination of the degree of environmental aging of Hercules 3501-6 resin. The results indicate that degradation occurs via hydrolysis, oxidation, and dehydration reactions at specific locations in the polymer chain. Of special interest is the unique reaction of the tertiary amine of the epoxy portion of the molecule.

## INTRODUCTION

Fiber-reinforced epoxy composites are rapidly gaining usage as replacements for metals in a number of structural applications where high strength combined with light weight is of critical importance. Examples are the outer skins of commercial and defense aircraft, which may contain in excess of 20% of total weight in fiber-reinforced composites. In such advanced applications the composite is expected to be exposed to physical fatiguing as well as to extremes of environment such as driving rain, freezing-thawing cycles, and thermal changes in excess of 100°C. This exposure is likely to have a deleterious effect on the organic matrix through oxidation, dehydration, and hydrolysis reactions, and result in a reduction in strength of the composite components.

A number of previous investigations have been concerned with the uptake of water by a variety of epoxy systems and its subsequent effect on the physical properties of the composite.<sup>1-10</sup> Nuclear magnetic resonance (NMR) studies indicate that epoxy matrices contain both bound and mobile water molecules.<sup>2,3,9</sup> Physical studies indicate that water absorption decreases glass transition temperatures ( $T_g$ ) and strengths of epoxy matrices, although these changes are largely reversible.<sup>4-7</sup>

Other investigators have monitored the effects of exposure to temperatures below  $T_g$  on the physical and chemical properties of epoxy resins.<sup>2,11-14</sup> These studies indicate that a loss of strength occurs after long-term exposure at elevated temperatures. Furthermore, mass spectrometric analysis of heated Hercules 3501-6 resin indicated that propenal (and other aldehydes) are the major volatile products of thermal degradation, although those experiments

were performed in the absence of oxygen.<sup>12</sup> Therefore, exposure to heat and moisture can cause changes in epoxy resin structure.

Another possible contribution to degradation in epoxy resins is exposure to sunlight, since many organic polymers are subject to free-radical reactions in the presence of ultraviolet light and oxygen.<sup>13-16</sup> A large number of products of photooxidation have been proposed for use as epoxies, depending on the epoxy type and amine type in the polymer. Also, the combined effects of heat, water, and sunlight are expected to be greatest on the surface where abundant supplies of oxygen and water are present. Therefore, a good method for following degradation mechanisms would be one which detects chemical changes on the surface and monitors their rate of penetration into the bulk of the resin material.

Reflectance infrared spectroscopy is becoming an increasingly popular method for studying organic polymers on surfaces.<sup>17,18</sup> Theories of reflectance infrared spectroscopy using internal reflectance elements (IRE's) indicate two important principles, as evident from Harrick's equation and a later paper by Hirschfeld:<sup>19,20</sup>

$$D_p = \frac{\lambda_1}{2\pi(\sin^2\theta - \eta_{21}^2)^{1/2}} \quad (1)$$

where

$$\lambda_1 = \frac{\lambda}{\eta_1} \quad \text{and} \quad \eta_{21} = \frac{\eta_2}{\eta_1}$$

where

$\eta_2$  = refractive index of sample

$\eta_1$  = refractive index of internal reflectance element

$\lambda$  = infrared wavelength

$\theta$  = angle of incidence of infrared beam

$D_p$  = depth of penetration into sample surface

The first is that as the refractive index of the reflectance element approaches the refractive index of the sample, the depth of penetration ( $D_p$ ) will increase. Therefore, by varying the crystal material one can probe to various depths of the sample surface. The second principle is that the smaller the angle of incidence of the infrared beam on the sample surface, the smaller the depth of penetration in the sample. Thus, the 30° IRE which corresponds to a 60° angle of incidence on the sample will produce a greater penetration into the sample surface than a 60° IRE of the same material.

The above considerations indicate that a judicious choice of IREs with various angles of incidence and made of materials with different refractive indices can be utilized to map chemical structures at various depths into the surface of an epoxy resin block. This theory has been tested recently and verified on thin films.<sup>21,22</sup>

The present report utilizes reflectance Fourier transform infrared spectroscopy (FT-IR) to probe the effect of sunlight and high humidity on a commonly used epoxy resin system, Hercules 3501-6 resin, which has its major components Ciba Geigy MY720 resin (70%) and diaminodiphenylsulfone (DDS,

30%). The MY720 resin contains 70% tetraglycidylether of methylenedianiline (TGMDA).<sup>12,23</sup> It is shown that the environmental degradation involves some specific chemical reactions, and that reflectance infrared spectroscopy can be used to estimate the rate of penetration of oxidation into the bulk epoxy resin from the surface.

## EXPERIMENTAL

### Preparation of Resin Samples

Epoxy resin was extracted from Hercules AS3501-6 graphite-reinforced prepreg using HPLC-grade acetone. The acetone was removed by flash evaporation, and residual volatiles were removed under a  $10^{-2}$  mm vacuum at 50°C for one hour. The resin was then cured by the normal procedure for preparing graphite-reinforced laminates (8 hours at 177°C using a vacuum press. The cured resin block was then cut into 2 cm × 5.0 cm × 0.5 cm specimens for infrared analysis.

### Accelerated Environmental Degradation of Samples

Resin blocks were mounted on a holder and placed in a UVCON Weather-Ometer for accelerated aging tests. The normal cycle for aging was 4 hours at 60°C in saturated water vapor under ultraviolet light followed by 4 hours at 40°C with the light off. The total exposure time per run was 72 hours, using 40 W of light between 280–350 nm. Spectra were obtained at exposure times of 0, 72, 144, and 216 hours of exposure in the weatherometer. Finally, to compare accelerated degradation techniques to normal degradation, a sample was placed in a glass chamber for one year under ambient laboratory conditions.

### Fourier Transform Infrared Analysis

Samples were mounted on a Perkin Elmer multiple internal reflectance apparatus using either germanium or KRS-5 multiple internal reflectance elements obtained from Harrick Scientific. In all, five different elements were used: KRS-5 at 45° or 60° incident angles and germanium elements at 30°, 45°, 60° incident angles. All spectra were recorded on a Nicolet 6000C FT-IR equipped with a wide-frequency range mercury cadmium telluride (MCT) detector. Spectra were collected at 4 cm<sup>-1</sup> resolution and a total of 500 scans were co-added to achieve a sufficiently high signal-to-noise ratio.

## RESULTS

### Depth of Penetration for Various Crystal Materials

Based on Eq. (1), depth of penetration by the infrared beam into the epoxy resin for each crystal material at each incident angle can be calculated provided the refractive indices of the epoxy and the various crystals are known. In the present case, the refractive index 3501-6 resin was determined by laser interferometry to be about 1.7, while the published values for Ge and KRS-5 crystals are 2.37 and 4.00, respectively, at 1000 cm<sup>-1</sup>.

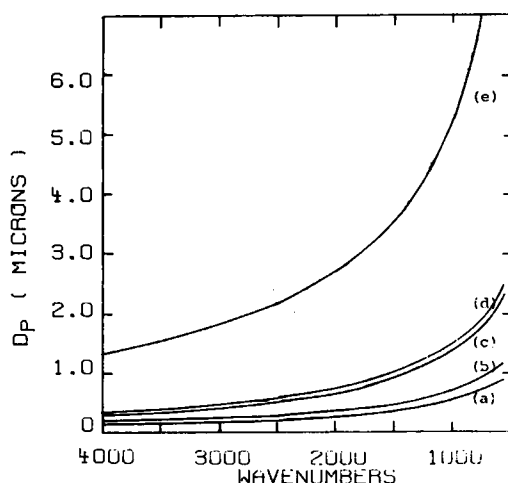


Fig. 1. Plots of depth of penetration of infrared light ( $D_p$ ) versus infrared frequency ( $\text{cm}^{-1}$ ) for internal reflectance elements with varying angles and refractive indices. (a) Ge at  $60^\circ$ ; (b) Ge at  $45^\circ$ ; (c) KRS-5 at  $60^\circ$ ; (d) Ge at  $30^\circ$ ; and (e) KRS-5 at  $45^\circ$ .

Inserting these values into Eq. (1) produces the curves in Figure 1. Notice that the depth of penetration increases substantially for all crystals at lower frequencies, and this becomes important when determining the rate of penetration of the oxidized layer in exposed epoxy. The other important fact to note is that, by using various crystals at various incident angles, one can essentially "depth profile" the surface structure of the epoxy from  $0.5 \mu\text{m}$  to greater than  $5.0 \mu\text{m}$  at  $1000 \text{ cm}^{-1}$ , or from  $0.7 \mu\text{m}$  to  $9.0 \mu\text{m}$  at  $700 \text{ cm}^{-1}$ . This ability to sample at various depths allows the rate of progression of degradation to be determined as a function of exposure time to ultraviolet light, moisture, and heat. In determining the depth of penetration of infrared light into the surface of the resin, however, it should be noted that, as a refractive index of the sample approaches the refractive index of the IRE, the depth of penetration increases dramatically. At this point, the degree of intimacy of contact between the sample surface and the IRE surface becomes critical in order to accurately determine the depth of penetration. Therefore, in the epoxy samples which are inflexible and cannot form the necessary intimate contact with the IRE, the accuracy of determination of the larger depths of penetration is diminished.

### Assignment of Bands in Epoxy Resin

Before the mechanism of degradation of the epoxy resin can be determined, the various bands in the infrared spectrum must be assigned to specific functional groups. The infrared spectra of the two major components of 3501-6 resin are shown in Figure 2, along with the infrared spectrum of the cured resin. The assignments of the major bands are given in Table 1. The table indicates that the bands in the cured resin are readily assigned to specific functional groups, and changes in their intensities or positions can give information on specific reactions involved in environmental degradation.

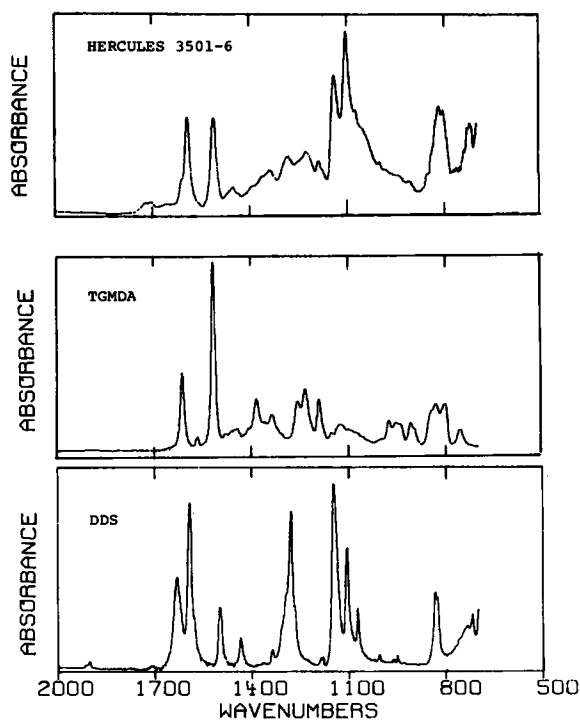


Fig. 2. The infrared spectra of tetraglycidylether of methylenedianiline (TGMDA), diamino-diphenylsulfone (DDS), and the cured Hercules 3501-6 resin.

TABLE I  
Assignment of Major Bands in the Infrared Spectrum of TGMDA Cured With DDS

Position ( $\text{cm}^{-1}$ )	Assignment
1710	carbonyl group of amide (amide band)
1670	amide band
1594	<i>p</i> -substituted benzene of DDS
1514	<i>p</i> -substituted benzene of TGMDA
1452	C—H bond deformation of aliphatic groups
1340	C—H bond of aliphatic secondary alcohol
1287	secondary amide group of DDS
1251	tertiary amide group of TGMDA
1225	tertiary amide group of TGMDA
1187	tertiary amide group of TGMDA
1142	sulfone group of DDS
1104	sulfone group, C—O bond of sec. alcohol
1075	sulfone group, C—O bond of sec. alcohol
817	<i>p</i> -substituted benzene of DDS and TGMDA
724	aromatic substitution of DDS

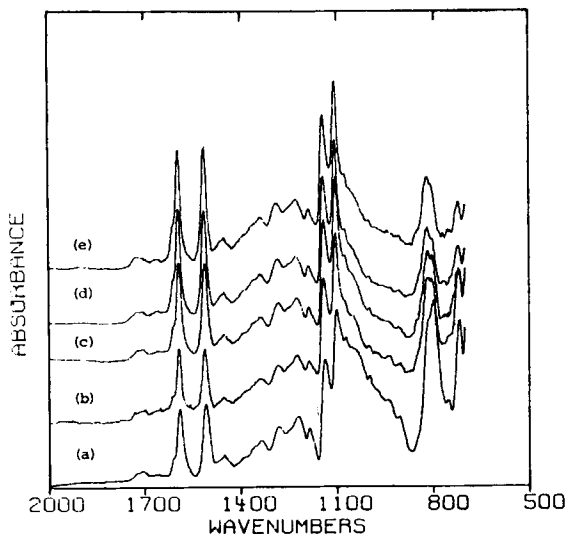


Fig. 3. Reflectance infrared spectra of cured Hercules 3501-6 resin before aging using internal reflectance elements of varying angles and refractive indices. (a) KRS-5 at 45°; (b) KRS-5 at 60°; (c) Ge at 30°; (d) Ge at 45°; and (e) Ge at 60°.

In the infrared spectrum of Hercules 3501-6 resin, three distinct portions of the polymer network can be monitored by specific infrared bands. These include the TGMDA portion of the molecule with its *p*-substituted benzene ring and tertiary amine group, the DDS portion containing a *p*-substituted benzene ring with secondary amine and sulfonyl group, and the aliphatic secondary alcohol formed during the cure reaction. Therefore, specific degradation products should be easily determined from changes in the infrared spectrum.

#### Reflectance Spectra as a Function of Aging

Figure 3 shows the infrared spectra obtained before aging using Ge and KRS-5 internal reflectance elements at various angles. Although there are some minor differences in the spectra, they are very similar in overall appearance. Therefore, differences which occur with environmental aging must be a result of changes in structure, and are not due to artifacts caused by the varying incident angles of the IRE crystals.

Figure 4 shows the spectra obtained on 30° Ge plates after various aging times in the Uvicon Weatherometer, and indicates that environmental weathering introduces a number of specific structural changes in the resin. Firstly, a number of peaks either diminish in intensity or broaden (Table II). Since the bands at 1517  $\text{cm}^{-1}$ , 1234  $\text{cm}^{-1}$ , and 817  $\text{cm}^{-1}$  are all associated with the aromatic to nitrogen bond in the TGMDA portion of the molecule, it can be concluded that a major point of degradation in the resin is at the tertiary amine bond in the polymer backbone. The mechanism for this breakdown will be considered in the discussion section. The band at 1103  $\text{cm}^{-1}$  is likely the secondary hydroxyl band associated with curing the epoxy.

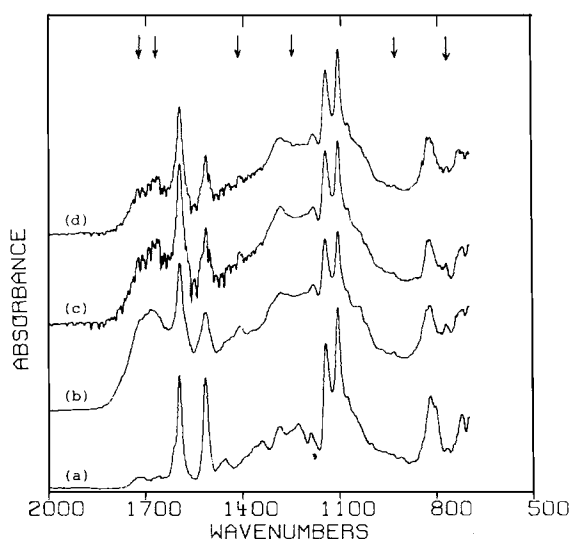


Fig. 4. Reflectance infrared spectra of cured Hercules 3501-6 resin after exposure to ultraviolet light and high humidity for various periods of time. The internal reflectance element shown is Ge at 45°. (a) 0 hours exposure; (b) 72 hours exposure; (c) 144 hours exposure; and (d) 216 hours. Arrows indicate bands that appear with degradation.

TABLE II  
Changes in Cured 3501-6 Resin Infrared Spectrum Accompanying Environmental Degradation

Bands appearing ( $\text{cm}^{-1}$ )	Bands disappearing ( $\text{cm}^{-1}$ )
1710	1514
1670	1452
1407	1340
1250-1200	1225
930	1104
771	810

others have suggested that dehydration of cured epoxies is a common reaction during heat degradation, and this is likely the case in the present example.<sup>11-14</sup>

Second, new bands appear in the infrared spectrum of the degraded sample, and they are indicated in Table II and by arrows in Figure 4. The peaks at  $1250\text{--}1200\text{ cm}^{-1}$ ,  $930\text{ cm}^{-1}$ , and  $771\text{ cm}^{-1}$  are consistent with the formation of a *para*-substituted phenol. As well, the band at  $1515\text{ cm}^{-1}$  is broadened and appears to contain at least three distinct bands (the original plus a band on either side) in environmentally exposed samples. Since *p*-substituted phenols have two bands in this region, the spectra are again consistent with the formation of this species. The bands at  $1710\text{ cm}^{-1}$  and  $1670\text{ cm}^{-1}$  have been previously attributed to the formation of an amide,<sup>14</sup> or a combination of double bonds from a dehydration reaction on the secondary alcohol group and oxidation to produce ketones and aldehydes.<sup>13</sup>

Third, the signal-to-noise ratios of the infrared spectra obtained decrease markedly as environmental degradation takes place, indicating that the surface layer is extensively degraded. This decrease of the signal-to-noise ratio in the

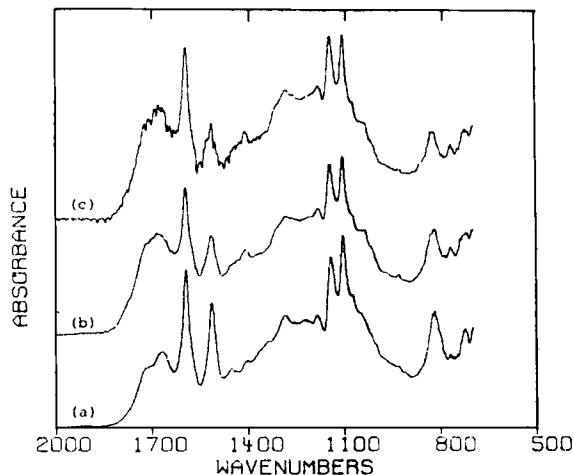


Fig. 5. A comparison of reflectance infrared spectra obtained at various angles with Ge plates after 72 hours exposure. (a) Ge at 30°; (b) Ge at 45°; and (c) Ge at 60°.

infrared spectrum correlates well with the observed "alligator skin" appearance of the resin surface and indicates that the surface is substantially degraded.

#### Depth of Penetration of the Oxide Layer in Accelerated Degradation Samples

As described above, the depth of penetration by the infrared beam into the epoxy surface can be controlled by varying the incident crystal angle and the refractive index of the crystal material. The spectra shown in Figure 4 from the 60° Ge crystal indicate that after a 72 hour exposure oxidation has penetrated to a depth of at least 0.5  $\mu\text{m}$ , while after 216 hours the surface above 0.5  $\mu\text{m}$  is almost completely degraded. Thus, the surface layer of the epoxy is largely degraded after only a short period of exposure to ultraviolet light and warm moisture.

Figure 5 shows the spectra obtained using Ge crystals with various incident angles after 72 hours of exposure. As is evident from this figure, there is substantial degradation in the spectrum obtained with the 45° Ge crystal. Therefore, after 72 hours the environmental breakdown has progressed to a level of 0.5–1.0  $\mu\text{m}$ . The spectrum from the 30° Ge crystal is only slightly changed, indicating that degradation is only beginning at a level of 0.7–1.5  $\mu\text{m}$ .

Although not shown here, spectra at various angles on Ge crystals after 144 hours of exposure indicate a further progression of the degradation layer. At this time, there is substantial degradation up to 2.0  $\mu\text{m}$ , and the layer up to 1.0  $\mu\text{m}$  is largely degraded.

In the final series of spectra at 216 hours of exposure, spectra were also obtained on KRS-5 crystals because of the greater depth of penetration. Figure 6 indicates that the spectra on all of the Ge crystals show substantial degradation, and even the spectra using the 45° KRS-5 crystal shows signs of structural changes. In these samples, the resin is highly degraded up to at



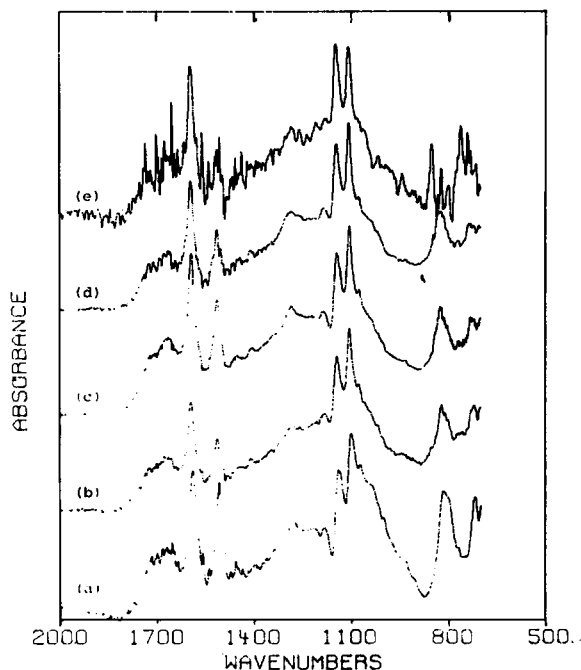


Fig. 6. A comparison of reflectance infrared spectra obtained at various angles with Ge and KRS-5 elements after 216 hours exposure. (a) KRS-5 at 45°; (b) KRS-5 at 60°; (c) Ge at 30°; (d) Ge at 45°; and (e) Ge at 60°.

least 0.7  $\mu\text{m}$ , as is evidenced by the high noise level in the spectrum using the 30° Ge crystal. Furthermore, the changes noted in the spectrum on the 45° KRS-5 crystal indicates that the degradation reactions have progressed to a depth of 5.0  $\mu\text{m}$  or more. Therefore, the degradation reactions are not confined to the extreme surface layer of the resin, but rather appear to progress at a measurable rate into the bulk of the resin block.

### Environmental Degradation in Room-Stored Samples

The environmentally degraded samples discussed above were obtained through accelerated aging experiments, and it is necessary to know if the results obtained are relevant to real-life environmental exposure. To compare the accelerated degradation products to normal exposure degradation products, a sample of 3501-6 resin was stored in a glass chamber for one year, during which time it was exposed to ambient room conditions. Although the glass attenuates the amount of ultraviolet light impinging on the sample, 10%–50% of the intensity between 300 nm and 350 nm does penetrate the glass. A comparison of the infrared spectra of this sample to those of the samples that were aged in the weatherometer should provide information on both the validity of the accelerated tests and any differences in the degradation products as a result of the different weathering methods. Figure 7 shows the infrared spectra at various angles on both Ge and KRS-5 crystals for the room-aged sample.

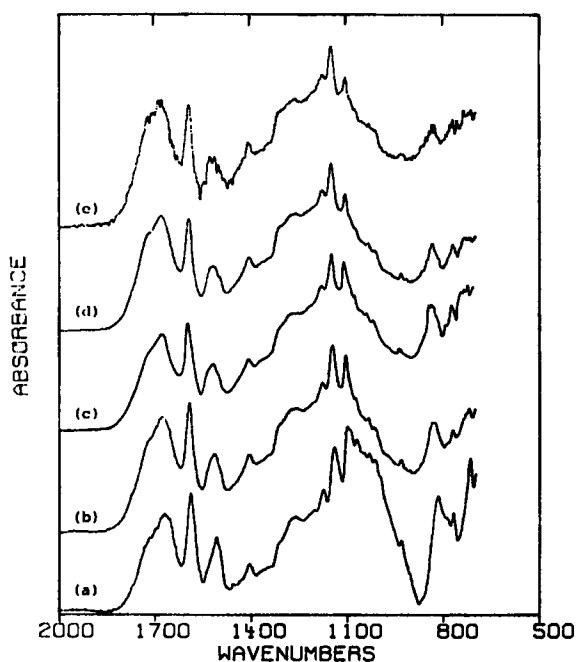


Fig. 7. A comparison of reflectance infrared spectra obtained at various angles with Ge and KRS-5 crystals after exposure in ambient room conditions for one year. (a) KRS-5 at 45°; (b) KRS-5 at 60°; (c) Ge at 30°; (d) Ge at 45°; and (e) Ge at 60°.

Two important results are apparent in this figure. First, the spectra are almost identical with those from the accelerated degradation samples. This finding suggests that the same degradation reactions can occur in the absence of high humidity and ultraviolet radiation provided the sample is exposed to air and a reasonable amount of light. Therefore, results obtained by accelerated degradation are applicable to normal exposure conditions.

Second, all of the spectra except one obtained on the 45° KRS-5 crystal are qualitatively similar. This suggests that one year of exposure to normal room conditions causes extensive surface degradation in 3501-6 resin to a depth of about 2.0  $\mu\text{m}$ . However, the spectrum of the one-year-aged sample obtained on the 45° KRS-5 crystal is substantially altered from the unaged sample, suggesting that degradation is continuing to penetrate to greater depths than 2.0  $\mu\text{m}$ . Therefore, the room aging experiment confirms the finding that the degradation reactions are not confined to just the extreme surface layers of the epoxy resin, and that the degradation reactions can take place even in mild environmental conditions.

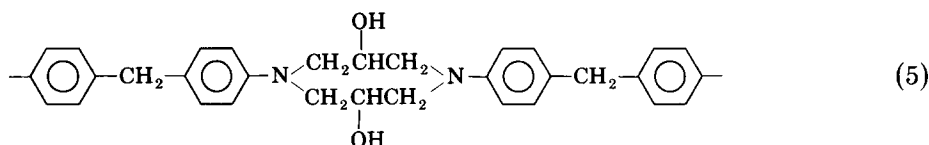
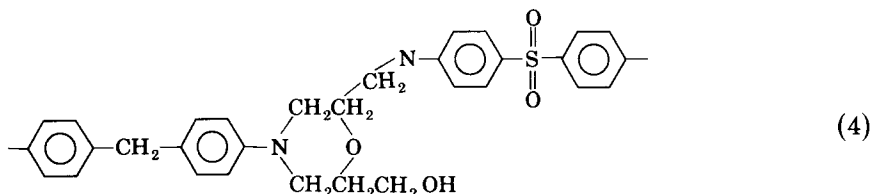
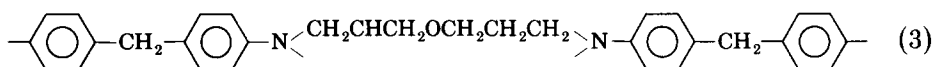
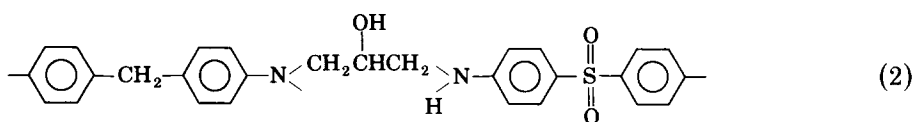
## DISCUSSION AND CONCLUSIONS

The present infrared study provides information on two important facets of environmental degradation of Hercules 3501-6 resin. The individual infrared spectra provide information on the products formed during breakdown, while a comparison of the spectra at various angles indicates the rate at which the

degradation process progresses from the surface to the center of the resin block.

### Degradation Products from Hercules 3501-6 Resin

The reactions which take place as indicated by changes in the infrared spectra can be divided into three distinct groups: oxidation reactions; dehydration reactions; and hydrolysis reactions. The position of oxidative attack in the resin backbone will be dependent on the structures produced during resin curing. Since the uncured resin contains an excess of epoxy groups over amine groups, four reaction products are possible during normal curing of the resin.



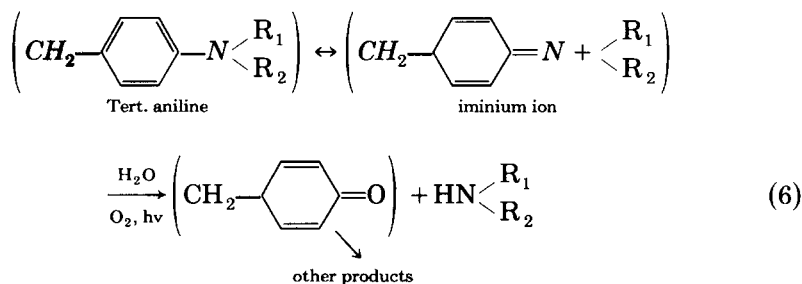
Of these the normal reaction of a DDS molecule with a TGMDA molecule is reaction (2), while reaction (3) is the homopolymerization of excess TGMDA molecules. Reaction (4) is the intercyclization of a glycidyl and the hydroxy group produced in reaction (2), while reaction (5) is produced by two homopolymerization reactions. Of these reactions, reactions (2) and (3) are most likely to occur.<sup>12</sup> Reactions (4) and (5) are not likely, since the brittleness of the cured resin suggest a high cross-link density which is not possible if cure reactions (4) and (5) are predominant. Therefore, only the more likely reactions (2) and (3) will be considered here.

A previous investigation using gas chromatography and mass spectrometry suggested that propenal is the major volatile component produced during heat

degradation of 3501-6 resin.<sup>12</sup> In the present experiments we could not identify it as a component for three reasons. Firstly, being a volatile component, propenal would evaporate from the resin during exposure and would not be seen in the infrared spectrum. Second, the previous experiments were performed in an apparatus which excludes oxygen, and therefore the degradation products are likely to be different. Finally, the degradation in the previous report<sup>12</sup> was a result of heating, while the present experiments tested the effects of light, moisture, and air on the resin.

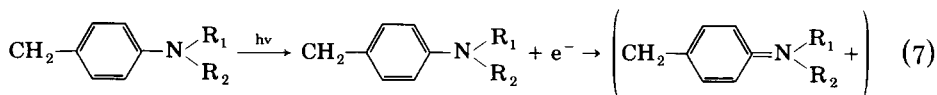
Numerous previous experiments have suggested that carbonyl compounds such as amides are formed during the oxidation of epoxy networks.<sup>14-16</sup> The authors suggest that oxygen, through a free radical mechanism, interacts with the carbon bonded to the amine group during the normal cure reaction. In our study there is also evidence of carbonyl formation, as indicated by the appearance of a band at  $1710\text{ cm}^{-1}$ . Although a previous report suggested that photooxidation of epoxies cured with DDS produced carbonyl compounds but not amides, the present infrared spectra have a strong band between  $1660$  and  $1670\text{ cm}^{-1}$ , which has been previously attributed to amide formation. This band could also be attributed to the formation of an alkenyl group during the dehydration of a secondary alcohol, but the low temperatures involved in this study tend to rule against this alternative. Therefore, these experiments suggest that Hercules 3501-6 resin does photooxidize to form amide products.

Some of the reactions postulated in this study are unique to epoxies containing amine groups. Two major commercial products contain this functional group: the presently studied TGMMA, and triglycidylether of *p*-aminophenol (TGPAP). Both are relatively unstable at room temperature and darken noticeably when exposed to ultraviolet light. This observation correlates well with our observed darkening of the exposed resin blocks and suggests that the degradation reaction may involve a portion of the molecule not related to the formation of epoxy/amine linkages. Our infrared spectra indicate that the degradation occurs between the aromatic ring and the tertiary nitrogen of the TGMMA portion of the molecule. A possible mechanism for this degradation is via an enamine reaction.



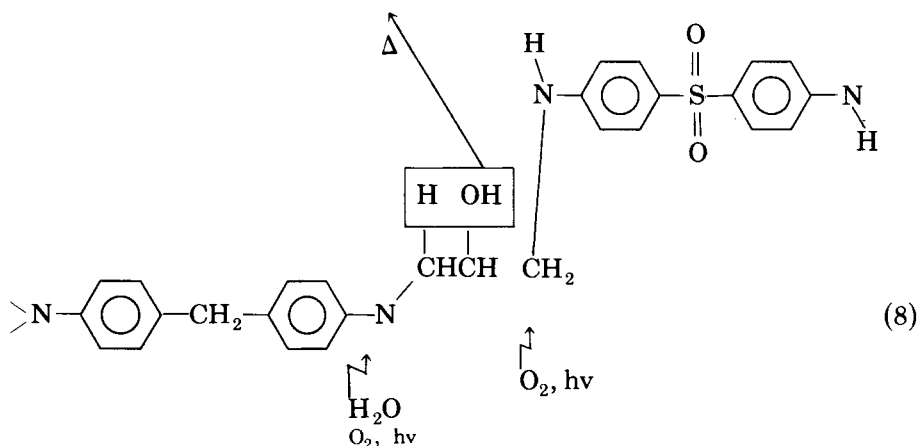
In this reaction the tertiary aromatic nitrogen has a resonance-stabilized structure which resembles an iminium ion. This iminium ion can then undergo hydrolysis or further free radical reactions to produce phenone or phenol groups plus a free secondary amine. The reaction must be catalyzed by light or oxygen or both since the same degradation products were formed in the room-aged sample where high humidity was not present. For the light-cata-

lyzed reaction, previous reports have indicated that light of wavelengths 250–340 nm can cause the abstraction of an electron from tertiary amines as shown below.<sup>24</sup> This allows an alternative mechanism to form the iminium ion shown in (6):



In this reaction mechanism only a tertiary aromatic amine can act as a starting material, since a secondary aromatic amine does not form the resonance-stabilized iminium ion. Instead, the secondary amine deprotonates to leave an uncharged amine.<sup>24</sup> This explains why the reaction is specific to the TGMMA portion rather than also occurring at the secondary amine adjacent to the aromatic ring in the DDS portion of the repeating polymer unit. The same enamine reaction is also possible in the homopolymerized epoxy of reaction (3).

The present discussion, therefore, suggests that three separate or combined degradation reactions are likely to take place in Hercules 3501-6 resin during environmental degradation. In the chemical groups formed by curing, photooxidation produces carbonyl-containing groups such as amides which may then undergo further degradation to form propenal as seen in mass spectral analysis. In the epoxies that have tertiary aromatic nitrogen groups, hydrolysis or photooxidation splits the nitrogen from the aromatic ring and produces a phenol or phenone which gives rise to the darkened color. Finally, dehydration of the secondary alcohol produced during cure can occur. The degradation points in Hercules 3501-6 resin are summarized below.



### Relation of Chemical Degradation to Physical Properties

The depth of penetration studies suggest that environmental degradation in epoxies takes place at a measurable rate and penetrates from the outer surface toward the interior matrix quickly. In Hercules 3501-6 the chemical break-

down is further promoted by the presence of the tertiary amine group. These degradation reactions can cause two major physical changes in the matrix material. Firstly, the glass transition temperature ( $T_g$ ) is lowered. Therefore, the operational service temperature is decreased. Secondly, the embrittlement and cracking of surface can cause loss of impact strength such as is seen in acrylic and polycarbonate transparencies. Therefore, the environmental degradation can have a deleterious effect on composite physical properties, and care should be excersised to prevent oxidation reactions from taking place in epoxy resins by making sure that they are coated with an environmentally stable coating. Furthermore, the choice of epoxy resins should be considered both from the point of maximum initial strength and environmental durability.

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Received September 10, 1985

Accepted April 8, 1986