

Irreversible Interactions Between Water and DGEBA/DDA Epoxy Resin During Hygrothermal Aging

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ABSTRACT: Two approaches were adopted to examine the irreversible interactions between water and a model epoxy resin (DGEBA/DDA). One was to employ XPS to investigate the changes of the chemical structure of the resin after immersion in water at a temperature of 90°C and followed by completely drying. The other was to use XPS and FTIR to characterize the degradation products formed during hygrothermal aging. The results clearly showed that irreversible interactions occurred between water and the resin at elevated temperature. Water can lead to the incorporation of C—O and N—CO—N groups in the resin and cut the epoxy backbone chain. Based on the results obtained, a tentative degradation mechanism is proposed and found to explain the results reasonably well. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 449–458, 1997

Key words: irreversible interactions; epoxy resin; water; XPS; FTIR; hygrothermal aging

INTRODUCTION

Epoxy resins are widely used as adhesives and as matrices in fiber-reinforced composites with applications in the automotive, aerospace, marine, and other industries. It is well known that epoxy resins absorb moisture from humid environments and that the absorbed water can have detrimental effects on their properties. Understanding of the mechanisms of hygrothermal aging can facilitate the design of reliable composite structures or adhesive joints. However, due to the complexity of epoxy systems, information about the interactions between water and epoxy resin at a molecular level is rather limited and sometimes contradictory.

By using proton nuclear magnetic resonance (NMR), Fuller et al.^{1,2} found that the absorbed

water molecules in an amine-cured epoxy resin are less mobile than in liquid water but more mobile than water molecules strongly bound in cellulose fibers. They² further hypothesized that the water absorbed by the resin is involved in an exchange between the hydrogen of the water and the hydrogen of the polymer. Other NMR studies^{3,4} also indicated that epoxy resin contains both bound and mobile water molecules. Using Fourier transform infrared spectroscopy (FTIR), Antoon et al.⁵ found that the absorbed water is held within the epoxy resin by hydrogen bonding and suggested that the interaction between water and epoxy is a completely reversible phenomenon.

However, Jelinski et al.^{6,7} reached different conclusions by using quadrupole echo deuterium NMR spectroscopy. Their results revealed that (a) water in epoxy resin is impeded in its movement; (b) there is no free water; (c) there is no evidence for tightly bound water; and (d) it is unlikely that the water disrupts the hydrogen-bonded network in the epoxy resin. The water molecules migrate

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from site to site, but the jumping motion does not involve a specific hydrogen-exchange mechanism. Studies by dielectric experiments⁸ also suggested that the water is not bound to polar groups in the resin or to hydrogen-bonding sites. There was only some clustering of water molecules in the polymer, rather than complete molecular separation.

Nevertheless, FTIR (internal reflectance mode) investigations⁹ on a diaminodiphenylsulfone (DDS)-cured tetraglycidylether of methylenedianiline (TGMDA) epoxy resin revealed that degradation might occur via hydrolysis, oxidation, and dehydration reactions at specific locations in the polymer chain. In addition, there is a unique reaction between the tertiary amine of the epoxy portion of the molecule with water. Previous work carried out at the Ecole des Mines¹⁰ also indicated that water can cause chain scission in DGEBA/DDA epoxy systems.

The controversy is believed to be due either to the different epoxy systems being studied or to the different aging conditions employed. Subject to the environmental conditions that the materials are exposed to, it is believed that absorbed water can either cause reversible property changes or lead to irreversible degradation of the resin or both. Clearly, irreversible processes are more detrimental in practical applications of epoxy adhesives or matrices, but the mechanisms of these processes are not well understood. The aim of this study was to gain better understanding of irreversible interactions occurring between water and epoxy resin.

In the present work, two approaches were used to examine the irreversible effects of water on a DGEBA/DDA epoxy resin system during hygrothermal aging. One was to employ X-ray photoelectron spectroscopy (XPS) to monitor the irreversible changes of the chemical composition of the resin. The other was to use both XPS and FTIR to investigate the degradation products leached out from the resin during the aging period.

EXPERIMENTAL

Sample Preparation

The epoxy resin employed was a model adhesive from CECA S. A. France, which consists mainly of diglycidyl ether of bisphenol A (DGEBA), dicyandiamide (DDA) as a curing agent, and a low

concentration of accelerators ($< 1\%$). A cure cycle of 30 min at 140°C was adopted with a temperature increase rate of 3°C min⁻¹. DSC studies showed that these curing conditions give the highest glass transition temperature. In addition, no further curing is detectable by subsequent DSC runs.

Three kinds of samples were prepared for analysis: two corresponding to the resin itself, and the other corresponding to the degradation products of epoxy/water interactions. One type of resin sample was simply cured bulk specimens of 1 mm thickness, used for FTIR analysis. Other resin specimens were prepared as coatings. Optical glass slides were selected as the substrates. These were cleaned by ultrasound with acetone, followed by thorough acetone rinsing and air drying. The slides were then dipped in the acetone solution of the uncured resin mixture (5% by weight) for 1 s and taken out and dried in the laboratory atmosphere. This procedure was repeated 20 times. The thickness of the coating prepared by this method is believed to be thin enough for the degradation products to leach out of the resin virtually instantaneously. The coated samples were then immersed in deionized water at 90°C for 6 days. After immersion, the specimens were put into an oven at 40°C and dried for 2 days. Before XPS analysis, there was no decomposition of the epoxy coating on the slides observable to the naked eye.

Degradation products were prepared in an acetone solution. Some thin films (of about 0.15 mm thickness) of the cured resin were immersed in deionized water for 2 weeks and then the immersion water transferred to a clean bottle (preparation corresponding to washing in acetone followed by heating to 600°C for 4 h and, finally, ultrasound cleaning in acetone). The water was then evaporated at 40°C to leave a residue corresponding to degradation products. Acetone was then added to dissolve the residue. The solutes were concentrated by evaporation of acetone and then used to prepare XPS and FTIR specimens.

XPS Analysis

An SSI SSX-100 "top hat" mounted on a vacuum system was employed to analyze the coating samples. The analyses were performed with monochromated AlK $\alpha_{1,2}$ X-rays. Analysis areas had a diameter of 600 microns. Elemental compositions were determined from peak areas using the manufacturer's software which assumes a constant analyzer transmission and a 0.7 power energy de-

pendence of mean free paths and makes use of Scofield's cross sections.

The degradation products were analyzed by a VG MK1 spectrometer, using an unmonochromated AlK $\alpha_{1,2}$ source. The analysis areas were 0.4 cm². Samples were prepared by dipping Al foil into the leaching substances—acetone solutions—and then drying at 40°C for 2 days. The surfaces of the dipped Al foil were analyzed. Elemental compositions were deduced from peak areas using sensitivities obtained with reference materials. For both XPS machines, a surveying scan and a high-resolution analysis of C_{1s}, O_{1s} and N_{1s} were performed.

FTIR Analysis

The unaged resin and the degradation products were analyzed by FTIR. A Bruker IFS25 spectrometer from Bruker Analytische Messtechnik was employed. The spectra were recorded from 4000 to 400 cm⁻¹.

For the unaged sample, the spectra were obtained by specular reflection and treated with the Kramers–Kronig transformation. The bulk samples of 1 mm thickness with smooth surfaces were used for this analysis.

For the degradation products, the transmission mode was used. Samples were prepared by placing the acetone solution of the leaching substances on a KBr disk and drying in air for at least 10 min. To exclude the possible effect of acetone remaining on the recorded spectra, a sample of pure acetone prepared in the same way was used as the background. Furthermore, the spectra of the sample were recorded twice with a 5 min time interval and were found to be the same, thus confirming that the spectra recorded only represent the degradation products.

RESULTS

Chemical Structures of DGEBA/DDA Epoxy Resin

Table I compares the elemental composition of the DGEBA/DDA epoxy system before and after immersion for 6 days in distilled water at 90°C. The analysis for the sample, having been immersed in water for 6 days, was repeated and the results are also listed in Table I. It can be seen that the reproducibility of the analysis was quite good. The aged samples showed trace amounts of Si, which is thought to be either from the substrate or con-

Table I Effect of Water Immersion on the Elemental Composition of DGEBA/DDA Adhesive (in 90°C Distilled Water and Then Dried)

Immersion Time	Elemental Ratio (% with Respect to C)			
	C	O	N	Si
0	100.00	17.5	7.0	0.0
6 days				
Sample 1	100.00	22.7	6.1	0.9
Sample 2	100.00	22.1	6.0	1.2

tamination or possibly due to leaching from the glass into the water and subsequent penetration into the polymer. Since its concentration was quite low, it is believed to be reasonable to neglect its effects on the XPS results.

As shown in Table I, before aging, the elemental composition was O/C = 0.17 and N/C = 0.07. After aging, the O/C ratio in the resin increased, while the N/C ratio decreased slightly. The increase of O/C may indicate that the epoxy resin gained oxygen through interactions with water, such as hydrolysis. However, the decrease of N/C, on the contrary, suggests that the N-containing part of the intercrosslink chain segment may be cut and leached out in the aging process or possibly that the resin contained an excess of hardener which could leach out during the aging process. Nevertheless, the infrared result of the unaged resin (as shown in Fig. 1) excludes the latter possibility since there is no doublet near 2200 cm⁻¹, which is characteristic of dicyandiamide (DDA).¹¹ Moreover, the spectrum in Figure 1 confirms that the resin studied in this work was fully cured by showing no characteristic absorption for the epoxy group in the spectrum (at ~ 916 cm⁻¹). Therefore, it is concluded that the changes of the chemical composition of the resin reported here reflect only the effects of hygrothermal aging.

To study further the effects of water, a high-resolution analysis of the C_{1s}, O_{1s}, and N_{1s} was carried out. Figure 2 compares the C_{1s} signal of an unaged sample and a typical aged sample. As can be seen, aging increased the shoulder at the higher energy side of the C_{1s} signal, confirming the previous statement that aging changes the chemical structure of the epoxy resin. Curve fitting of the C_{1s} signal requires three components, with binding energies of 285.0, ~ 286.6, and ~ 287.7 eV, respectively. The component at 285.0

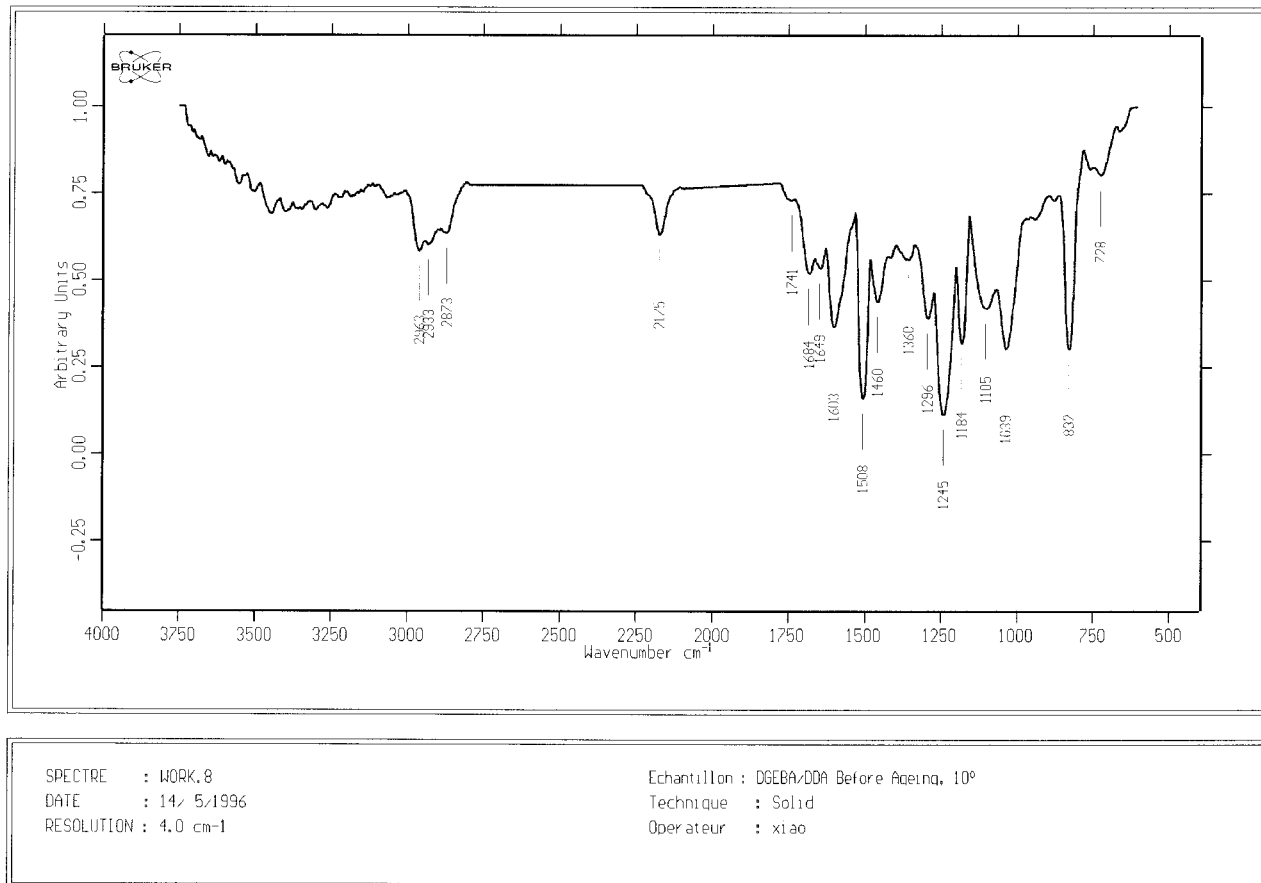
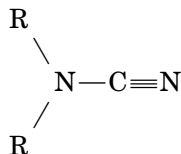


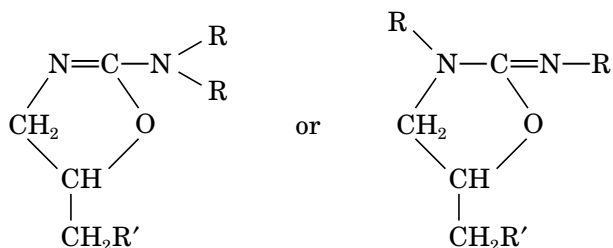
Figure 1 Infrared spectrum of unaged DGEBA/DDA epoxy resin.

eV is the reference in this work, corresponding to carbon bonded to itself and/or hydrogen only. Due to the complexity of the structure of the cured epoxy resin, it is difficult to assign the other two signals. This is particularly so for the nitrogen-carbon bonds. Petrat et al.¹² listed the binding energies for different carbon-nitrogen bonds from various literature and found that the scatter of data was considerable, and in some cases, indications were contradictory.

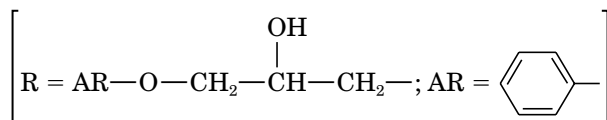
According to Zahir,¹³ the reaction of epoxide resin with dicyandiamide leads mainly to products with two different structural units, namely, a dialkyl cyanamide:



and an organic base, derivative of 2-amino-2-oxazoline (or its tautomer 2-imino-oxazolidine);



where



In addition, urea carbonyl and urethane ester groups may be formed in the resin via intramolecular and (or) intermolecular rearrangement reactions of the above products.¹³

Taking into consideration Ref. 14 and the work of Petrat et al.¹² here we tentatively assign

~ 286.6 eV to —C—O and —C—N and the signal at ~ 287.7 eV to carbon atoms bonded to more than one nitrogen atom, such as N≡C—N, N=C—N, and N—CO—N. The results of this analysis are listed in Table II.

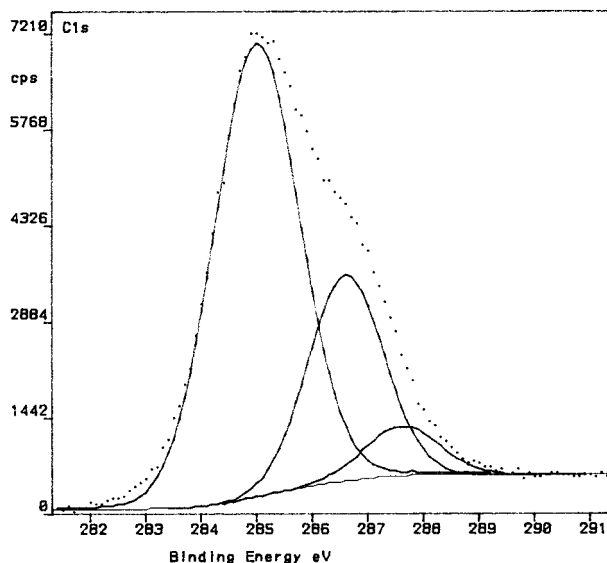
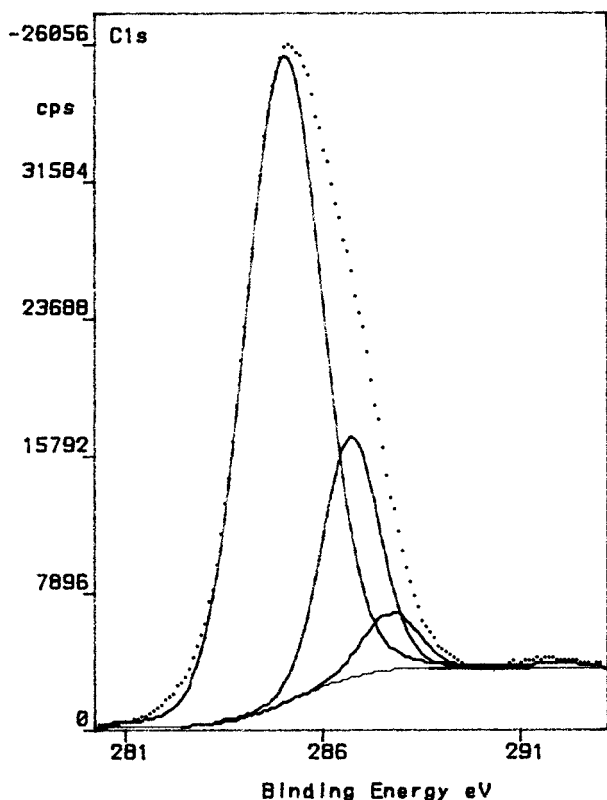


Figure 2 Effects of aging on the C_{1s} signals of DGEBA/DDA epoxy system: (a) before aging; (b) in 90°C water for 6 days and then dried.

Table II High-resolution analysis of C_{1s} Signal of DGEBA/DDA System Before and After Aging (in 90°C Distilled Water and Then Dried)^a

Immersion Time	Binding Energy (eV)		
	285.0	286.6	287.7
0	100.00	27.5	6.2
6 days			
Sample 1	100.00	39.2	9.3
Sample 2	100.00	42.6	8.2

^a Values at 286.6 and 287.7 eV are given as percentage of the signal at 285.0 eV.

Surprisingly, we could not find signals appearing at ~ 289.6 eV, which is the characteristic signal for —COO groups.^{14,15} This result suggests that there were no —COO groups in the cured epoxy resin or that their concentration was too low to be detected. However, the result is not in agreement with Zahir,¹³ who suggested that when DGEBA/DDA was cured at a temperature over 120°C ester groups could be formed in the resin.

The results in Table II show that the signal at ~ 286.6 eV was significantly enhanced after aging, while the signal at ~ 287.7 eV was enhanced only slightly. Since aging only increased the concentration of oxygen in the resin, it is believed that the enhancement of these signals was due mainly to the introduction of some oxygen-containing functional groups, particularly C—O groups. In addition, perhaps rather surprisingly, there was no signal characteristic of ester groups appearing in the C_{1s} peak of the aged resin.

Figure 3 shows the O_{1s} signal of both an unaged and an aged sample, respectively. It can be seen that the curve fitting for the O_{1s} signal needs two components, one at ~ 531.9 eV and the other at ~ 533.4 eV. Based on Ref. 14, the peak at the lower binding energy is tentatively assigned to N—CO—N (including carbon oxygen single and double bonds), while the peak at the higher binding energy, to C—O groups. The results are listed in Table III. The results are scattered, but do suggest that aging does not have significant effects on the relative concentrations between N—CO—N groups and C—O groups, which could be due to the fact that hygrothermal aging produces both C—O and N—CO—N groups on the polymer chain.

For the N_{1s} signal, the curve fitting also might need two components, i.e., ~ 398.5 and ~ 400.4 eV (as shown in Fig. 4). As there is no signal

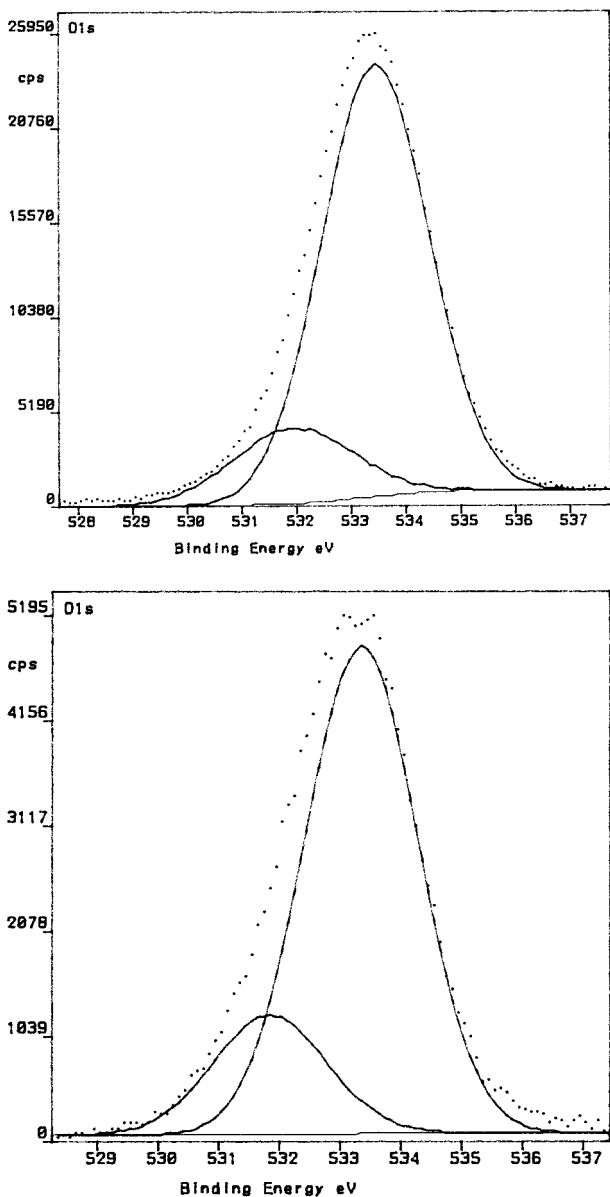


Figure 3 Effect of aging on the O_{1s} signal of DGEBA/DDA resin: (a) before aging; (b) in 90°C water for 6 days and then dried.

appearing at binding energies over 402 eV, we can exclude the existence of oxidized nitrogen functions (such as $-\text{ONO}_2$, ~ 408 eV; $-\text{NO}_2$, ~ 407 eV; and $-\text{ONO}$, ~ 405 eV) in the epoxy resin before and after aging. Moreover, 398.5 eV is too low for most nitrogen functionalities, which give N_{1s} binding energies in the narrow region of 399.0–401.0 eV,¹⁵ including C–N, $-\text{NH}_2$, $-\text{O}-\text{CO}-\text{NH}$, and $-\text{CO}-\text{NH}_2$, suggesting that the curve fitting might be artificial. Hence, the curve-fitting results of the N_{1s} peak were not

Table III High-resolution Analysis of O_{1s} Signal of DGEBA/DDA Epoxy System Before and After Aging (in 90°C Distilled Water and Then Dried)^a

Immersion Time	Binding Energy (eV)	
	~ 531.9 eV	~ 533.4 eV
0	19.8	100.00
6 days		
Sample 1	24.6	100.00
Sample 2	18.8	100.00

^a Values at 531.9 eV are given as percentage of the signal at 533.4 eV.

taken into consideration. However, it has been found that water immersion moves the N_{1s} signal to a higher binding energy, as shown in Table IV. Since the signals representing nitrogen carbon bonds are usually shown at the lower binding energy side of the N_{1s} peak,^{12,14} the results may indicate that the relative concentration of nitrogen-carbon bonds compared with nitrogen-carbon-oxygen-containing functional groups, such as N–CO, decreased after hygrothermal aging.

Therefore, the XPS studies have shown that water can induce irreversible changes in the chemical structure of DGEBA/DDA epoxy resin at elevated temperature. These involve increasing oxygen concentration in the resin, which is in the form of C–O and N–CO–N groups, and the slight decrease of nitrogen concentration.

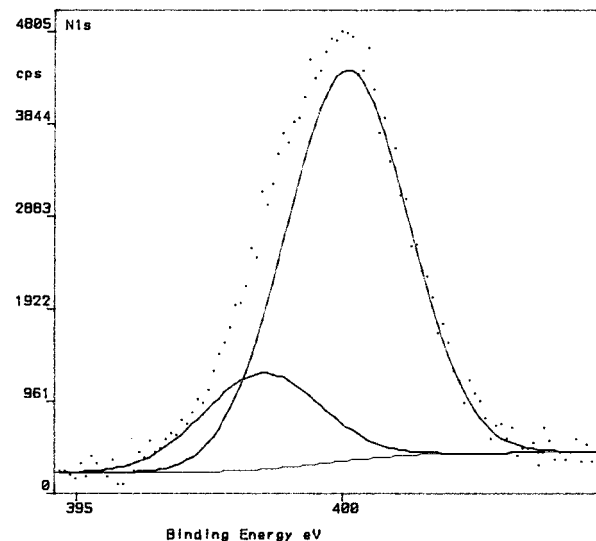


Figure 4 Curve fitting of N_{1s} peak (before aging).

Table IV Effect of Water Immersion on the Binding Energy of N_{1s} Signal (in 90°C Distilled Water and Then Dried)

Immersion Time	Binding Energy (eV)
0	399.8
6 days	
Sample 1	400.2
Sample 2	400.2

Degradation Products

Table V shows the percent relative signal intensities of O_{1s}, N_{1s}, and Al_{2p} with respect to C_{1s}. As can be seen, Al can be detected, which suggests that the amount of extracted substance on the Al foil is very low. Due to the Al foil containing a high concentration of Al oxide, the concentration of oxygen detected in this test may not be very meaningful. The control sample shows some C, possibly indicating some contamination or adsorption of organic matter. However, the results show that the leaching products contain a high concentration of nitrogen, which can only be from the epoxy resin—hence, confirming that water immersion induces chain scission in the epoxy resin and that the degradation products can leach out.

Table VI compares the positions of N_{1s} signals for the leaching substances and the unaged resin. The results show that the N_{1s} signal for the leaching substances is situated at a lower binding energy compared with the unaged resin, suggesting that the degradation products contain a higher concentration of nitrogen carbon bonds than do the unaged resin. By considering the results in both Tables VI and IV, it may be reasonable to postulate that there are some unusual reactions involving nitrogen-containing functional groups which occur during hygrothermal aging. These reactions produce nitrogen-carbon-oxygen-containing functional groups in the resin and nitrogen-carbon bonds in the leaching substances.

The leaching substances were also studied by

Table V Relative Percentage XPS Peak Areas of the Leaching Products Deposited on Al Foil

Sample	O _{1s} /C _{1s}	N _{1s} /C _{1s}	Al _{2p} /C _{1s}
Leaching substances	3.4	0.85	0.49
Control ^a	6.4	0.00	1.2

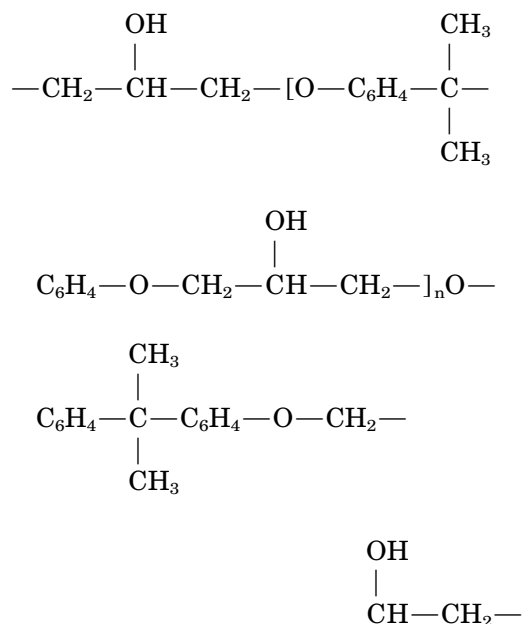
^a Al foil immersed in acetone.

Table VI Binding Energy of N_{1s} Signals

Sample	Binding Energy (eV)
Epoxy before aging	399.8
Leaching substance	399.1

FTIR. Figure 5 gives their spectrum. Compared with the spectrum of the unaged resin (Fig. 1), several noteworthy features are apparent:

- (A) The leaching substances have all the characteristic signals for the backbone structure of DGEBA:



i.e., 1508 and 831 cm⁻¹ for the *p*-phenylene group, 1183 cm⁻¹ for the bridge between the benzene rings, 1249 cm⁻¹ for the aromatic ether, and 2966, 2929, and 2876 cm⁻¹ for —CH₃ and —CH₂ groups. The result confirms that the backbone chains of DGEBA/DDA epoxy resin can be cut by hygrothermal aging and that segments leach out of the resin.

- (B) There is a very strong and broad signal between 3000 and ~ 3600 cm⁻¹. This signal can be assigned to the stretching of —OH and —NH groups, its broad range indicating the existence of intermolecular hydrogen bonds. Moreover, the existence of a new absorption at ~ 1556 cm⁻¹ for the leaching substances also confirms the

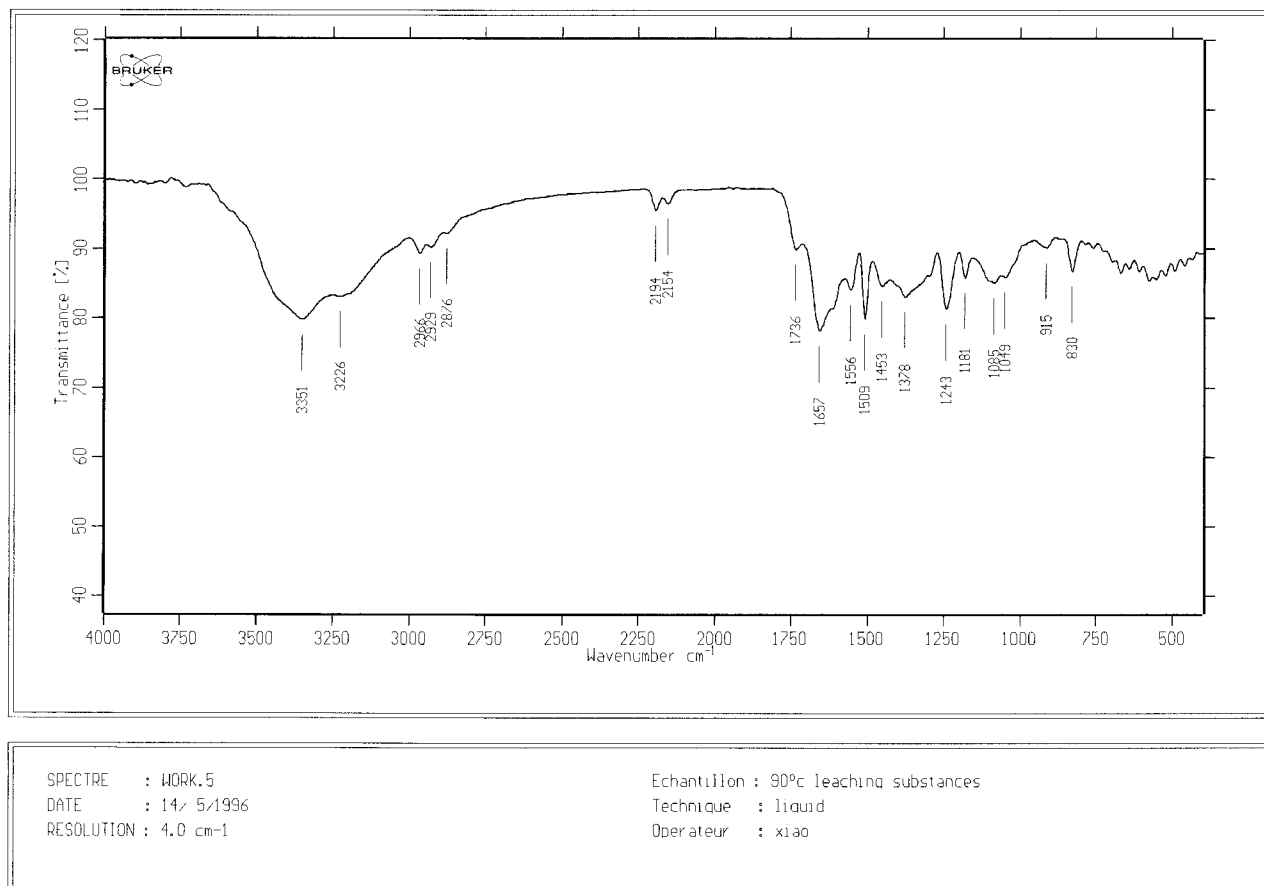


Figure 5 FTIR spectrum of the leaching substances from DGEBA/DDA resin.

- existence of —NH groups in the degradation products.
- (C) For the leaching substances, there is a doublet at 2194 and 2154 cm^{-1} . This signal is characteristic of the —NH—C≡N section in DDA,¹¹ while the unaged sample has only one peak at 2175 cm^{-1} , which is the absorption of nitrile groups.¹³
- (D) A strong absorption appears at 1736 cm^{-1} for the leaching substances compared with the unaged resin, which has only a small shoulder at the same position. The assignment of this signal is controversial, as reviewed in Ref. 10. Zahir¹³ assigned it to a urethane ester group, while some other researchers assigned it to a carbonyl group.^{16,17} Since XPS results do not suggest that there are —COO groups in the resin before and after aging, we also tentatively assigned it to carbonyl group.

Therefore, both XPS and FTIR results confirm

that the epoxy backbone chains can be cut during water immersion and then segments leach out. The leached-out segments have different chemical structures from those of the aged and unaged samples. They contain the —NH—C≡N structure, —OH groups, and a higher proportion of C—N, N—H, and —C=O groups.

DISCUSSION

Hygrothermal aging at 90°C induces irreversible changes to the chemical structure of the DGEBA/DDA epoxy resin. The results show that water not only brings about the incorporation of oxygen into the epoxy resin, particularly in the form of C—O and N—CO—N groups, but also produces the —NH—C≡N structure, a higher concentration of nitrogen carbon groups, and N—H groups in the degradation products. These results led us to postulate that the tertiary amine groups in the cured resin may well be the weakest points, re-

acting with water via hydrolysis and causing dissociated chain segments by scission, as shown in Scheme 1.

The low molecular weight scission products of this degradation reaction can leach out of the bulk resin; hence, we can find —OH, —NH, —NH—C≡N, and the main structure of DGEBA in the leaching substances. Moreover, the hydrolysis reaction introduces C—OH groups into the polymer chain, which could explain the XPS result of hygrothermal aging increasing the C—O group in the resin.

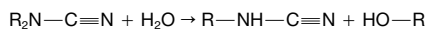
The increase in concentration of N—CO—N groups in the aged resin may be explained by analogy with one of the intermolecular rearrangement reactions occurring during the curing of DGEBA/DDA resin,¹³ as shown in Scheme 2.

It is conceivable that the hydrolysis product in Scheme 1 might provide the —OH groups and (or) —NH—C≡N groups to facilitate the above reaction. Since this reaction further crosslinks the resin, it would be difficult for the reaction products to leach out. Therefore, the resin would have more N—CO—N groups after aging. Furthermore, this reaction changes nitrogen—carbon bonds to nitrogen—carbon—oxygen bonds and, hence, might explain why the aged resin has a higher binding energy for the N_{1s} signal. The existence of —C=O groups in the leaching substances can also be explained by Scheme 2 since it is also conceivable that water might provide the —OH groups with which to react.

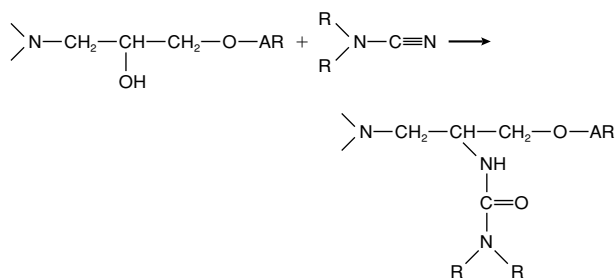
However, even though the mechanism proposed here is in good agreement with the experimental results obtained, it should not be regarded as the sole possible degradation mechanism. Other degradation reactions might also occur during hygrothermal aging.

CONCLUSIONS

1. The techniques of XPS and FTIR have been used to characterize the irreversible interactions between a DGEBA/DDA epoxy resin and water. The results clearly show that the epoxy backbone chains can be cut and segments leach out during hygrothermal aging.



Scheme 1



Scheme 2

2. After aging, the epoxy resin gains oxygen while losing some nitrogen. The increased oxygen content in the resin is mainly in the form of C—O and N—CO—N functional groups.
3. The degradation products contain not only the backbone structure of DGEBA, but also the —NH—C≡N structure, a higher concentration of carbon—nitrogen bonds, and —NH groups.
4. It is believed that water cuts the crosslink chains by hydrolysis reactions. Water reacts with the tertiary amine groups in the resin to form N—H and —OH bonds in the polymer chains. The reaction products might undergo further reactions either with each other or with the crosslink chains.

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