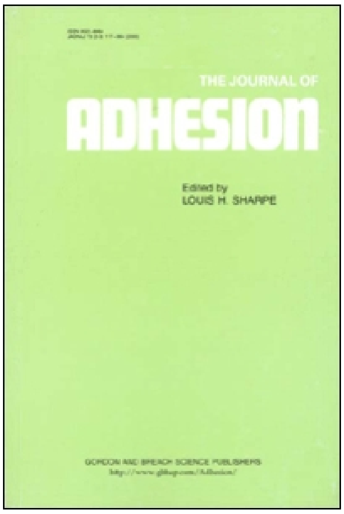

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# Factors Affecting the Processing of Epoxy Film Adhesives II. Moisture Content

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# Factors Affecting the Processing of Epoxy Film Adhesives

## II. Moisture Content

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Dielectric and thermomechanical analysis, infrared spectroscopy, and mechanical testing were used to study the changes which occur in the cure behavior of a 178°C (350°F) epoxy film adhesive, Hysol EA-9649. The response of the system was compatible with the catalyst type employed. The overall effect of increasing moisture content was an increase in flow accompanied by lower $T_g$ values in the cured film with no loss in ambient temperature tensile lap shear strength. These effects are interpreted in terms of the dicyandiamide portion of the adhesive catalyst system reacting with the absorbed moisture resulting in a cured adhesive of different structure but equivalent in bonded joint strength to those made with low moisture content adhesive.

## 1. INTRODUCTION

One of the major factors which control adhesive response during fabrication is the moisture content of the adhesive film. There have been limited reports in the literature alluding to the effects of moisture in resin/adherend systems including several suggested mechanisms related to the cure of epoxy resins with dicyandiamide. One of these involves interaction of water with a carbodiimide type intermediate to produce guanylurea.[1]

Dielectric analysis has been used to identify changes in an adhesive during cure using FM-73.†[2a] Both the plasticizing effect and resin advancement (cure) of the adhesive system containing moisture were identified but not explained in chemical terms.

A recent study describes the effect of moisture content on adhesive cure as measured by oscillating rheometry techniques in terms of dynamic viscosity,

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† An epoxy film adhesive made by American Cyanamid Co., Stamford, CT.

storage and loss modulus.[2b] The results showed a plasticizing effect at temperatures below 100°C. Above this temperature level an effect referred to as "an acceleration of the cure reaction" in the vicinity of 130°C indicated by an increase in viscosity was found. Moisture levels above 1.0 weight % gave the above described viscosity response. No chemical explanation as to the cause of the observed changes was given nor were the five adhesives identified.

The type of film adhesive used in the present study is normally shipped and stored at low temperatures to avoid catalyst activity prior to use. However, no specifications as to moisture content of the films are stipulated by the user or supplied by the vendor. Thus, under conditions where a roll of adhesive is repeatedly used and restored at low temperatures, the moisture content could vary as much as 1 to 2%. This is particularly true during the summer months if adequate precautions are not taken to control humidity levels.

The objective of the described investigation was to determine the effect of moisture content on the cure behavior and ultimate cure level of the commercially available 178°C (350°F) epoxy film adhesive Hysol EA-9649. This adhesive, available in supported and unsupported form, is an aluminum powder-filled epoxy system cured, in part, using dicyandiamide. Aging characteristics of the adhesive have been previously described.[3]

The effect of varying moisture content was investigated in both forms of the adhesive over a two weight percent range. The relationship between moisture level, adhesive softening point, adhesive flow and resulting bonded joint strength was determined.

Dielectric analysis and infrared spectroscopy were used to define the changes which occurred at varying moisture levels. Differences in the cure behavior of the films were related to the extent of reaction between the dicyandiamide catalyst and moisture that produced a new reactive catalyst which ultimately resulted in bonded joint assemblies of equivalent strength to those fabricated using low moisture content adhesive.

## 2. MATERIALS AND TECHNIQUES

The EA-9649 adhesive film used in the study was kindly supplied by the Hysol Division, Dexter Corporation, Pittsburgh, CA.[3]

The infrared spectra were obtained by dissolving a portion of the uncured adhesive in methyl ethyl ketone, centrifuging and evaporating the resulting solution under vacuum on a standard sodium chloride disk. The spectrometer was a Perkin-Elmer model 457. Comparative absorption band heights were obtained by ratio of changing bands with a static band to eliminate any film thickness effects.

Thermomechanical analysis ($T_g$) was carried out using a DuPont 990 thermal analyzer at a heating rate of 10°C/min.

Dielectric analysis was carried out as previously described.[3] Temperature was automatically recorded by using a thermocouple inserted directly into the two-ply adhesive lay-up.

Tensile lap shear specimens were prepared using 2024 aluminum alloy etched with FPL etchant. Six specimens were fabricated at once in a gang mold under compression. Suitable stops were employed to insure a bond line thickness of 5–7 mils. Tensile specimens were 1.27 cm (0.5 in.) overlap, 10.16 cm (4.0 in.) long, 2.54 cm (1.0 in) wide and 0.635 cm (0.25 in.) in thickness. The thick adherends were used to minimize the peel effect associated with thinner material. Testing was carried out on a MTS 810 test system at a crosshead speed of 0.127 cm/min.

Moisture content of the adhesive was determined by the Karl Fisher (aquametry) technique. The adhesive was dissolved in a 1:3 methanol/chloroform solution prior to addition to the standardized Karl Fisher reagent.

## 3. RESULTS AND DISCUSSION

The changes which took place in the adhesive films when cured at various moisture levels are listed in Tables I and II. Identifiable changes are in terms of increase in surface area (flow), shift in major softening point, moisture evolution and minor changes in resin gel point as measured by dielectric analysis. In addition, the initial dissipation factor of the film increased with increasing moisture level, as shown in Figures 1 and 2.

The steady increase in flow was found with both types of film indicating the absorbed moisture acted as a plasticizer. This was also reflected in a lowering of the major melting point of the adhesive before cure. Thus, the time between

TABLE I

Moisture effects on EA-9649 supported adhesive

| Exposure time (hr) | Moisture content (weight %) | ISA[a] (flow %) | Major softening[b] point (°C) | Moisture evolution[b] (°C) | Gel point[b] (Time, min) |
|---|---|---|---|---|---|
| "as received" | 0.6 | 70 | 76 | — | 81 |
| 1 | 1.1 | 78 | 68 | 88 | 80.5 |
| 4 | 1.6 | 90 | 60 | 88 | 79 |
| 6 | 1.4 | 138 | 58 | 75–100 | 76 |

[a] ISA = increase in surface area.

[b] Dielectric analysis, heating rate = 2.5°C/min.

TABLE II

Moisture effects on EA-9649 unsupported adhesive

| Exposure time (hr) | Moisture content (weight %) | ISA[a] (flow %) | Major softening[b] point (°C) | Moisture evolution[b] (°C) | Gel point[b] (time, min) |
|---|---|---|---|---|---|
| "as received" | 0.5 | 25 | 79 | | 81 |
| 1 | 1.3 | 31 | 55 | 90 | 80.5 |
| 4 | 3.5 | 45 | 55 | 90 | 80 |
| 6 | 1.9 | 55 | 50 | 95–120 | 78.5 |

[a] ISA = increase in surface area.

[b] Dielectric analysis, heating rate = 2.5°C/min.

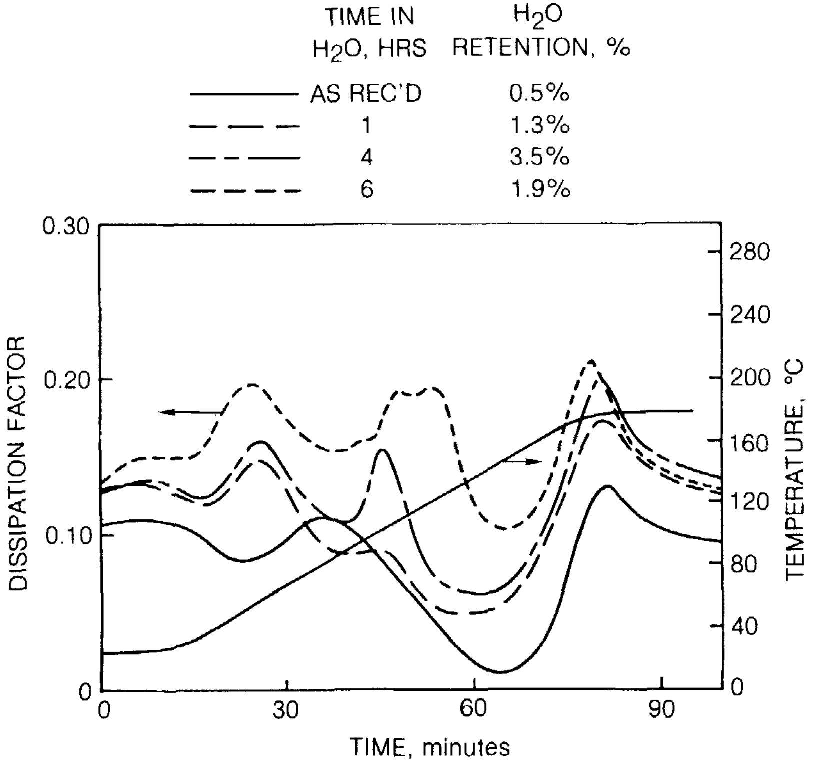


FIGURE 1 Dissipation factor *vs.* time EA9649 unsupported.

softening and gelation was increased resulting in a longer flow period at low viscosity. The loss of absorbed moisture during heatup was more evident with the unsupported film than the supported film at the lower moisture levels. This was probably due to the difference in film thickness as well as the absorption of water by the nylon scrim cloth used in the supported adhesive.

The unexpected change (decrease) which occurred in measured moisture level with increasing exposure in both types of film indicated the possible interaction of water with one of the active catalysts in the adhesive system. Six separate adhesive film samples produced the same result, a decrease in measured moisture level after exposure for a given time period.

Accompanying these changes in resin behavior was the higher dissipation factor shown by all samples compared to "as received" adhesive with relatively minor changes in final gel temperature. These results are indicative of a different final molecular structure in either a fully or partially cured state. This is more fully discussed below.

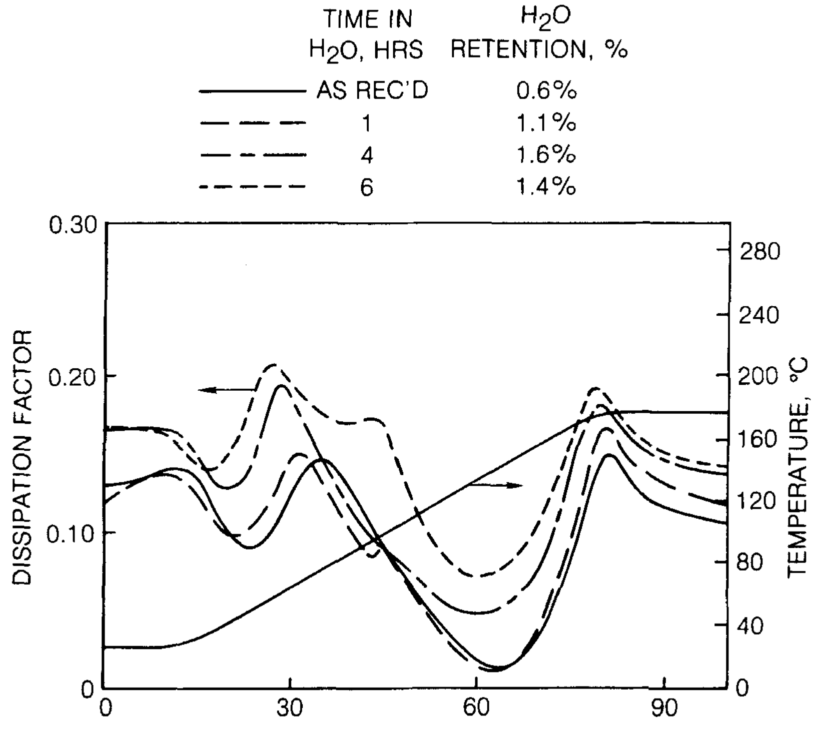


FIGURE 2 Dissipation factor *vs.* time—EA9649 supported.

TABLE III

Effect of initial moisture content on $T_g$ of cured EA-9649 adhesive[a]

| Moisture conditions | $T_g$, °C Unsupported | $T_g$, °C Supported |
|---|---|---|
| "as received" | 200 | 220 |
| 1-hr soak | 183 | 213 |
| 4-hr soak | 180 | 205 |
| 6-hr soak | 185 | 200 |

[a] Determined on cured film by TMA analysis.

The effect of initial moisture content on the $T_g$ of the cured film samples obtained during dielectric analysis is shown in Table III. In both cases, a decrease in $T_g$ to a lower nearly constant value was found to occur compared to the "as received" adhesive, particularly in the case of the unsupported film. These results would indicate that a fully cured structure of different crosslink density or chemical structure was obtained as a result of the absorption of moisture. Thus, the initial moisture content of the film not only affects the rheological properties of the curing film, but also influences the resulting structure or cure level obtained at a given set of conditions.

Examination of the infrared spectra of the moisture containing films showed that changes occur in four spectral regions as illustrated in Figures 3 and 4.

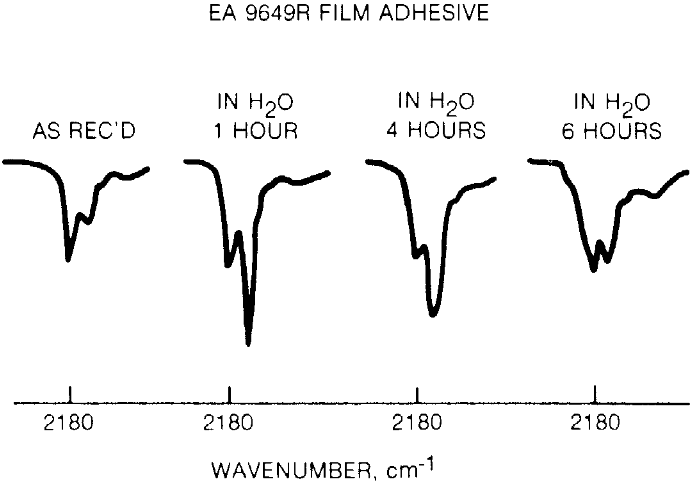


FIGURE 3 Change in dicyandiamide absorption with moisture content.

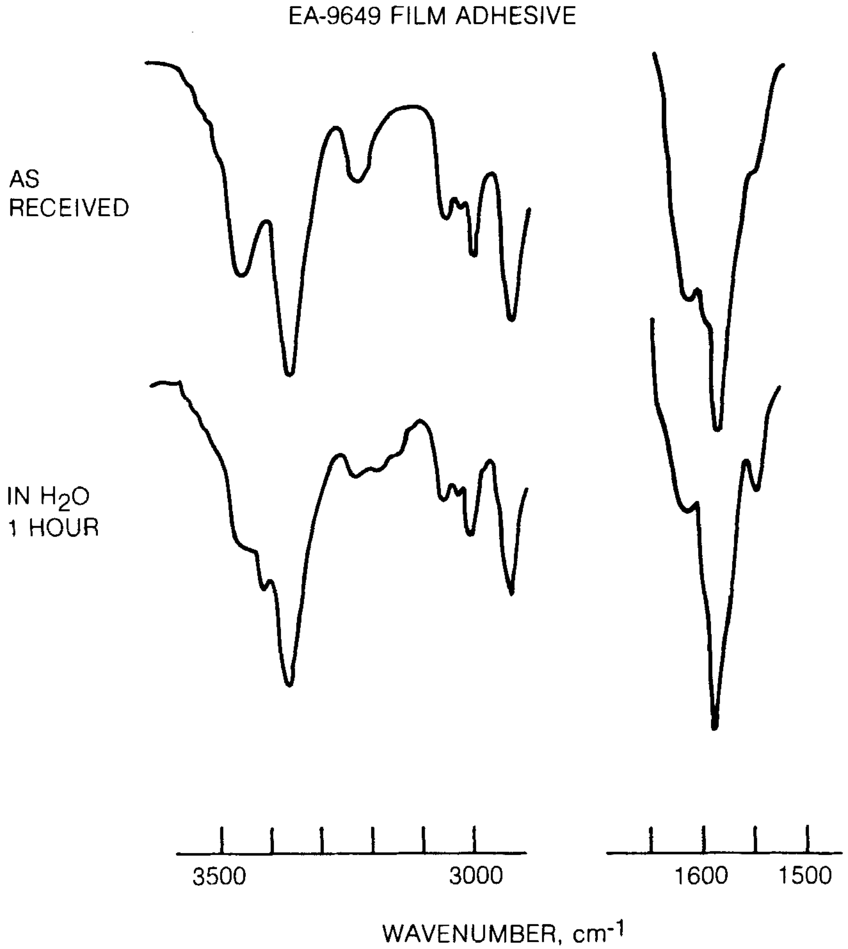


FIGURE 4 Change in EA-9649 absorption spectrum with moisture.

These changes are briefly summarized as follows:

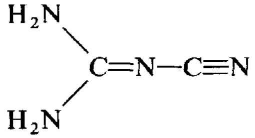
3500–3400 cm$^{-1}$—The initial single peak at 3460 cm$^{-1}$ in the 1- and 4-hr time period changes to two peaks; a sharp, weak 3420 peak and a weaker 3460 peak. After 6 hr this peak again becomes a single peak identical to the starting material.

3250–3140 cm$^{-1}$—The initial single peak at 3230 cm$^{-1}$ in the 1- and 4-hr time period becomes a broad band having three weak absorption peaks at 3230, 3180 and 3140 cm$^{-1}$. Again, as above, after 6 hr this spectral area returns to a single peak identical with the starting material.

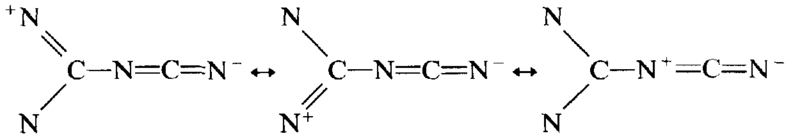
2180–2140 cm$^{-1}$—Initially, the 2180 cm$^{-1}$ peak is more intense than the 2140 cm$^{-1}$. Within one hour exposure the relative peak intensities are reversed with the 2140 cm$^{-1}$ peak becoming much stronger. After the 6-hr time period the relative intensities have become almost equivalent and weaker.

1550 cm$^{-1}$—Initially there is essentially no absorption in this area, only a very weak shoulder on the strong absorption at 1590 cm$^{-1}$. After 1 hr the shoulder resolves into a distinct sharp, although weak, band at 1550 cm$^{-1}$ which is also present in the 4-hr spectra. After 6 hr the peak intensity decreases to an easily seen shoulder of the strong band at 1590 cm$^{-1}$ (stronger than in the "as received" spectra).

Crystallographic,[4] infrared[5] and nuclear magnetic resonance[6] evidence has been reported describing the structure of solid dicyandiamide as having a planar, conjugated structure containing only one type of nitrile, *i.e.*,



The doublet at 2180–2140 cm$^{-1}$ has been interpreted as being due to the electronic resonance forms:[7]



all of which contain the carbodiimide (N=C=N) type linkage. Based on bond length calculations there is considerable delocalization of the $\pi$ electrons extended over the whole six atom system indicating that the molecule is a resonance hybrid.[6] A similar interpretation has been cited for the existence of the doublet in the spectrum of cyanamide.[7] Disubstituted carbodiimides have strong absorption at 2150–2100 cm$^{-1}$.[7]

The fact that the 2180–2140 cm$^{-1}$ doublet is affected by addition of polar groups to an epoxy adhesive system has been reported.[8] Increases in polarity concentration were found to result in decreases in the longer wavelength absorption peak. This is analogous to the changes seen in Figure 3 with water absorption in that a decrease in one band (2180 cm$^{-1}$) was accompanied by an increase in the other (2140 cm$^{-1}$). Addition of water to the dicyandiamide molecule could also account for the spectral changes noted in the 3500–3400 and 3250–3140 cm$^{-1}$ regions. The initial intermediates could contain as many as 2 C=NH moieties. Of particular interest is the emergence of the band at 1550 cm$^{-1}$. Absorption in this region has been interpreted to be due to the

CNH grouping found in amidines and mono-substituted amides.[9] One of the possible protonated tautomers of dicyandiamide would contain this group.

An important factor to consider in the interpretation of these results is that it is only that portion of the dicyandiamide which has been dissolved in the epoxy resin system or the absorbed water or both which undergoes the spectral changes cited above. The material which remains in solid form is probably not affected. It has been shown that dicyandiamide solubility is enhanced by resin additives and low molecular weight amine-epoxy adducts.[10] Thus, the level of soluble dicyandiamide could be quite high in the EA-9649 adhesive formulation. The solubility of dicyandiamide in water is 3% at room temperature. There is the added possibility that as dicyandiamide interacts with water additional material dissolves in the system to give increasing concentrations of soluble compound.

Based on the reported literature interpetations as to the structure of solid dicyandiamide,[4,5,6] it is assumed that the electronic structure of dicyandiamide in solution is the weighted average sum of the resonance and proton tautomer structures which could exist. All of these contain either a nitrile or a carbodiimide moiety capable of undergoing hydrolysis to yield amido groups.

Water does react with dicyandiamide to produce guanylurea as the initial reaction product in dilute acidic or basic solutions.[11,12] Since the adhesive film system used in our study is essentially a non-aqueous environment extremes in hydrogen ion activity can be expected which could result in greatly enhanced hydrolysis rates. Thus, there is every possibility that a reaction between dicyandiamide and water could take place at room temperature.

Based on these considerations, it is postulated that the dissolved dicyandiamide undergoes a hydrolysis reaction to produce guanylurea. Such a reaction could proceed by two possible routes. First, via reaction of water with the carbodiimide-like resonance forms by a mechanism similar to that proposed for disubstituted carbodiimides.[13] Secondly, *via* the direct hydrolysis of the nitrile group involving the protonated tautomer.[14]

Because of the need of further investigation to define the exact mechanism, the hydrolysis of dicyandiamide is presented as shown in Figure 5. This representation would account for the changes associated with the 1550 cm$^{-1}$ and 2140 cm$^{-1}$ peaks which increase on water uptake then decrease as reaction proceeds to guanylurea formation which, in the electronically favored state, contains no CNH amide or carbodiimide type linkages. That guanylurea is best represented by the structures shown is based on the effect of conjugation in analogy to the accepted structure for dicyandiamide. An alternate possibility is that only hydrated dicyandiamide results from the absorption of water and the peak shifts at 2180–2140 cm$^{-1}$ account for this change in compound polarity. The additional spectral changes noted, however, appear to preclude this interpretation. In addition, during cure of the adhesive, water

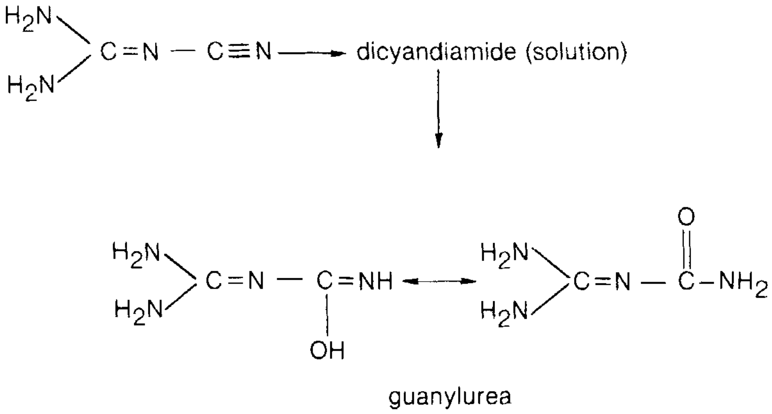


FIGURE 5 Hydrolysis of dicyandiamide.

could react with dicyandiamide at elevated temperatures and produce guanylurea. Unfortunately, the carbonyl region does not reveal any discernible differences which may be due to formation of a reaction product of water and dicyandiamide. This is undoubtedly due to masking of any such absorption bands by the strong absorption resulting from the major peaks formed with the other catalyst and epoxy as well as unaffected dicyandiamide. Since substituted guanidines have been suggested as the explanation for the appearance of the 1730 $cm^{-1}$ peak which emerges on cure of epoxy with dicyandiamide, the inability to see any differences in the final cured spectra of the "as received" and water soaked samples is not surprising.

The rate at which the conversion of dicyandiamide to the guanylurea occurs will depend on the concentration of solubilized dicyandiamide, moisture diffusion rate, viscosity of the medium, epoxy resin type, and the affinity of the scrim cloth (supported film) and filler for moisture. A longer time period for inversion of the cyano absorption peaks was noted in the supported adhesive. Based on the change in the infrared spectra, the time required is approximately one hour at a moisture level greater than one weight percent for the unsupported adhesive. More exact measurements than those used in this study will be required to establish accurate reaction rates and the effect of added substituents on the interaction of dicyandiamide with water.

The suggested mechanism would account for the measured free water concentration decreasing after a given time period. The sharp decrease noted in the 2140 $cm^{-1}$ absorption peak would occur with formation of the guanylurea since this compound contains no cyano grouping. The remaining peak intensity at 2180–2140 $cm^{-1}$ relates to the presence of non-dissolved dicyandiamide.

The guanylurea formed during the interaction with water should function as an active catalyst in the cure of the adhesive and may explain the "accelerated cure" effects previously cited.[2] It would be anticipated, however, that because of the difference in structure, the final cured state of the adhesive from a structural standpoint would be different from that associated with a dicyandiamide cured system. This could result in a different glass transition point as indicated in Table III. The reported studies on epoxy resin systems, in which competing network-forming reactions having different reaction rates led to different molecular structures, would explain the results found in the present study.[15]

An alternate explanation for the lower $T_g$'s is the possible reaction of water directly with epoxy groups to act as a chain stopper or crosslinker. Two factors appear to eliminate this possibility. First, from the dielectric spectra the loss of free water is clearly evident prior to reaching the gel point of the curing system. Secondly, the ratio of the broad hydroxyl band (3400 cm$^{-1}$) formed on curing the "as received" and soaked films to the aliphatic and aromatic C—H bands in the spectrum is the same. It would be expected that the hydroxyl band would be stronger in the soaked sample spectra if significant hydroxyl end blocking had occurred.

In order to determine the effect of the added moisture on ultimate bond strength, a series of tensile lap shear specimens were fabricated using supported adhesive exposed to water for the same time periods indicated above. The results are listed in Table IV. It was found that there was essentially no change in bond strength at any of the varying moisture levels. There was a slight increase in porosity in the high moisture content bonded specimens compared to the standard. The porosity level was less than 3% in all cases.

Examination of the dielectric spectra reveals that essentially all of the free moisture is eliminated from the adhesive film prior to gelation. Thus, due to the high gel temperature of the resin, the unreacted water is lost during the programmed heatup in the low viscosity region of the adhesive cure schedule producing a low level of porosity. The guanylurea produced which replaced, at

TABLE IV

Effect of initial moisture content on tensile lap shear strength of EA-9649 adhesive[a]

| Moisture content % | TLS, psi | (MPa)[b] |
|---|---|---|
| standard, 0.5 | 4944 | (34.1) |
| 1 hr, 0.8 | 5362 | (36.9) |
| 4 hr, 2.1 | 4841 | (33.4) |
| 6 hr, 1.6 | 4961 | (34.2) |

[a] Aluminum 2024 alloy, supported film.
[b] Average of five samples.

least in part, the dicyandiamide results in a cured structure having bond strengths equivalent to that normally associated with EA-9649 adhesive.

Resin adhesive systems which cure at lower temperatures [*i.e.*, 126°C (250°F)] and contain moisture sensitive catalysts have been found to be adversely affected by the presence of excess moisture and result in bonded joints having lower strengths.

The ultimate proof as to whether a water-dicyandiamide reaction does occur must be the isolation and structural identification of the postulated product. Variations of the liquid chromatography procedures described for the quantative analysis of dicyandiamide[10] will be investigated and reported when complete.

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