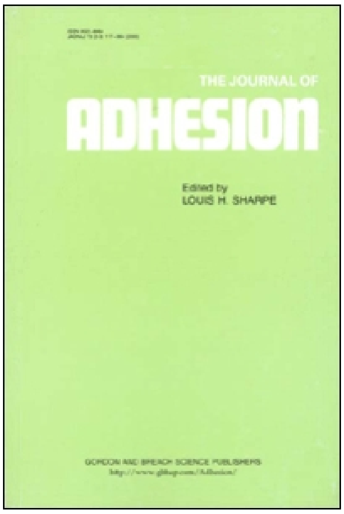

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Factors Affecting the Processing of Epoxy Film Adhesives: I. Room Temperature Aging

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Factors Affecting the Processing of Epoxy Film Adhesives

I. Room Temperature Aging

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Differential scanning calorimetry, dielectric analysis, and infrared spectroscopy were used to study the changes which occur at room temperature in an epoxy film adhesive cured, in part, with dicyandiamide. The principal reaction involved interaction of the catalyst with the lower molecular weight resins in the formulation. The overall effect was demonstrated by an increase in resin viscosity, softening point and overall cure time, accompanied by a decrease in resin flow and ultimate bonded joint strength.

INTRODUCTION

The degree of room temperature shelf-aging which occurs in an adhesive between time of manufacture and actual use in a bonding application is one of the factors controlling the fabrication parameters required to achieve optimum bond strength. Ultimate bond strengths can also be affected if extended aging has taken place, regardless of the fabrication process employed. The objective of the described investigation was to determine the effect of room temperature shelf-aging on the properties of the commercially available 178°C (350°F) epoxy film adhesive, Hysol EA-9649. This adhesive, available as supported or unsupported film, is an aluminum powder-filled epoxy system cured, in part, using dicyandiamide.

The room-temperature aging of both types of film was studied over a three-month period. The relationship between aging time, adhesive softening and gel point, and the resulting effect on adhesive flow was determined.

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Differential Scanning Calorimetry (DSC), dielectric analysis and infrared spectroscopy were used to define the changes which occurred on aging. Differences in the cure behavior of the aged films were related to the extent of reaction between the dicyandiamide catalyst and the epoxy resins in the adhesive which produced an initial resin configuration differing from that normally encountered using non-aged adhesive.

MATERIALS AND TECHNIQUES

The EA-9649 adhesive films used in the study were obtained in both supported and unsupported form from the Hysol Division of Dexter Corp., Pittsburg, CA. This adhesive is a rubber-modified, aluminum powder-filled epoxy resin-type cured, in part, with dicyandiamide and designated as a 178°C (350°F) curing system. Aging was carried out at room temperature, 26°C, with the protective cover films removed just prior to testing.

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 the changing bands with a static band to eliminate any film thickness effects.

Differential Scanning Calorimetry (DSC) measurements were carried out using a DuPont 990 Thermal Analyzer at heating rates of 5, 10 and 20°C/min. Samples were heated in standard closed aluminum cups in an air atmosphere. The instrument was calibrated for temperature with indium. Gel temperatures were designated as the peak temperature obtained during the exothermic portion of the cure curve.

Dielectric analysis curves were obtained using a Tetrahedron, Inc. Audrey Model 203 dissipation factor bridge and a small laboratory press. Two plys of the adhesive, 7.6 × 7.6 cm square, between two aluminum electrodes, were used to determine the increase in surface area (flow) which occurred during cure. Teflon-coated glass cloth and Kapton film were used to separate the electrodes from the adhesive surface. A heating rate of 2.5°C/min was maintained during the cure schedule up to 180°C. Pressure was maintained at 50 psi. After the gel point, the temperature was held constant for an additional 30 minutes. All scans were carried out at 1 KHz.

RESULTS AND DISCUSSION

The changes which took place in the adhesive films during the aging period are listed in Tables I and II. Identifiable changes are in terms of increase in surface area (flow) during cure, initial and major softening point, and resin

TABLE I

Room temperature aging effects on EA-9649 supported adhesive

Aging time (days)	ISA[a] (flow %)	Initial softening[b] point, °C	Major softening[b] point, °C	Gel point[b] time, min	Gel point[c] DSC (°C)
0	73	23·5	72	66 (178°C)	194
30	54	30.5	81	64	190
66	32	48	97	62.75	188.5
100	30	61	98	61.5 (173°C)	186.5

[a] ISA = Increase in surface area
[b] Dielectric analysis, heating rate = 2.5°C/min
[c] DSC, heating rate = 5°C/min

TABLE II

Room temperature aging effects on EA-9649 unsupported adhesive

Aging time (days)	ISA[a] (flow %)	Initial softening[b] point, °C	Major softening[b] point, °C	Gel point[b] time (min)	Gel point[c] DSC (°C)
0	21	25	76	66 (178°C)	190
30	20	32	84	64.5	188
66	14	47	98	63.5	187
100	13	58.5	102	61.25 (174°C)	186

[a] ISA = Increase in surface area
[b] Dielectric analysis, heating rate = 2.5°C/min
[c] DSC, heating rate = 5°C/min

gel point as measured by dielectric analysis and DSC. Essentially no change in ISA (flow) was found to occur in the unsupported tape over the first thirty-day aging period although there was a small increase in the initial softening point accompanied by an increase in the major softening point (8°C) with a very slight decrease in gel point. The supported tape showed a nineteen per cent decrease in flow with a 9°C increase in the major softening point.

During the next aging period, 30 to 66 days, there was a marked drop in ISA (flow) in both the supported and unsupported tapes accompanied by a slightly larger increase in both initial and major softening points. A slight decrease in gel point was also noted. Thus, during the second aging period, the time difference between the softening and gelation temperature decreases. This could account for the decrease in flow since the time to allow flow has decreased and the viscosity of the system increased through the temperature range where movement of the resin film can occur.

After the 66-day aging period, there were minor changes in the flow and softening point of the two adhesive systems. These results indicate the rate of resin advancement decreased sharply after the 66-day period. This is probably related to the increase in viscosity of the system resulting in a lower diffusion rate of reactive catalyst as well as a concentration effect.

The differences in degree-of-flow between the two types of adhesive films is attributable to the difference in initial film thickness. The unsupported tape had an average thickness 54 % that of the supported adhesive.

The changes which occurred in the adhesive gel point over the aging period are identified by a shift to a lower gel temperature, as illustrated in Figures 1 and 2, using DSC analysis. Similar techniques have been reported for defining

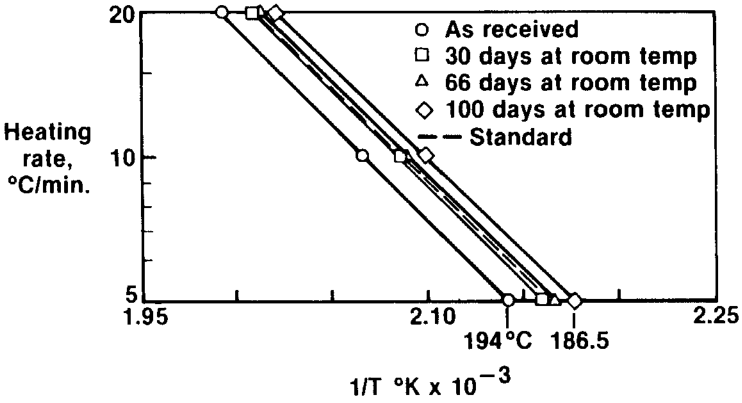

FIGURE 1 Change in gel temperature with heating rate—EA-9649 supported.

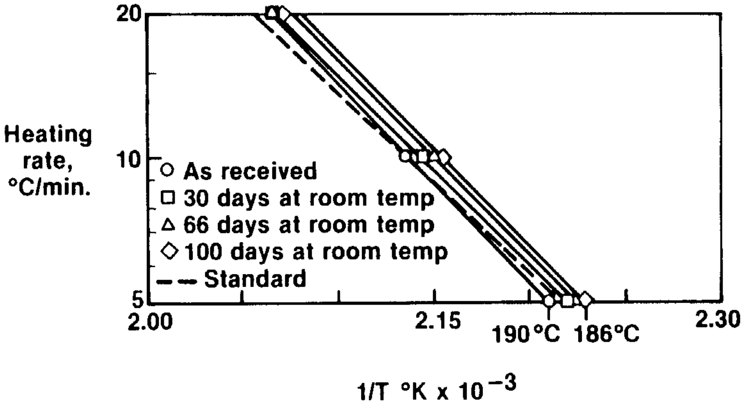

FIGURE 2 Change in gel temperature with heating rate—EA-9649 unsupported.

cure advancement in fiber-reinforced epoxy composite systems.[1] The temperature shifts are in agreement with those determined by dielectric analysis at a slower heat up rate. As expected, the more rapid heat up rate resulted in gelation at a higher temperature. Comparison with what has been identified as standard EA-9649 is indicated for each adhesive type. The unsupported film was initially the same as the standard sample while the supported film gelled at a higher temperature than the standard at a given heat up rate. Based on additional studies, both at Hysol and UTRC, this variation from the standard is due primarily to a difference in catalyst content. Thus, the supported adhesive used in this study had a slightly lower catalyst content than the standard sample. It should be noted that the DSC technique cannot be used to distinguish between variations in catalyst content and changes which occur due to the shelf-aging prior to adhesive usage since both effects cause gel point shifts over the same temperature range. Once a specific lot of adhesive has been received and "fingerprinted" by DSC, any variations which do occur on aging can be readily detected.

Dielectric analysis has been used extensively in the study of eopxy resin polymerization reactions, as demonstrated with reinforced prepregs,[2] coatings,[3] casting compounds,[4] and model systems.[4] Dielectric curves obtained on each of the aged adhesive films simultaneously with the flow of measurements, are shown in Figures 3 and 4. With the supported EA-9649, two resin softening temperatures are evident. The initial shallow drop in dissipation showed peak temperatures progressing from 23.5 to 61°C as

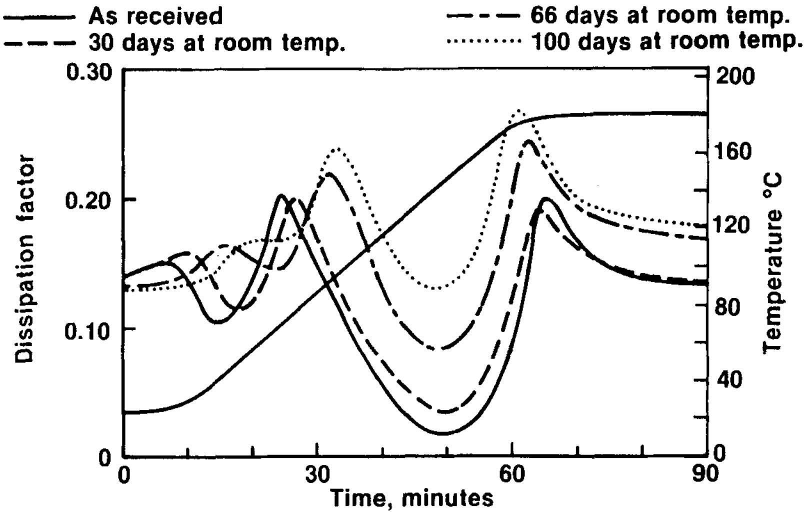

FIGURE 3 Dissipation factor vs. time—EA-9649 supported.

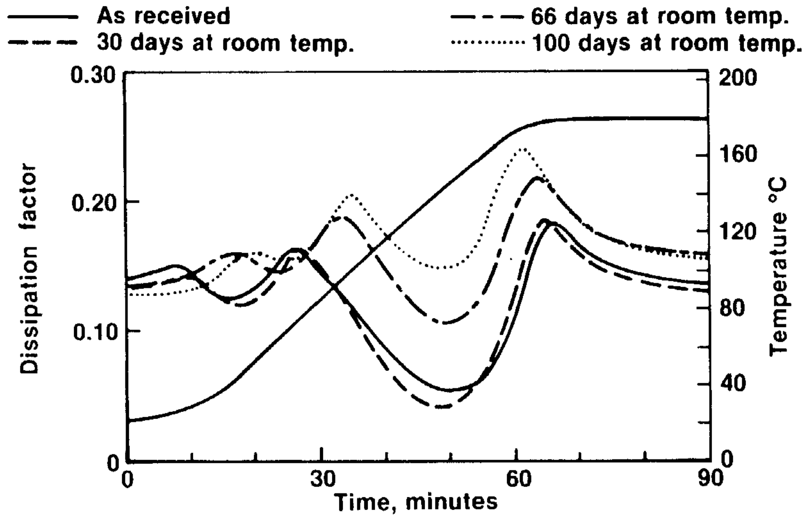

FIGURE 4 Dissipation factor *vs.* time EA-9649 unsupported.

aging time increased. The last two time periods resulted in less change in the dissipation factor profile, indicating less variation in the viscosity through the temperature range. In both cases after 100-day aging, there was essentially no drop in viscosity. The initial softening point is probably due to the lower molecular weight epoxy resins used in the adhesive. The major adhesive softening peak indicated by a large drop in dissipation factor varied over a range of 72° to 98°C with the largest change evident between the 30- and 66-day aging periods. As at the lower temperatures, the degree of change in dissipation factor between the softening point and the gelation peak decreased as aging time progressed.

A similar change was found to take place in the two resin softening temperature regions with the unsupported tape, Figure 4. The temperature variations were over the same range as in the supported system. The viscosity increase shown by a decrease in dissipation factor profile between melting and gelation was also evident.

Accompanying these changes in resin behavior was the decreased time-period between the major softening temperature and the gel peak. Thus, the degree of additional cross-linking or branching required to reach gelation appears to be less the longer the aging time, indicating some branching has occurred in the adhesive. The higher dissipation factor shown by the 66- and 100-day samples at the end of the heating cycle is indicative of a different final molecular structure which, because of steric considerations, would require a longer heating cycle or higher temperature to reach complete cure. This is more fully discussed below.

The aged adhesive films exhibited complete solubility in methyl ethyl ketone. The resulting solutions were used to prepare coated sodium chloride disks for infrared analysis. Examination of the infrared spectra showed a decrease in oxirane (epoxy) ring content, 910 cm^{-1}, with an increase in the cyano absorption, 2180 cm^{-1}, as aging progressed. There was also a noticeable increase in the hydroxyl absorption, 3430 cm^{-1}, while the —C=NH imino absorption at 1625 cm^{-1} slowly decreased throughout the aging period.

The marked change which occurred during aging in the doublet associated with dicyandiamide at 2180 and 2140 cm^{-1} in both adhesive tapes is shown in Figure 5. Reported studies on the structure and reactions of dicyandiamide[5,6] have alluded to the two tautomeric forms associated with these absorption peaks being due to the cyano group conjugated with unsaturation, 2140 cm^{-1}, and the nonconjugated form, 2180 cm^{-1}, as illustrated in Figure 6. The conjugated form predominates in the solid-state in equilibrium with the nonconjugated form which exists primarily in solution. The possible existence of a carbodiamide structure in solution has also been suggested.[7] The partial solubility of dicyandiamide in epoxy resins is well-known and the effect of particle size and solublizers on the effectiveness of dicyandiamide cure of bisphenol-A-epoxy systems has been reported.[8]

The fact that dicyandiamide is partially soluble in the resin matrix as the adhesive film is fabricated would explain the existence of the doublet shown

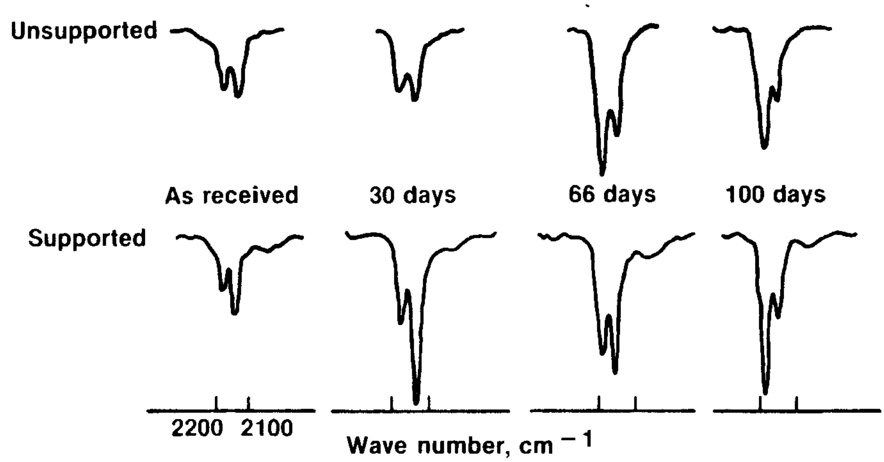

FIGURE 5 Change in dicyandiamide absorption with room temperature aging—EA-9649 adhesive.

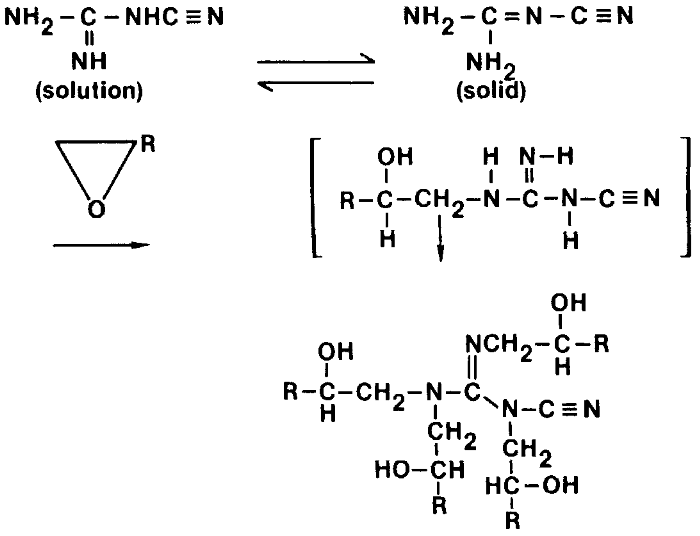

FIGURE 6 Room temperature reaction of dicyandiamide with epoxy resin.

in the infrared spectrum. Solution in an aprotic solvent, followed by evaporation, would not be expected to drastically change the ratio of the two tautomeric forms in the resulting film. Thus, the shift in absorption intensities of the 2180 and 2140 cm^{-1} peaks suggests the further solublization of solid dicyandiamide in the resin mixture as reaction at room temperature of soluble catalyst proceeds. The time differences associated with spectral changes in the two tapes may be due to variation in particle size or degree of dispersion of the catalyst in the adhesive film.

The reaction of dicyandiamide with the epoxide ring has been described as proceeding with formation of α-hydroxy-N-alkylcyano guanidines which ultimately results in the four available hydrogens of dicyandiamide being reacted during the cure process.[9] This proposed mechanism could account for the observed changes in the infrared spectra of the aged samples. Reaction of the nonconjugated (soluble) tautomerer with epoxy groups would cause a shift in the initial solubility equilibrium allowing more dicyandiamide to solublize as reaction proceeds at room temperature, thus causing a decrease in concentration of the conjugated form with the resulting decrease in the absorption of the 2140 cm^{-1} peak. Increased polarity of the resin system due to guanidine formation would be expected to facilitate catalyst solubility. That complete solublization of the catalyst during the aging period did not occur is indicated by the presence of the 2140 cm^{-1} absorption peak after the 100-day aging period. The extent to which the available reactive hydrogens in the catalyst are reacted at room temperature has not been determined in the present study. Additional investigation is in progress to define the extent of this reaction. However, it is apparent that since the epoxy resins used in the adhesive are at least di- or tri-functional, or possibly higher, an increase in molecular weight has taken place due to cross-link formation or branching but at a level below that required for gelation.

Interpretation of the data in Tables I and II and the dielectric curves in Figures 3 and 4, suggests that up to the 30-day period although a significant increase in resin softening (melting) point has occurred, sufficient reaction which would lead to a high level of branching and produce a large viscosity increase has not taken place, as indicated by the small change in resin flow in the unsupported system. The decrease in flow in the supported tape is more evident due to the large volume of resin in the test specimen. At some point between 30 and 66 days, this critical level was reached, as shown by the marked drop in resin flow and an increase in the resin softening point above 90°C for both systems. After this time period, further decrease in resin flow did not occur, possibly due to a decrease in reactivity of soluble dicyandiamide because of steric considerations or diffusion due to the structures formed which produce the higher viscosity. Both the dielectric and DSC curves reflect the increase in molecular weight of the total system as aging time increased.

Reported studies in epoxy systems have shown that if there are competing network-forming reactions having different reaction rates than it would be anticipated that different molecular structures should result.[10] The intermediate structures formed by reaction of the epoxy resins with catalysts during room temperature aging could be quite different from those found under normal curing conditions at elevated temperature. In addition, studies with epoxy coatings[3] have shown that the higher the initial molecular weight of the epoxy resin, the higher the initial softening point and a longer cure time is required for complete reaction if advances in molecular weight occur at a lower than standard cure temperature.[11,12] These factors, higher initial molecular weight prior to cure and a different molecular structure than encountered under normal circumstances, would be reflected by a higher dissipation factor at the end of the standard cure cycle, as indicated in Figures 3 and 4. Thus, it would be expected that these effects, combined with a decrease in flow capability, would result in a lower bonded joint strength compared to a normally-processed joint. Bonded joints prepared from the 100-day aged samples showed a 25 percent decrease in tensile lap shear strength compared to specimens fabricated from non-aged adhesive.

Determination of *Tg* points, using DSC analysis on the processed films at the end of each aging period, also reflected the effect of room-temperature aging. The *Tg* decreased from 210°C to 203°C over the aging period. In addition, the curves for the 66- and 100-day samples showed the presence of unreacted dicyandiamide catalyst having a melting point of 220°C at the 10°C/min heat-up rate used for the analysis.

The lower bonded joint strengths and the decrease in *Tg* together with the higher final dissipation factor at the end of the cure cycle suggest that the principal reaction involved in room-temperature aging of the EA-9649 adhesive film is one of increasing molecular weight due to reaction of the dicyandiamide catalyst with the lower molecular weight resins used in the formulation. The structural changes which occur at room temperature affect resin flow and produce a different final resin configuration than encountered using standard cure conditions which not only affects the ultimate bond strength but requires a modified cure cycle to achieve complete cure.

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