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FACTORS AFFECTING THE PROCESSING OF EPOXY FILM ADHESIVES

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ABSTRACT

The increasing awareness that adhesive performance is controlled not only by the condition of the adherend surface but also the condition or "state" of the adhesive and the process parameters used during fabrication is expected to result in improved reliability as well as bond performance. The critical process variables which have been found to control adhesive bond formation and ultimate bond strength in 250°F and 350°F curing epoxy adhesives will be described in terms of fabrication parameters and adhesive characteristics. These include the heat-up rate and cure temperature during processing and the adhesive moisture content and age condition (degree of advancement). The diagnostic methods used to delineate the effects of these process variables on adhesive performance will be illustrated. These are dielectric, thermomechanical (TMA) and dynamic mechanical (DMA) analyses. Correlation of test results with measured mechanical tensile lap shear strengths of bonded joints will be presented and the results briefly discussed in terms of the additives and hardeners used in the adhesive systems.

DEFECTS IN ADHESIVE BONDS

- Porosity/internal voids
- Disbonds (adhesive failure)
- Improper cure
- Inclusions/foreign material
- Bond line variation

Control and an understanding of how processing variables affect the adhesive and final joint properties are mandatory if high levels of reproducibility and reliability are to be achieved. Processing variables can be separated into two classes; those related to the fabrication parameters:

- Pressure/temperature control
- Part design
- Heat-up rate

and those related to the adhesive:

- Adhesive quality (lot-to-lot component variations)
- Surface primer condition
- Moisture content
- Age condition of the adhesive

Studies at UTRC have addressed the effect of aging[1], and moisture content[2] on EA-9649 performance during bond fabrication. These factors are directly related to the condition of the adhesive at time of bonding. Fabrication parameters, such as variation in cure temperature, have also been identified as critical to the ultimate performance of bonded joints[3], as has heat-up rate, one of the important fabrication variables which affect the processing of epoxy adhesives[4]. Non-optimized conditions related to any of these four variables can result in one or more of the above identified defects.

AGING EFFECTS

- Resin soluble portion of catalyst reacts with epoxy to produce:
  - Increased viscosity (decreased flow)
  - Lower level of cure
  - Decreased bond strength

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

(From ref. 1)

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 the 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. The changes which took place in the adhesive film during the aging period are listed above. Identifiable changes are in terms of increase in surface area (flow) during cure, initial and major softening point, and resin gel point as measured by dielectric analysis and DSC. The supported tape showed a nineteen per cent decrease in flow with a 9°C increase in the major softening point over the first thirty day aging period.

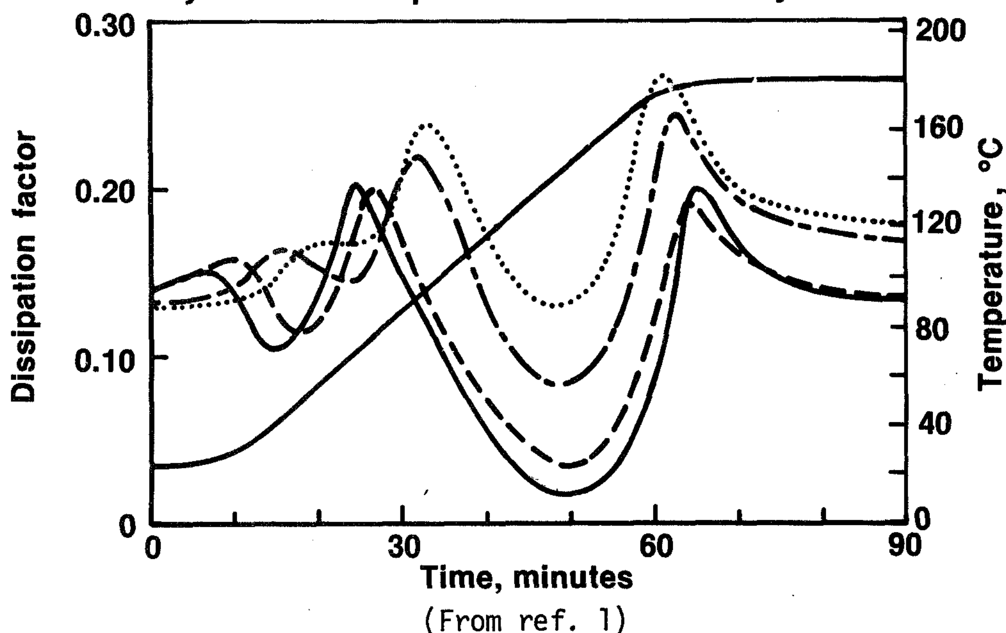
During the next aging period, 30 to 66 days, there was a marked drop in ISA (flow) in the supported tape accompanied by a slightly larger increase in both initial and major softening points. A slight decrease in gel point was also noted. Thus, during the second aging period, the time difference between the softening and gelation temperatures 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 adhesive. 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.

DISSIPATION FACTOR vs TIME

EA 9649 film adhesive, supported

——— As received — — — 66 days at room temp.
— — — 30 days at room temp. ·········· 100 days at room temp.



(From ref. 1)

Dielectric curves obtained on the aged adhesive film simultaneously with the flow measurements are shown above. 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 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. 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.

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. This not only affects the ultimate bond strength but requires a modified cure cycle to achieve complete cure.

CURE TEMPERATURE EFFECTS

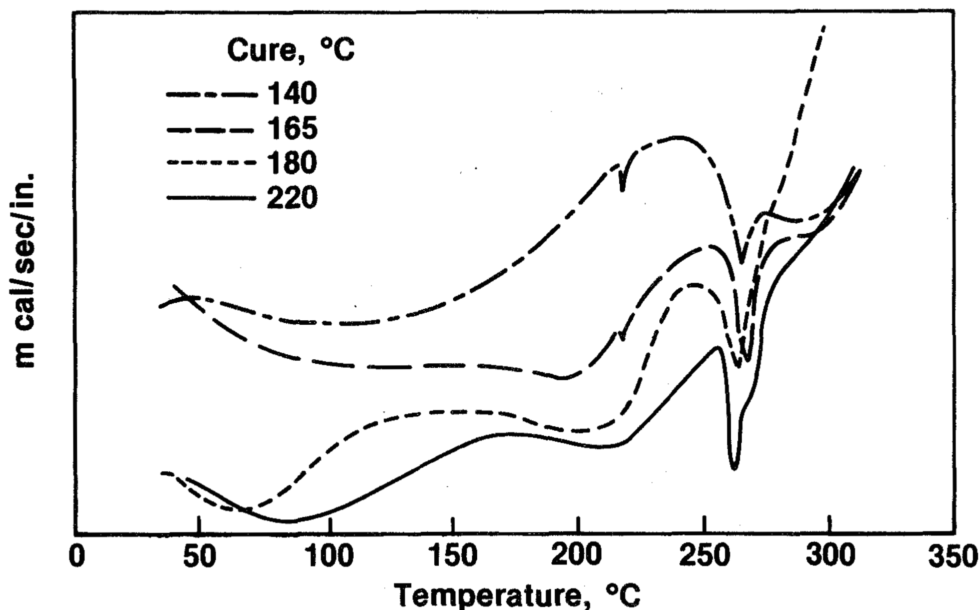
Changes in reaction temperature produce

- Flow changes
- Lower cure level
- Lower bond strengths

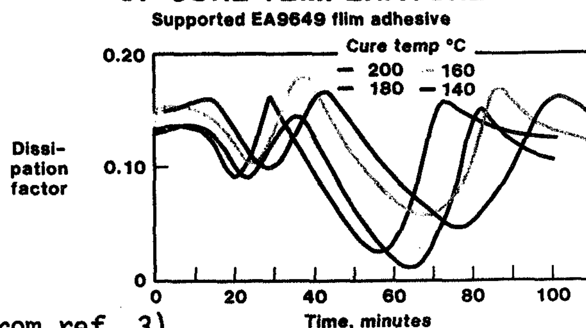
Three methods were used to assess the effect of varying cure temperature on both supported and unsupported EA-9649 adhesive film in terms of flow, gel time and final Tg. These were dielectric and TMA analysis of the neat adhesive and fillet length measurements of the reticulated unsupported adhesive film in a bonded honeycomb structure.

EFFECT OF CURE TEMPERATURE ON DEGREE OF CURE (DSC)

EA-9649 Adhesive/6061 Al



DSC analysis of the cured adhesive showed the presence of unreacted catalyst at the 140°C and 160°C temperatures. This was apparent from the slight endotherm (melting) which occurred at approximately 220°C. The melting point of dicyandiamide is 216°C at the heat-up rate used for the analysis. Thus, at temperatures below 180°C the adhesive appears to be only partially cured. The marked effect of cure temperature on flow related to resin viscosity, cure kinetics and temperature rise indicates the necessity of careful monitoring of process parameters to achieve reproducibility in bonded structures.



(From ref. 3)

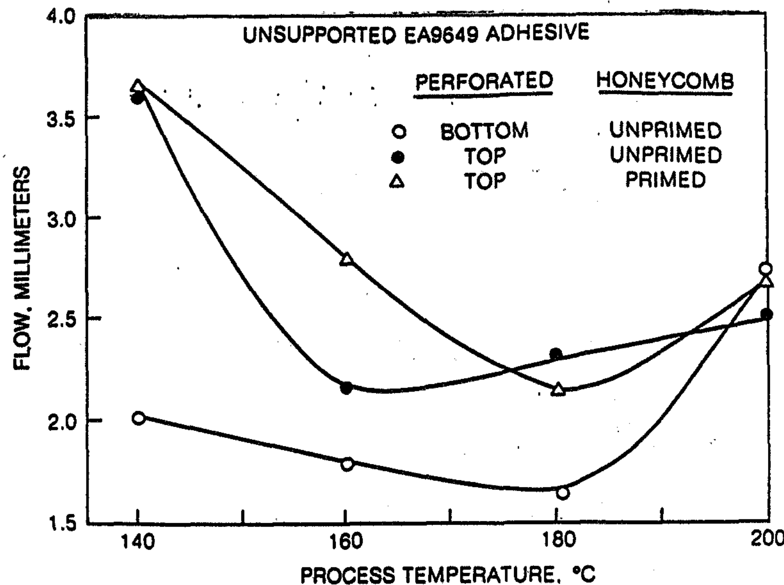
The dissipation factor profile curve obtained on the supported adhesive film is illustrated above. The pertinent data are listed in Table I.

Table I. Cure Temperature Effects on EA-9649 Adhesive-Dielectric Analysis[a]

	Cure Temp, °C	ISA[b] (%flow)	Time to gel, minutes	Tg, °C[c]
Supported Adhesive				
	200	97	72	246
	180	70	81.5	220
	160	89	86	203
	140	71	101	139
Unsupported Adhesive				
	200	45	70	239
	180	25	81	205
	160	35	90	185
	145	42	102.5	142

a. Analysis run at 1000 Hz, 50 psi pressure, 2 ply lay-up.
b. ISA = Increase in surface area.
c. Measured by TMA on the cured sample.

For the unsupported adhesive, an increase in Tg point and decrease in time to gel with increasing cure temperature were observed as expected. The flow, as measured by the increase in surface area during cure, was found to be minimum at the specification 180°C level. Higher flow was experienced above and below this temperature. The supported adhesive in general gave a similar cure response with varying cure temperature. Minimum flow was again found to occur at 180°C. The low flow associated with the 140°C cure is probably due to the effect of the support scrim coupled with the higher viscosity of the adhesive. Accompanying these changes in resin behavior was the higher final dissipation factor obtained by samples cured at temperatures other than the specification 180°C. This is indicative of a different final molecular structure in either a fully or partially cured state.



(From ref. 3)

Adhesive fillet length (in terms of flow) vs processing temperature.

In order to correlate the flow response obtained by dielectric analysis with fillet formation in a bonded honeycomb structure, measurements of fillet length were made on the reticulated unsupported adhesive using specimens fabricated at the four curing temperatures with primed and unprimed honeycomb. The results are shown graphically above. The degree of flow obtained on the primed honeycomb with perforated plate on top was in exact agreement with the dielectric analysis results, i.e., a minimum flow was obtained at the 180°C cure temperature with longer fillets being formed at cure temperatures above and below the specified cure temperature. The flow on the unprimed honeycomb showed a slight minimum at 160°C indicative of the different response of the spreading characteristics of the adhesive to a metal or resin surface. Reversing the honeycomb construction so that the perforated plate was on the bottom (adhesive flows up) gave a minimum flow condition at 180°C on the unprimed surface. Thus, varying cure temperatures produce trends in adhesive flow and final cured state properties which affect the mechanical properties of a bonded joint.

MOISTURE EFFECTS

- Moisture reacts with catalysts to produce:
  - EA-9649
    - Increased flow (plasticizer)
    - New slower reacting catalyst
    - Porosity
    - Lower bond strengths

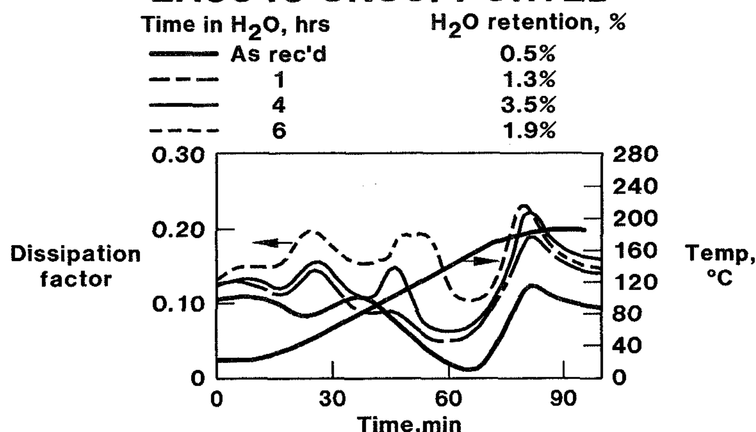
EFFECT OF INITIAL MOISTURE CONTENT ON Tg OF CURED EA 9649 ADHESIVE[a]

	Tg, °C	
Moisture conditions	**Unsupported**	**Supported**
As received	200	220
1 hour soak	183	213
4 hour soak	180	205
6 hour soak	185	200

[a]**Determined on cured film by TMA analysis**

(From ref. 2)

The effect of initial moisture content on the Tg of the cured film samples obtained during dielectric analysis is shown above. In both cases, a decrease in Tg 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.



(From ref. 2)

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

(From ref. 2)

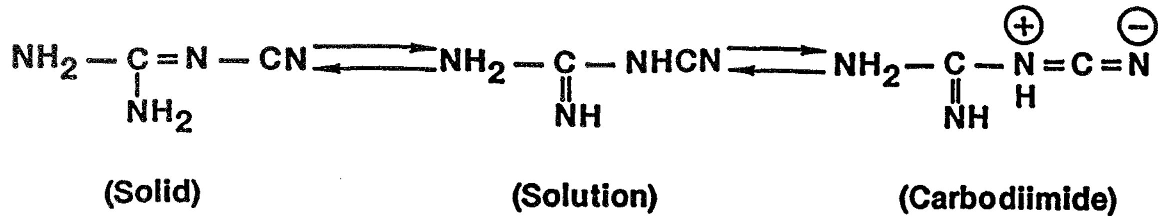
a. ISA = increase in surface area.
b. Dielectric analysis, heating rate = 2.5°C/min

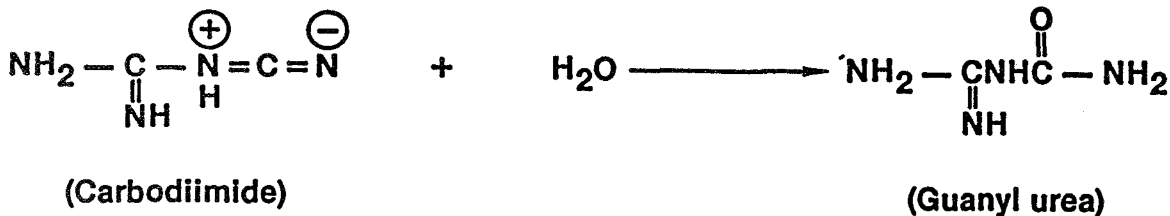
A steady increase in flow was found with both types of film indicating the absorbed moisture acted as a plasticizer. This was also reflected in a lowering of the major melting point of the adhesive before cure. Thus, the time between softening and gelation was increased resulting in a longer flow period at low viscosity. The loss of absorbed moisture during heat-up 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.

DICYANDIAMIDE — EFFECT OF MOISTURE





Water does react with dicyandiamide to produce guanyl urea as the initial reaction product in dilute acidic or basic solution. 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 guanyl urea. 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, and second, via the direct hydrolysis of the nitrile group involving the protonated tautomer.

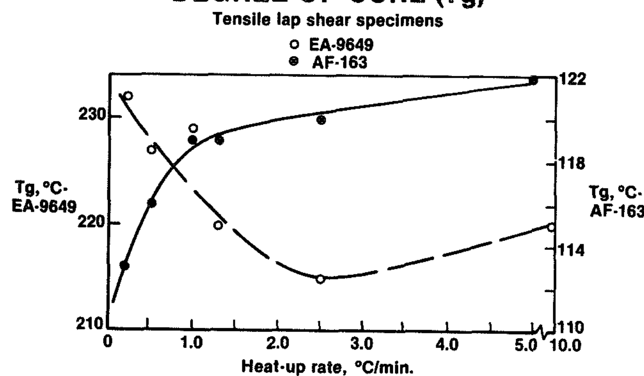
The rate at which the conversion of dicyandiamide to the guanyl urea occurs will depend on the concentration of solubilized dicyandiamide, moisture diffusion rate, viscosity of the medium, epoxy resin type, and the affinity of the scrim cloth (supported film) and filler for moisture. A longer time period 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.

HEAT-UP RATE EFFECTS

- Resin reacts with catalysts at varying rates to produce:
  - Flow minimum at intermediate heat-up rate
  - Decreased TG with increasing rate (EA-9649)
  - Increasing TG with increasing rate (AF-163)
  - Bond strength decrease (both adhesives)



(From ref. 4)

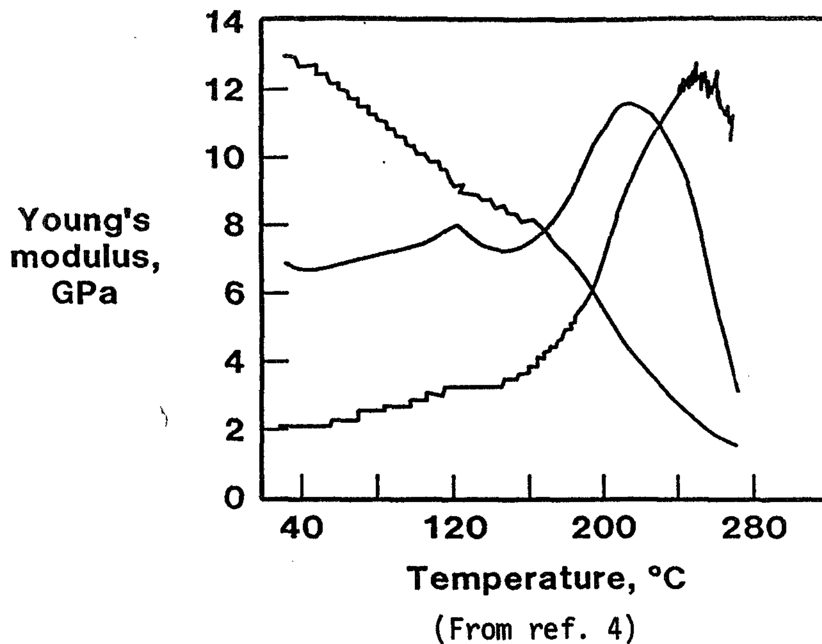
Comparison of the Tg's of cured AF-163 with those obtained from EA-9649 shows the opposite effect in terms of heat-up rate. As is shown above at faster heat-up rates, the Tg of AF-163 increased while that of EA-9649 decreased.

The cause of the increasing Tg with heat-up rate could be due to several possibilities. These are: a) the precipitation of the rubber toughener may be affected by heat-up rate, thus at fast rates the effectiveness is lost producing a more brittle system, b) the exotherm generated by rapid reaction of the catalyst could lead to excessive crosslinking, producing a resin structure of low molecular weight having a high crosslink density which would yield a higher Tg. Since the gel temperature is reached more rapidly at faster heat-up rates the tendency to produce a brittle undercured system would be enhanced. Which of these factors is the major cause of increased Tg cannot be delineated at the present time.

EA-9649 is cured in part with dicyandiamide. Studies have shown that reaction with this catalyst is a two step process, an initial rapid exothermic reaction involving ring opening of the epoxy groups to produce N-alkylguanidines followed by a slower high temperature (110-200°C) reaction resulting in guanyl urea formation. Once the gel point is reached the rate of the second reaction would be considerably reduced. Thus, short gel times at fast heat-up rates could lead to incomplete crosslink formation, resulting in reduced bonded joint strength.

Reactions of aromatic amines with the diglycidyl ether of bis-phenol A have also shown a dependence of gel time on cure temperature, the gel time at a given temperature being dependent on the structure of the amine. The second catalyst in EA-9649 is one which has slower reaction kinetics. Thus, if short gel times occur at the fast heat-up rates, the cure reaction becomes diffusion controlled which, if all specimens are heated for the same total time, would lead to incomplete cure at the rapid heat-up rates, ultimately producing lower Tgs and lower strengths. In a simpler system than EA-9649 the effects noted at the rapid cure levels have been attributed to the fact that the resulting network is less highly crosslinked since competing reactions produce different networks, a characteristic which cannot be corrected by post-curing.

DMA



(From ref. 4)

The use of DMA to measure that dynamic modulus and mechanical damping characteristics of adhesives has been reported. A typical response curve from RT to 280°C of dynamic modulus and mechanical damping (tan δ) of a specimen molded at the 1°C/minute heat-up rate is shown above. The modulus curve is in agreement with that reported for EA-9649. The mechanical damping (tan δ) of the adhesive is the corrected ratio of the viscous loss of energy to the stored elastic energy per cycle. The measurement detects molecular relaxation processes which are controlled by the structure of the adhesive's molecular network. Tan δ reaches a maximum in the glass-rubber transition region and therefore is associated with Tg. Thus, the higher the tan δ peak temperature the higher the maximum temperature at which an adhesive will maintain its structural integrity.

DAMPING PEAK CHANGE WITH HEAT-UP RATE*

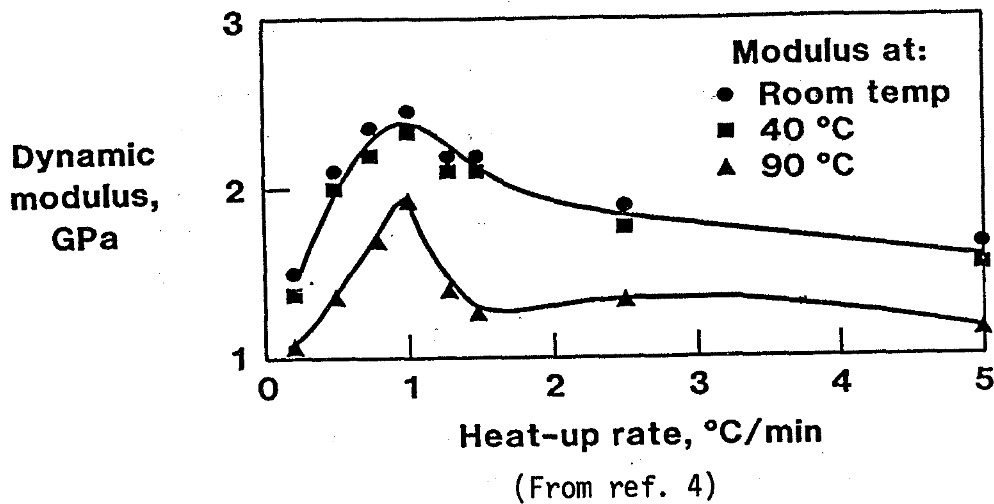
Heat-up rate, C/min	Sample vol mm^3	Tan δ peak area, mm^2	Peak area/ sample vol, mm^{-1}
0.2	35.4	132.3	3.74
0.5	31.0	120.6	3.89
1.0	34.1	157.4	4.62
2.5	31.7	136.8	4.32
5.0	34.8	120.0	3.45

*AF-163 supported adhesive 2-ply sample from dielectric analysis

(From ref. 4)

As was the case with EA-9649 the maximum modulus was obtained at the 1.0°C/min heat-up rate. An indication that permanent differences in the formation of the molecular network, using varying heat-up rates, did occur was shown by comparison of the damping peak area (tan δ) normalized to constant volume. The data listed in the table shows that the maximum value was obtained at the 1.0°C/min rate. Thus, it appears that a specified heat-up rate which accommodates the cure kinetics of the reaction must be used to achieve optimum adhesive performance.

EFFECT OF HEAT-UP RATE ON DYNAMIC MODULUS

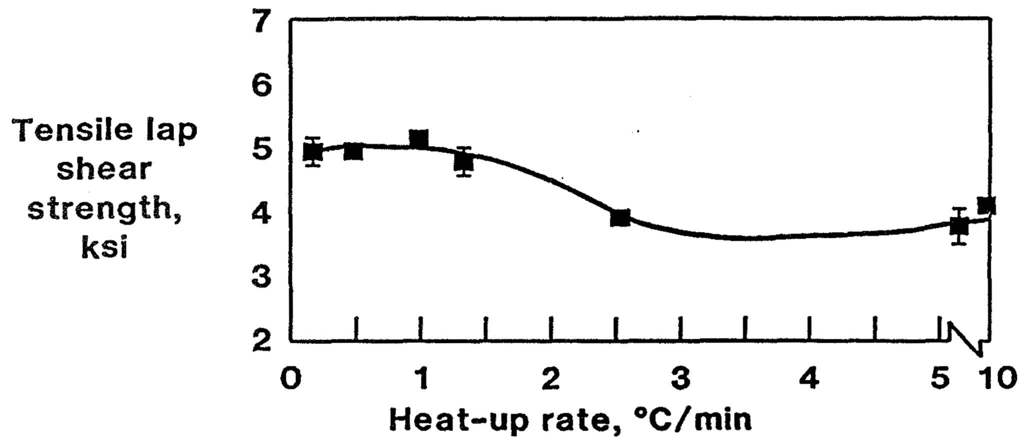


(From ref. 4)

Dynamic mechanical analysis was carried out on the neat resin AF-163 specimens obtained from the dielectric analysis runs. The tan δ peak temperature which is associated with Tg showed the same general trend of high Tg with increasing heat-up rate as was shown by the Tg values obtained from fractured joint specimens. The highest initial RT modulus and modulus retention at 40° and 90°C were exhibited by the 1°C/min heat-up rate specimen as shown above.

CHANGE IN TENSILE LAP SHEAR STRENGTH WITH HEAT-UP RATE

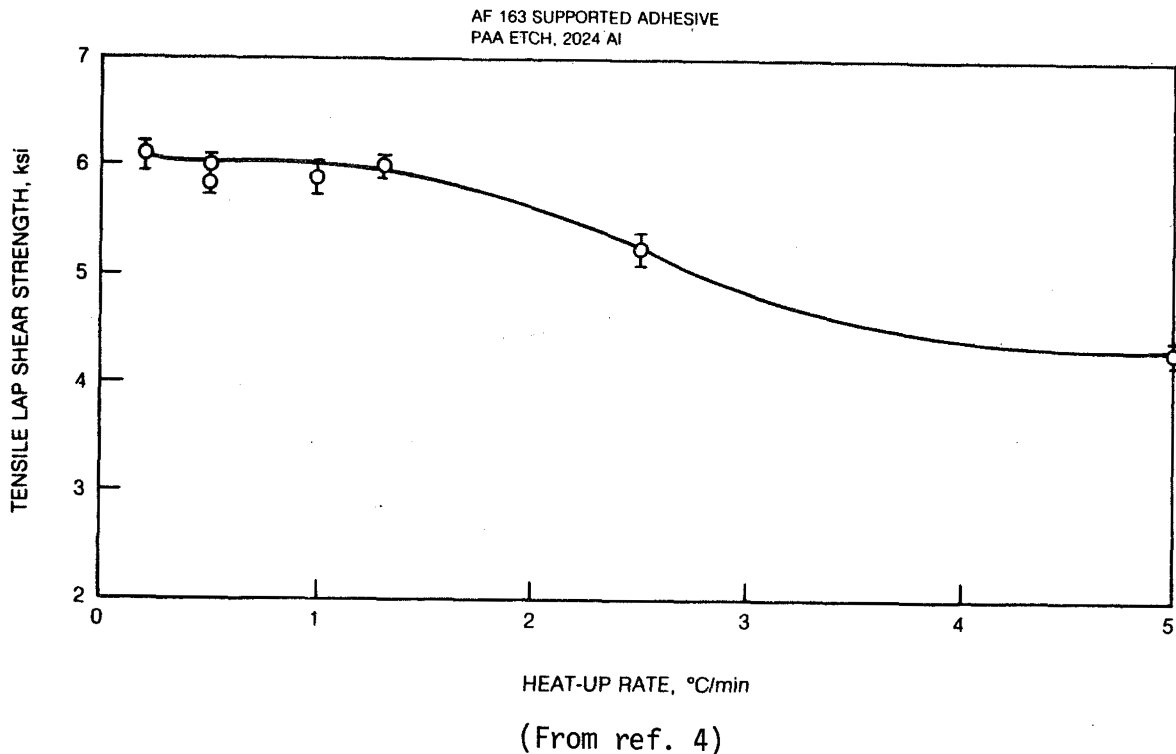
EA 9649 supported adhesive
FPL etch, 2024 Al



(From ref. 4)

The changes in tensile lap shear strength with heat-up rate are shown above. Each data point is an average of six specimens. These results showed that a twenty-five percent drop in tensile lap shear strength had occurred by increasing the heat-up rate from 1.3°C to 2.5°C/minute. The largest change in Tg occurred between 1° and 2.5°C/minute.

CHANGE IN TENSILE LAP SHEAR STRENGTH WITH HEAT-UP RATE



(From ref. 4)

The results of heat-up rate are reflected in the tensile lap shear strength of bonded joints fabricated at varying heat-up rates. The data are shown graphically above. As was the case with EA-9649, a reduction in shear strength occurred above a heat-up rate of 1.3°C/min. The lap shear strengths obtained at the slower rates are in agreement with those reported for AF-163. The decrease in strength, as indicated, may be the result of excessive embrittlement due to poor rubber dispersion and/or excessive crosslinking due to the reaction kinetics of the catalyst system.

CONCLUSIONS

The marked effect of processing parameters and adhesive condition on bonded joint properties has demonstrated the necessity of "knowing" the adhesive system being employed so that optimized bond strengths can be achieved. Potential analytical techniques have been identified which can be used for QC testing as well as tools for studying adhesive compositions.

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