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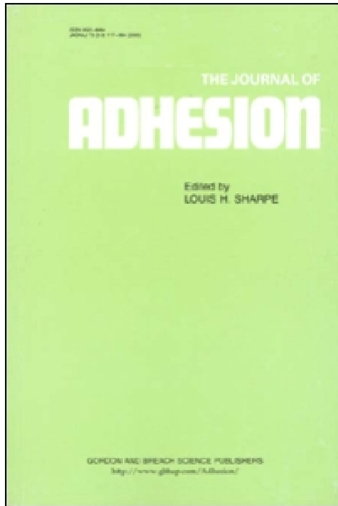

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Factors Affecting the Processing of Epoxy Film Adhesives III. Heat-Up Rate

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Factors Affecting the Processing of Epoxy Film Adhesives III. Heat-Up Rate

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Dielectric, thermomechanical (TMA), dynamic mechanical analysis (DMA) and mechanical testing were used to study the changes which occurred due to varying heat-up rate during fabrication of two commercially available epoxy film adhesives, 3M Co. AF-163 and Hysol EA-9649. The mechanical strength of bonded joints decreased by approximately twenty-five percent when processed above a critical heat-up rate. The glass transition temperature (Tg) of the cured adhesive bonds was found to change in opposing directions with increasing heat-up rate for the two adhesives. This different response has been interpreted in terms of the chemistry associated with the rubber additive and catalysts used in the adhesive formulations.

INTRODUCTION

As part of a continuing investigation of epoxy film adhesives, their properties and processing characteristics, the effect of varying heat-up rate used in the fabrication of bonded structures has been defined for two commercially available expoxy film adhesives, 3M Co. AF-163 and Hysol EA-9649.

Control and an understanding of how processing variables affect the adhesive and final joint properties is 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

Previous studies 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]

This study addresses heat-up rate, one of the important fabrication variables which affect the processing of epoxy adhesives. Heat-up or cure rate effects during fabrication have been alluded to by a number of workers in terms of internal stress levels[4], rheological cure behavior[5], tensile lap shear strength[6], and dynamic thermomechanical properties[7]. Reported studies in epoxy systems have also shown that if there are competing network forming reactions having different reaction rates it would be anticipated that different molecular structures would result.[8] The intermediate structures formed during cure of the epoxy adhesives at slow heat-up rates would be expected to be different from those generated at fast heat-up rates. Such structural changes should be reflected in the mechanical response of the adhesively bonded joints. That changes in molecular structure due to aging or advancement in molecular weight at lower than standard cure temperature do effect the final cured properties of epoxy systems has been demonstrated.[1,9,10,11]

Heat-up rate specifications supplied by these adhesive manufacturers generally extend over a 0.55°C to 8°C/minute (1.0°F to 15°F/minute) range. With an adhesive such as EA-9649 the specified range is narrower, 1° to 5°C/minute (1.8°F to 9°F/minute). With such a wide temperature/time domain the performance of a given adhesive in terms of viscosity (flow) and final chemical structure would be expected to vary considerably, thus influencing the ultimate properties of the bonded joint. This would occur especially in cases of poor process control.

The objective of the described investigation was to determine the effect of heat-up rate on the strength properties of bonded joints using the two identified adhesives and to correlate the response with energy damping and flow capabilities of the neat adhesives.

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MATERIALS AND TECHNIQUES

The two commercially available adhesives used in the present study, Hysol EA-9649, 178°C (350°F) and 3M Company AF-163, 121°C (250°F) curing systems are available in supported and unsupported form.

The EA-9649 adhesive film used in the study was kindly supplied by the Hysol Division of Dexter Corporation, Pittsburg, CA. This adhesive is a rubber-modified, aluminum powder filled epoxy resin cured with dicyandiamide and an aromatic amine. The supported form uses a woven scrim cloth. The AF-163 film adhesive is a rubber modified system consisting of a mixture of brominated epoxy, bis-phenol A based epoxy resin, and a chromium containing compound. The supported form uses a knitted scrim cloth.

Tensile lap shear specimens were prepared using 2024 aluminum alloy etched with FPL or PPA (phosphoric acid anodized). Six specimens were fabricated at once in a gang mold under compression. Suitable stops were employed to insure a bond line thickness of 0.127–0.178 mm (5–7 mils). Tensile specimens were 1.27 cm (0.5 in.) overlap, 12.7 cm (5.0 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 conducted using a MTS 810 test system at a crosshead speed of 0.127 cm/min.

Thermomechanical analysis (TMA) was carried out using a DuPont 1090 thermal analyzer with a 943 TMA module at a heating rate of 10°C/min. Dynamic mechanical analysis (DMA) was carried out using the DuPont 981 DMA module at a heating rate of 5°C/minute. Dielectric analysis was performed as previously described.[1] All runs were monitored at 1000 Hz.

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RESULTS AND DISCUSSIONS

A. EA-9649

The changes which took place in the dielectric analysis profiles at varying heat-up rates are listed in Tables I and II for the two EA-9649 adhesives. Identifiable changes are in terms of temperature and time shifts in major melting and gel points as well as the amount of flow. Composite dielectric curves at all heat-up rates are shown in Figures 1 and 2. The flow of both types of adhesive, as measured by the depth of the dissipation curve profile divided by the time between the major melting and gel peak, was found to increase with heating rate. This effect was

TABLE I
Heat-up rate effects on cure of EA-9649 supported adhesive by dielectric analysis

Heat-Up Rate[a] °C/min	Major Softening Point, °C, minutes	Gel Point °C, minutes	Curve Depth/[b] time, mm/min
0.3	88°, 190	144°, 365	0.185
0.5	80°, 110	154°, 249	0.185
1.0	80°, 53	170°, 140	0.57
3.0	70°, 13	178°, 53	1.62
5.0	76°, 7.6	7 min at 178°, 33	2.55
10.0	78°, 4.5	8 min at 178°, 23	2.49

[a]Dielectric analysis run at 1000 Hz.
[b]Flow, as indicated by depth of curve profile between major melting and gel peak divided by time to progress from melting to gel peak.

TABLE II
Heat-up rate effects on cure of EA-9649 unsupported adhesive by dielctric analysis

Heat-Up Rate[a] °C/min	Major Softening Point, °C, minutes	Gel Point °C, minutes	Curve Depth/[b] time, mm/min
0.3	84°, 210	134°, 370	0.07
0.5	82°, 120	140°, 240	0.12
1.0	80°, 55	164°, 132	0.24
3.0	80°, 19	178°, 54	0.74
5.0	76°, 10	5 min at 178°, 34.5	1.06
10.0	88°, 7	10.5 min at 178°, 26.5	1.87

[a]Dielectric analysis run at 1000 Hz.
[b]Flow, as indicated by curve profile between major melting and gel peak divided by time to progress from melting to gel peak.

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accompanied by decreased time to the gel point. The temperature of gelation increased with increasing heat-up rate. Thus, rapid heat-up cycles produced a lower viscosity allowing greater adhesive flow to occur within an overall shorter time span. An indication that the level of cure or final resin structure obtained varied with heat-up rate was noted by the decrease in dissipation factor after gelation. At rapid heat-up rates this change was significantly less than at the slower rates.

The results of the dielectric analysis of EA-9649 adhesive indicated that the heat-up rate may markedly influence the final cured resin properties which would be reflected in the mechanical response of bonded joints. This is in contrast to results obtained using rheological tests for 178°C and 121°C curing adhesives (unidentified) where only minor shifts in viscosity and gel point were detected, indicating that a 1°C to 10°C/min heat-up rate would have little influence on final bonded properties.[5]

HEATING RATE, °C/min.	TIME TO GEL PEAK, min	GEL TEMPERATURE, °C
0.5	249	153
1.0	140	170
3.0	53	178
5.0	33	178
10.0	23	178

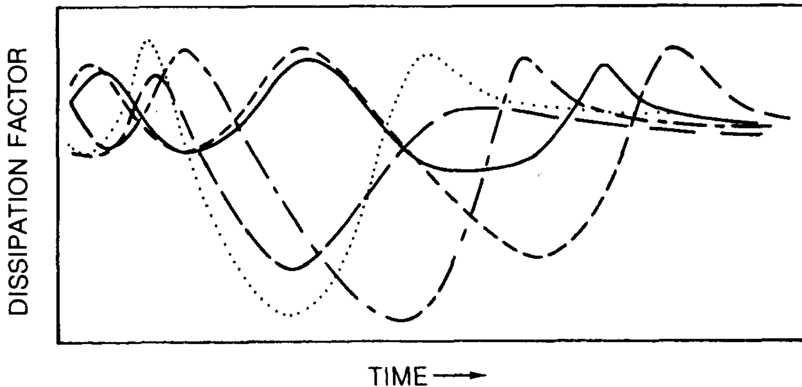

FIGURE 1 Dielectric Analysis of EA-9649 Supported Film Adhesive.

To define the extent of the mechanical property changes which did occur both tensile lap shear strengths and Tg of the cured adhesive were determined. The Tg variations are listed in Table III and shown graphically in Figure 3. The EA-9649 adhesive gave a decrease in Tg with increasing heat-up rate. This same decrease in Tg with varying heat-up rate has been previously noted in a less complex system, Epon 836 cured with 2,4-tolylene -1, 1-bis-3,3 dimethyl urea.[7] In that case the Tg decreased from 140° to 109°C over a heating rate range of 0.5 to 5.0°C/minute. The changes in tensile lap shear strength are shown in Figure 4 and listed in Table IV. 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.

Further evidence that heat-up rate influenced the mechanical proper-

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HEATING RATE, °C/min	TIME TO GEL PEAK, min	GEL TEMPERATURE, °C
——— 0.5	240.0	140
---- 1.0	132.0	164
— — — 3.0	54.0	178
.... 5.0	34.5	178
—— —— 10.0	26.5	178

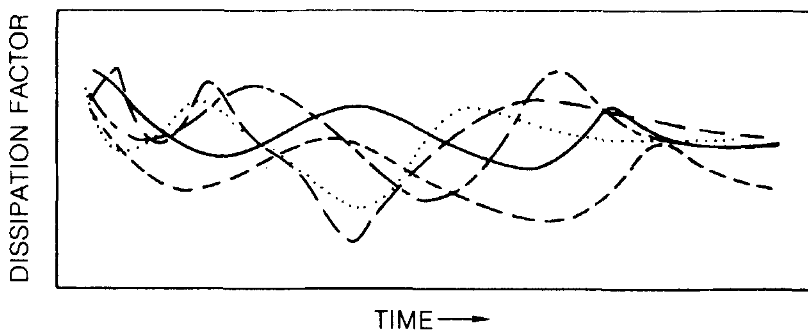

FIGURE 2 Dielectric Analysis of EA-9649 Unsupported Film Adhesive.

TABLE III
Effect of heat-up rate on degree of cure (Tg)[a]

Heat-Up Rate °C/min	Tg, °C EA-9649/FPL	Tg, °C AF-163/Anodized
0.2	232	113
0.5	227	116
1.0	229	119
1.3	220	119
2.5	215	120
5.0	218	122
10.0	220	—

[a] 2024 Al alloy, tensile lap shear, 0.250 in. thick adherends.

ties of the cured adhesive was obtained using dynamic mechanical analysis (DMA) on the sheets of the cured supported film adhesive obtained from the dielectric analysis runs. The use of DMA to measure that dynamic modulus and mechanical damping characteristics of

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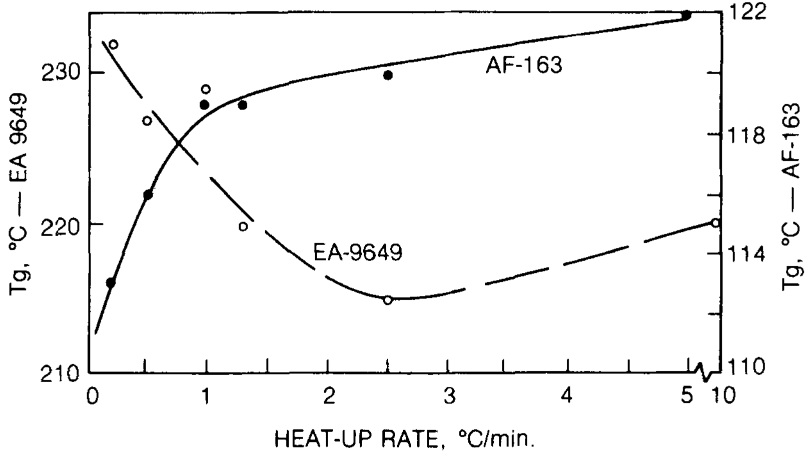

FIGURE 3 Effect of Heat-Up Rate on Degree of Cure (Tg).

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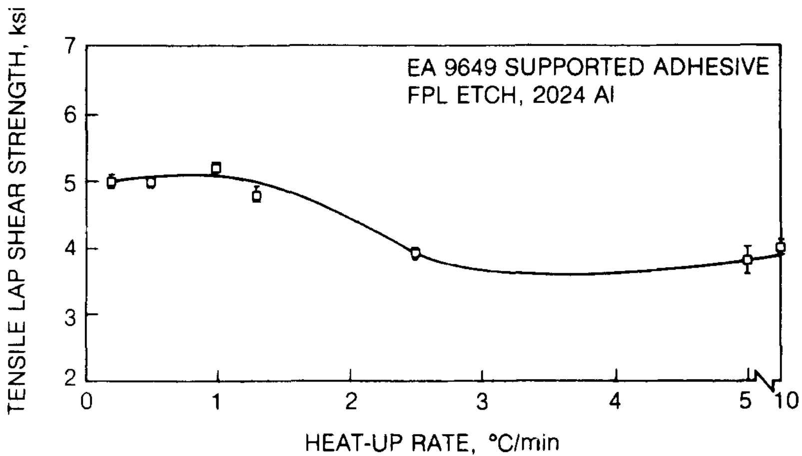

FIGURE 4 Change in Tensile Lap Shear Strength with Heat-Up Rate.

adhesives has been reported.[12] 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 in Figure 5. The modulus curve is in agreement with that reported for EA-9649.[12] The peak temperature of the tan δ curve indicated that changes in

TABLE IV
Effect of heat-up rate on tensile lap shear strength of EA-9649 supported adhesive[a]

Heat-Up Rate °C/min	Tensile Lap Shear Strength[b]	
	MPa	Psi
0.2	34.45	5000 ± 73
0.5	34.77	5046 ± 155
1.0	35.82	5200 ± 89.5
1.3	33.16	4810 ± 163
2.5	26.92	3900 ± 168
5.0	26.2	3800 ± 100
10	27.9	4050 ± 173

[a] 2024 Al alloy, 0.250 in. thick adherends, 0.5 in. overlap FPL etch.

[b] All tests at room temperature. Each value is an average of six specimens.

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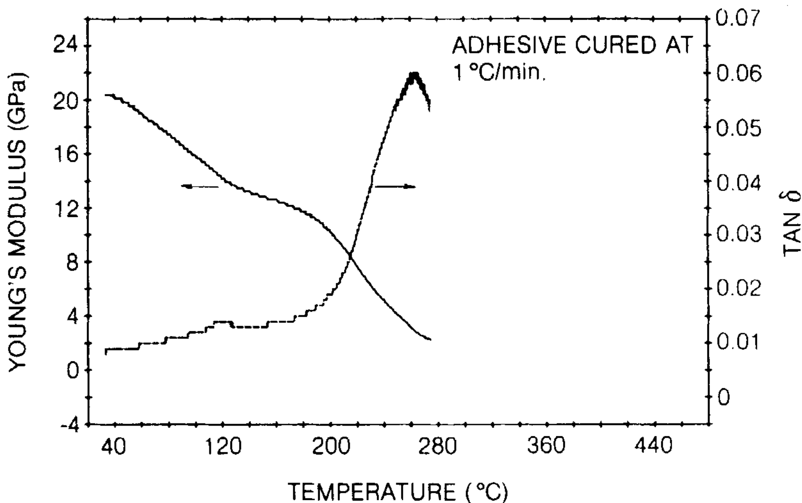

FIGURE 5 DMA of Supported Neat EA-9649 Adhesive.

mechanical damping of the neat adhesive occurred at varying heat-up rates similar to those found for both the Tg and strength measurements on the bonded joints. This result is shown graphically in Figure 6. As before, a maximum appeared at the 1°C/min rate with decreasing tan δ peak temperatures at higher heat-up rates.

The mechanical damping (tan δ) of the adhesive is the corrected ratio

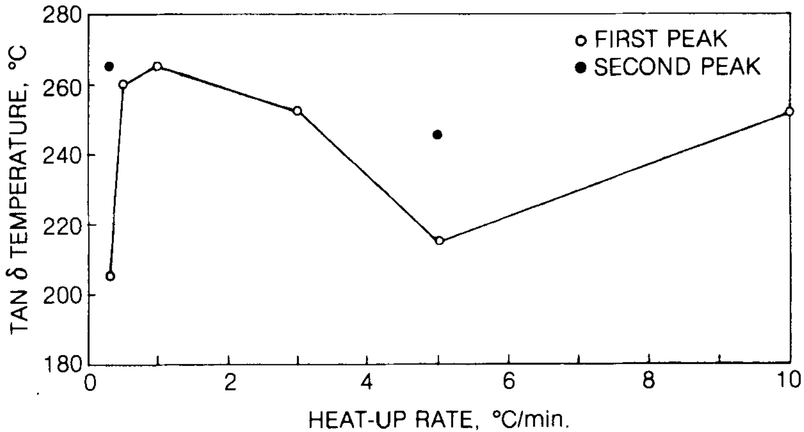

FIGURE 6 Heat-Up Rate vs Tan δ—EA-9649 Supported Film Adhesive.

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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.[12] Thus, the higher the tan δ peak temperature the higher the maximum temperature at which an adhesive will maintain its structural integrity.

It was found that at the 0.3° and 5°C/min rates the tan δ profiles gave two peaks as shown in Figures 7 and 8 over the temperature range evaluated. This response indicated the possible existence of more than one network structure formed during the curing process. At 0.3°C/min the initial peak (lower temperature) had the highest amplitude. However, at 5°C/min both peaks were of nearly the same amplitude with the second slightly higher. The EA-9649 adhesive contains more than one catalyst component, thus the resin structure resulting from varying cure rates would be expected to vary depending upon the reaction rates of the catalysts with the glycidyl ether entity of the epoxy resins. The level of cure and crosslink density attained would be affected by such a reaction rate response. That reaction rates at varying temperatures affect crosslink density formation and degree of cure obtained in amine and anhydride cured epoxy systems has been demonstrated under isothermal conditions.[13,14] Varying heat-up rate would also be expected to influence these resin properties because of the effect of the reaction rate kinetics involved. This was also reflected in the dynamic modulus

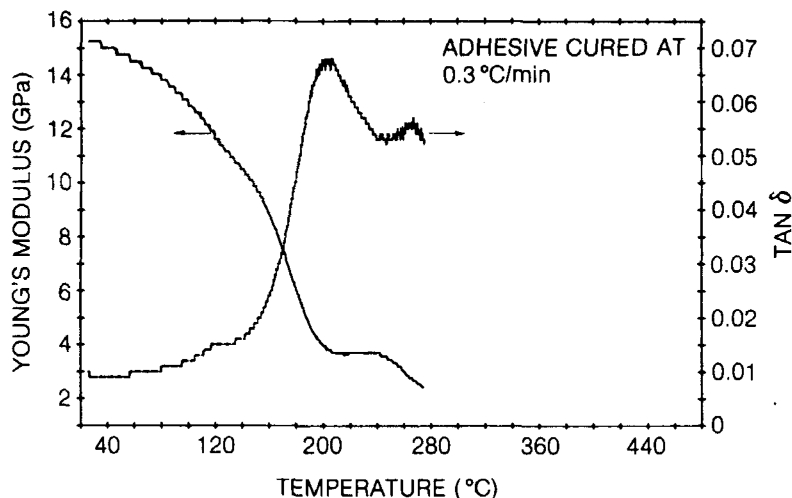

FIGURE 7 DMA of Supported Neat EA-9649 Adhesive.

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TABLE V
Effect of heat-up rate on dynamic modulus EA-9649 supported adhesive

Heat-Up Rate, °C/min	Dynamic Modulus, GPa[a] RT	Dynamic Modulus, GPa[a] 160°C	% Mod. Retn. at 160°C
0.3	15.2	8.8	58.0
0.5	13.4	8.4	62.7
1.0	18.2	11.4	62.6
3.0	12.0	7.5	62.5
10.0	12.8	8.0	62.5

[a]Analysis run at 5°C/minute.

curves obtained at each cure condition. Comparison of dynamic modulus at room temperature and 160°C shows the 1°C/min heat-up rate specimens maintained the highest modulus with increasing temperature as shown in Table V.

EA-9649 is cured in part with dicyandiamide.[1,2] 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

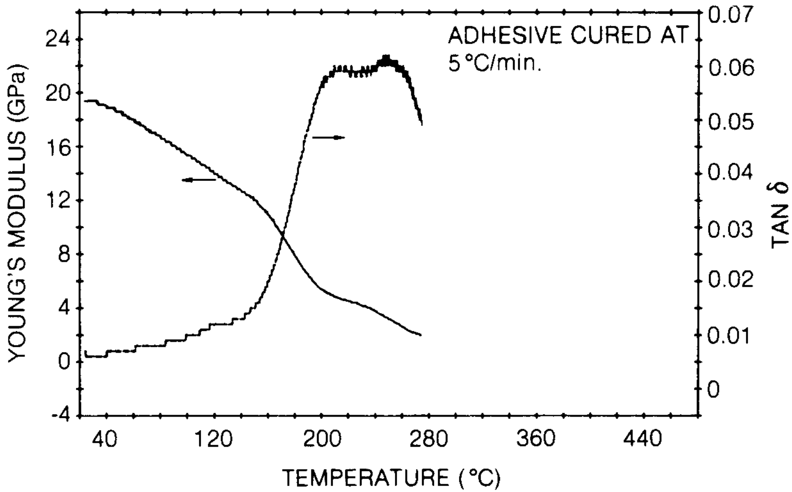

FIGURE 8 DMA of Supported Neat EA-9649 Adhesive.

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produce N-alkylguanidines followed by a slower high temperature (110-200°C) reaction resulting in guanyl urea formation.[17] 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 cross-link 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,[13] 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.[7]

These results, both from adhesively bonded joints and neat cured adhesive films, clearly demonstrate the effect that heat-up rate can produce in bonded systems.

Although the DMA results indicated that 1.0°C/min was the optimum heat-up rate, it is suggested that due to the relatively low percentage change (approximately 8%) in Tg and the similarity in tensile lap shear strength, within the data spread from 0.2–1.0°C/min, that 1.0°C/min should be considered a critical heat-up rate. Thus, cure of the system at slower heat-up rates would produce equivalent strength properties.

B. AF-163

AF-163, 3M Company 250°F curing epoxy adhesive, has been formulated to eliminate reductions in peel properties after the adhesive has been exposed to humidity prior to cure.[15] To some extent this has been achieved. Tests at UTRC do indicate that control of adhesive moisture content prior to cure is important since moisture does effect the catalyst used in the system. 3M has attributed peel strength reduction due to moisture to decreased particle size of the precipitated rubber toughening agent when the moisture content of the AF-163 is too high. Smaller particles are poor crack arrestors. That such rubber particles should be in a definite size domain to be effective has been reported.[16] The effect of processing temperatures on the morphological structure of rubber modified epoxy adhesives has also been reported.[10]

The effect of heat-up rate on the physical and mechanical properties of supported AF-163 was determined using the techniques described above for the EA-9649 adhesive.

The pertinent data obtained from the dielectric analysis curves at

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TABLE VI
Heat-up rate effects on cure of AF-163 supported adhesive by dielectric analysis[a]

Heat-Up Rate °C/min	Major Softening Point, °C, minutes	Gel Point °C, minutes	Curve Depth[b] Time, mm/min
0.3	78°, 175	125°, 360	0.11
0.5	90°, 118	30 min at 126°, 220	0.18
1.0	79°, 62	110°, 93	0.39
2.5	80°, 23	120°, 40	1.17
5.0	104°, 14.2	4 min at 120°, 25	3.15

[a] Analysis run at 1000 Hz.
[b] Flow, as indicated by depth of curve profile between major melting and gel peak divided by time to progress from melting to gel peak.

varying heat-up rates for supported film is listed in Table VI and illustrated in Figures 9 and 10.

As with EA-9649, the flow of AF-163 increased with increasing heat-up rate. This effect was primarily due to the lower resin viscosity obtained and the reaction kinetics which, under the higher heat rates,

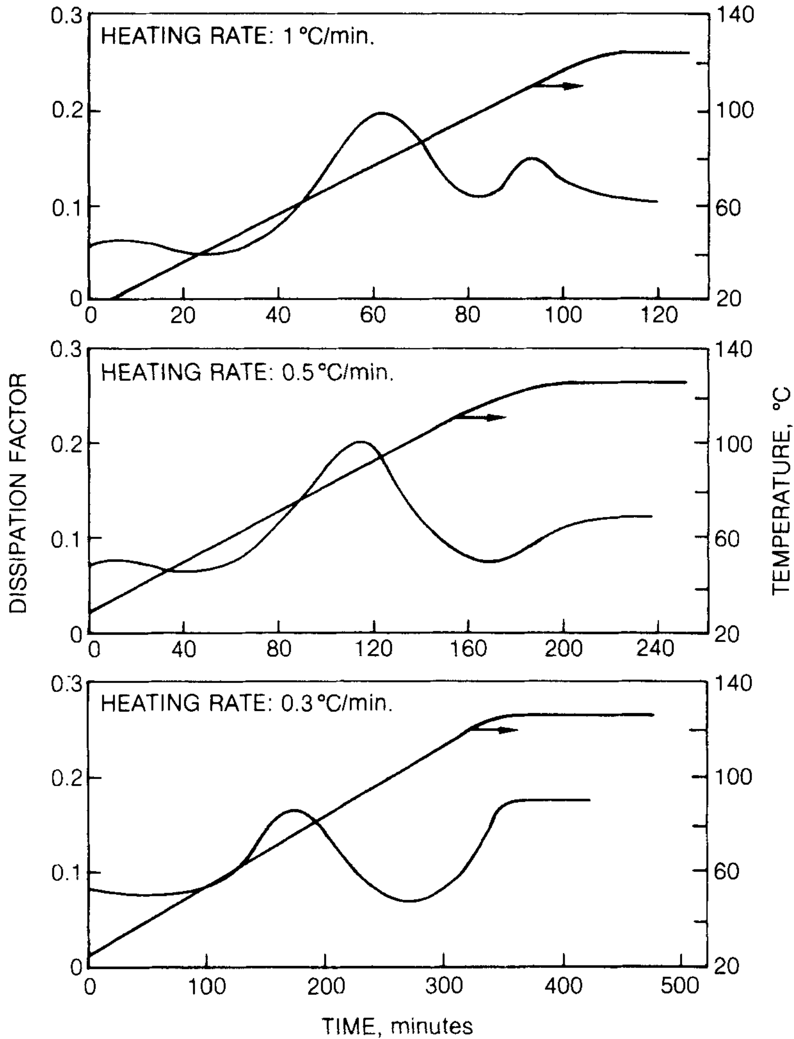

FIGURE 9 Dielectric Analysis of AF-163 Supported Film Adhesive.

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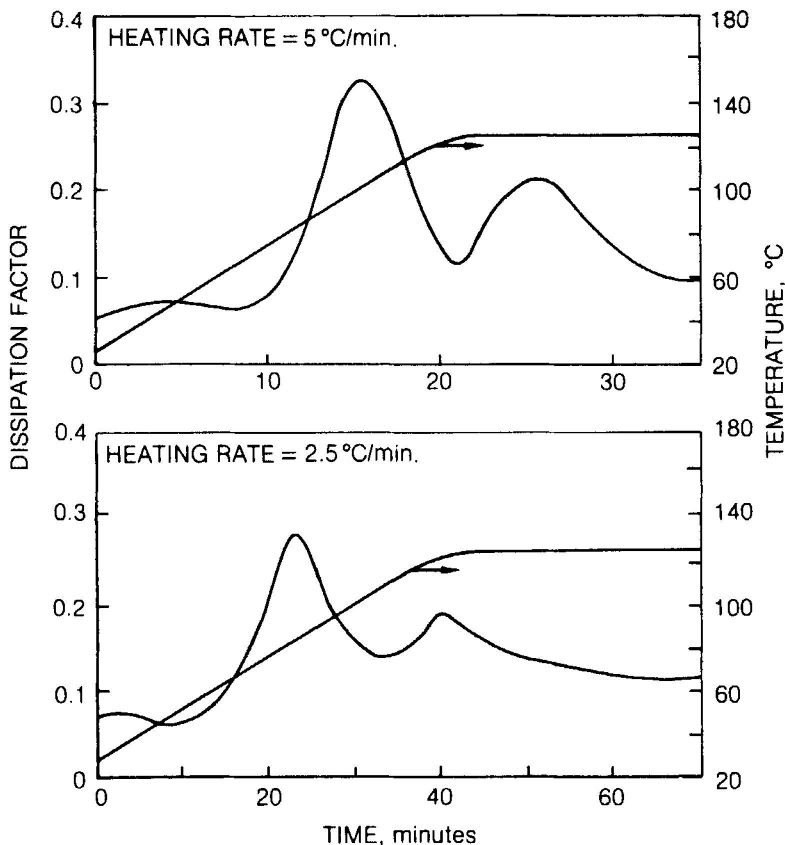

FIGURE 10 Dielectric Analysis of AF-163 Supported Film Adhesive.

did not generate sufficient molecular weight build-up to reduce flow. It was interesting to note that the gel temperature was the lowest at the 1°C/min heat-up rate indicating that the kinetics involved in the cure of the adhesive are such that a specific heat rate must be maintained to achieve optimum reproducibility and flow characteristics. Also note the change in amplitude of the melting peak, which increased with increasing heat-up rate due to the exothermic reaction of the catalyst with more heat being generated at the faster rates.

Comparison of the Tg's of cured AF-163 listed in Table III with those obtained from EA-9649 shows the opposite effect in terms of heat-up rate. Thus, at faster heat-up rates the Tg of AF-163 increased

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while that of EA-9649 decreased. The 3M Company reported Tg value, obtained by dynamic mechanical analysis, is 120°C.[15] The difference in response of the two adhesives is illustrated graphically in Figure 3.

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.

Scanning electron microscopy (SEM) analysis of failed joints revealed that a reduction of rubber particle precipitation in the 0.1–10 μm range had occurred at fast heat-up rates. The toughness properties of epoxy adhesives have been attributed to a dispersed phase of rubber particles in this size range. Thus, rubber particle formation may be in part responsible for the heat-up rate effect found with the AF-163 adhesive system.

It has been previously reported[10] that as the heat-up rate is increased the time to reach the gel point decreases (see Table VI) and that this has a direct influence on the precipitation of the rubber additive. The rubber particles nucleate and grow during the curing process. Stopping the diffusion of rubbery material to the growing domains of rubber, which occurs as gelation takes place, prior to the time of reaching adequate size would tend to produce mechanical response effects similar to a resin containing little or no rubber additive. This would account for the loss in strength and increased Tg found in the AF-163 adhesive.

The results of these effects are reflected in the tensile lap shear strength of bonded joints fabricated at varying heat-up rates. The data are listed in Table VII and shown graphically in Figure 11. 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 above, 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.

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TABLE VII
Effect of heat-up rate on tensile lap shear strength AF-163 supported adhesive[a]

Heat-Up Rate °C/min	Tensile Lap Shear Strength[b] MPa	Psi
0.2	42.0	6100 ± 60.5
0.5	40.3	5850 ± 93
0.5	42.0	6100 ± 105
1.0	40.65	5900 ± 99
1.3	41.34	6000 ± 110
2.5	36.2	5250 ± 123
5.0	29.6	4300 ± 114

[a] Al-2024 thick adherends, PAA etch.
[b] Each value an average of six specimens.

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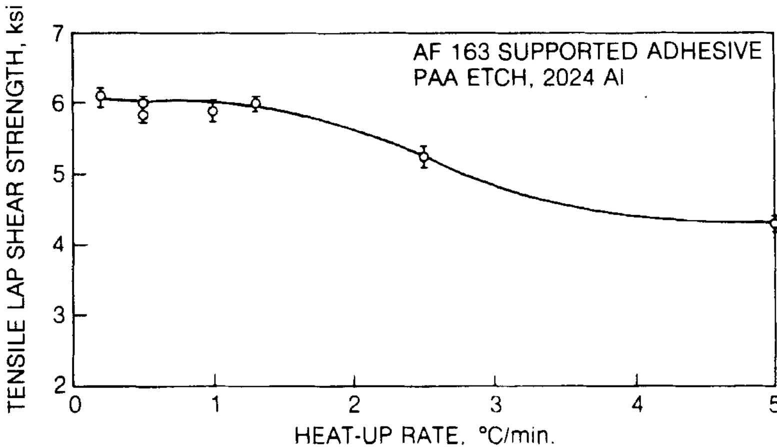

FIGURE 11 Change in Tensile Lap Shear Strength with Heat-Up Rate.

Dynamic mechanical analysis was carried out on the neat resin specimens obtained from the dielectric analysis runs. The pertinent data are listed in Table VIII and representative curves are illustrated in Figures 12–14. The tan δ peak temperature which is associated with Tg showed the same general trend of higher Tg with increasing heat-up rate as was shown by the Tg values obtained from fractured joint specimens, Table III. The highest initial RT modulus and modulus retention at 40° and 90°C was exhibited by the 1°C/min heat-up rate specimen as shown in Figure 15.

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

TABLE VIII
Effect of heat-up rate on dynamic modulus AF-163 supported adhesive

Heat-Up Rate °C/min	Dynamic Modulus, GPa RT	Dynamic Modulus, GPa 90°C	% Mod. Retn. at 90°C	Tan δ Peak Temp, °C
0.2	1.42	0.91	64	115
0.5	2.08	1.34	64.4	116.5
0.8	2.46	1.6	65.0	112
1.0	2.63	1.9	72.2	120
1.5	2.16	1.7	63	118
2.5	1.8	1.5	69	120
5.0	1.52	1.04	68.4	122

[a] Analysis run at 5°C/min.

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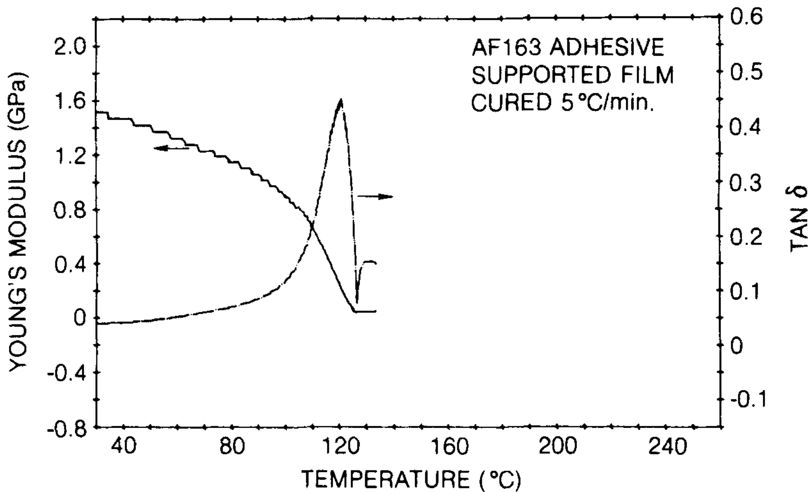

FIGURE 12 DMA of Supported AF-163 Film Adhesive.

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 Table IX show 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.

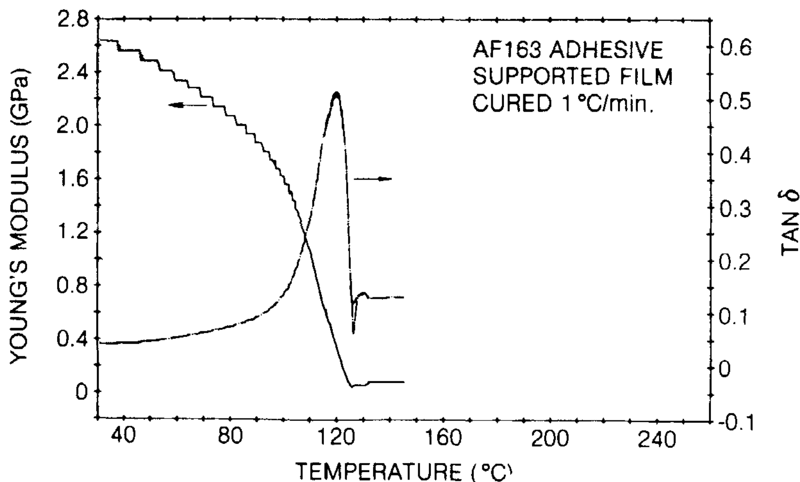

FIGURE 13 DMA of Supported AF-163 Film Adhesive.

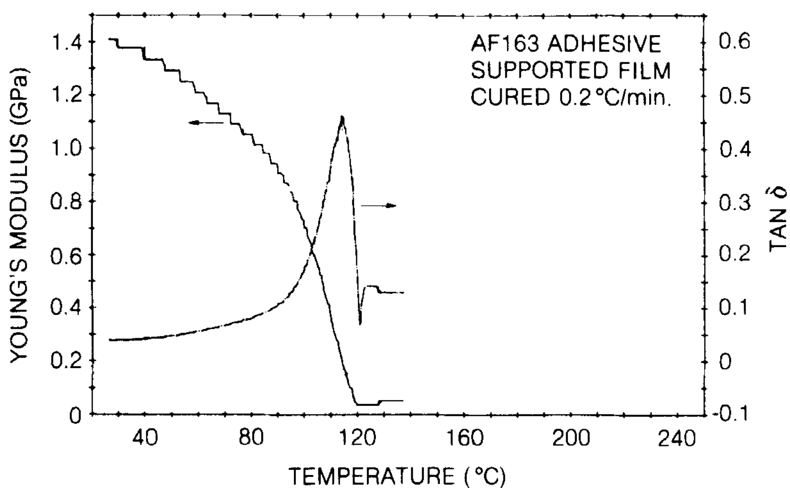

FIGURE 14 DMA of Supported AF-163 Film Adhesive.

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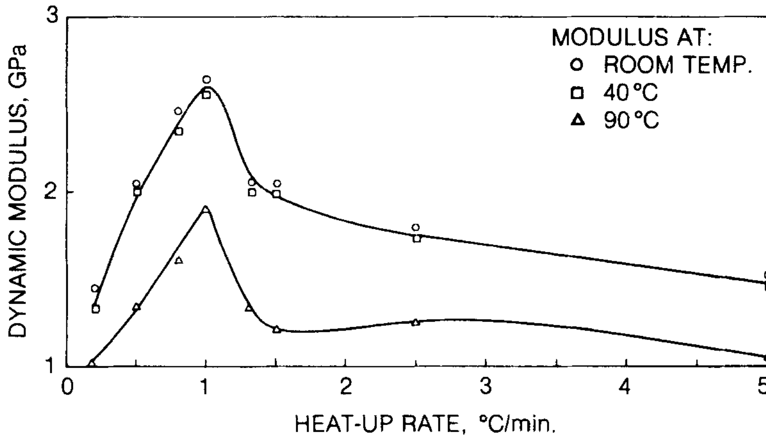

FIGURE 15 Effect of Heat-Up Rate on Dynamic Modulus.

TABLE IX
Damping peak change with heat-up rate[a]

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

[a]AF-163 supported adhesive 2-ply sample from dielectric analysis.

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These DMA results are in concert with Tg and strength measurements and reflect the necessity of maintaining specified heat-up rates to achieve reproducibility and optimum mechanical strengths in bonded joints.

CONCLUSIONS

The overall heat-up rate effects found with both adhesives are undoubtedly related to changes in network morphology. Each adhesive system will be influenced to varying degrees, depending upon the chemical composition and reaction kinetics of the catalysts and additives employed. In depth investigations similar to those reported

on microgel formation[18] will be required to elucidate the exact role of each constituent in structuring the final cured adhesive properties.

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