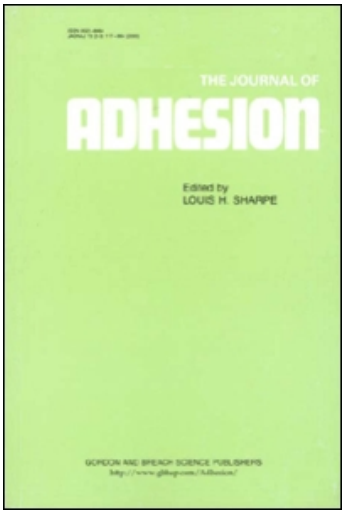

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Room Temperature Curing Epoxy Adhesives for Elevated Temperature Service. Part III. The Effect of Silane Coupling Agents*

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The effect of silane coupling agents incorporated into the bulk of previously-developed room-temperature-curing epoxy adhesives[8,9,10] was studied. The physical and mechanical properties of corresponding aluminum bonded joints were characterized in ambient and humid-hot environments. Experimental results have demonstrated significant advantages of silane addition to the performance of these epoxy adhesives, especially under exposure to humid atmosphere. Thermal analysis of the polymerization processes, taking place during curing of the various low-temperature-curing formulations containing silane coupling agents, indicates that curing is not complete after seven days at room temperature, showing an exotherm at 80–100°C and a residual small one at 120°C. The basic formulation, comprising a tetra- and trifunctional epoxy resin blend and a multifunctional amine and ATBN cross-linking mixture, developed a three-phase matrix-rubber microstructure when the silane was added to the system.

KEY WORDS elevated temperature service; room temperature curing epoxy adhesives; silane coupling agents; thermal analysis; rubber toughening; three-phase morphology; durability; hot/wet exposure; bonded joints.

INTRODUCTION

Application of coupling agents for surface modification of fillers and reinforcements incorporated into polymer composites has generally been directed towards improved mechanical and chemical properties.[1–5] The resulting chemical bond occurs by virtue of the coupling agent functional groups which react both with the filler and the polymer. One of the most common cases comprises silanes and glass fibers. In this case, the mechanical properties of the polymer composite, as well as its chemical characteristics, are enhanced to a large extent. It is well accepted that water primarily degrades the glass fiber/polymer interface *via* hydrolysis of the silane coupling agent in addition to its secondary effect(s) on the polymer matrix and filler.

Organosilanes of the general formula, $R_n Si X_{4-n}$, are composed of two functional end-groups. The first (X) is a hydrolyzable end group such as amine, alkoxy, etc. The second (R) is a non-hydrolyzable, organofunctional end group.

*One of a Collection of papers honoring John D. Venables, the recipient in February 1991 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

Due to their unique composition organosilanes are commonly used as coupling agents between organic and inorganic components.

The application of silanes involves a few steps. First, the hydrolyzable end groups are exposed to water for hydrolysis. Following hydrolysis, oligomers are formed in a condensation reaction. The oligomers may interact with inorganic compounds through hydrogen bonding with OH groups present on the surface, or form covalent bonds in other cases. The organic end group may react with the polymer components.

Strategies for optimization of interfacial adhesion must take into account the chemical and physical composition and properties of the components involved and select, accordingly, the silane with the appropriate end groups.

Silane coupling agents are also used as additives for adhesion promotion of polymers to adherends at levels of 1% or less.[3] In this case, they function in the same way as coupling agents or primers provided that there is a driving force for their migration to the interface.

Selection of the appropriate coupling agent for a given polymer/substrate combination is complex. Factors such as wetting, surface energies, polar absorption, acid-base interaction, interpenetrating network formation and chemical reactions have to be taken into consideration.

Even the best coupling agent for a given system may perform poorly if it is not applied properly. Orientation of the molecules at the interface and their physical properties can be controlled by the method of application, and may be as important as the chemistry of the selected silane.[6] Silane coupling agents have been used to improve adhesion and durability of polyurethane adhesives exposed to aggressive environments.[7] The general conclusion of the latter study is that silanes are very effective when incorporated into polyurethanes, especially with respect to durability.

The present study is aimed at evaluating the effect of silane coupling agents incorporated into room temperature curing epoxies which were evaluated for elevated temperature service.[8-10] Balanced performance with respect to shear and peel adhesion properties was obtained for a system composed of a tetra- and trifunctional epoxy blends cross-linked by a mixture of a multifunctional amine and an amino-terminated elastomer on aluminum adherends treated by a silane coupling agent.

This basic formulation developed a typical two-phase matrix-rubber microstructure. A third phase was observed when an epoxy-terminated silane was added to the bulk adhesive.[9] The unique microstructure was presumed to be the result of the specific polymerization kinetics and thermodynamic interaction between the system reactants and the silane used. Hence, in the present study two other silanes were incorporated into the basic epoxy formulation in order to achieve better insight into the relationship between microstructure, mechanical, and durability properties.

EXPERIMENTAL

a. Materials and Processes

The compounds used in this work are listed in Table I. In all cases studied, one part is a blend of two epoxy resins and the other part includes the amine curing agent

which is partially composed of an amine-terminated reactive liquid rubber.

Adhesive compositions were first characterized by determining their lap shear and peel properties. Test specimens were prepared from aluminum (AL-2024-T351) that had been chromic acid anodized without sealing in accordance with MIL-A-8625, Type I, Class I. Before the application of adhesive, the substrates were vapor degreased in a TP-35 solution (manufactured by Du Pont) for 5–10 minutes. Silane Primer (2% A-187 in 80/20 V/V ethanol/water) was applied by dipping, and allowed to dry for ½ hour at room temperature (RT) and 1 hour at 100°C. The adhesive was applied by brushing. The carrier (Table I) was impregnated with the adhesive, evacuated for 5 minutes at 5 mm Hg (absolute pressure) and excess resin was squeezed out. The test specimens were allowed to cure at ambient temperature for 6 days, prior to testing. The 90°C and 120°C test data are reported after a 10-minute soak at testing temperature. The effect of soaking time at the elevated testing temperatures on lap shear strength was previously evaluated[8] and found to be of secondary importance.

Lap shear specimens were placed in the humidity chamber at 50°C/95% RH for 90 days and then tested.

b. Sample Preparation

Typical formulations (Table I) were prepared as described earlier.[8] In the cases where the silane was studied, it was added to the epoxy mixture (0.5% or 2% w/w) and remixed to an homogeneous blend.

Three silanes were used. The first (A-187, Union Carbide) included epoxy end groups. The second (A-1100, Union Carbide) was an amine-terminated silane, and the third one (Z-6032, Dow Corning) was a vinyl-terminated silane.

TABLE I
Epoxy Formulations Studied

Component[a]		Formulation Component Weight (gr or %)			
Materials	Manufacturer	1	2	3	4
Epoxy Resins					
MY 720	CIBA Geigy (USA)	50	50	50	50
ERL 510	CIBA Geigy (USA)	40	—	40	—
EPON 815	Miller Stephenson (USA)	—	74	—	74
Curing Agents					
TETA	Miller Stephenson (USA)	18.6	18.6	18.6	18.6
ATBN 1300×35	BF Goodrich (USA)	36	36	36	36
Silane Coupling Agents					
A-187	Union Carbide (USA)	0	0	0.5%/2%	0.5%/2%
A-1100	Union Carbide (USA)	0	0	0.5%/2%	0.5%/2%
Z-6032	Dow Corning (USA)	0	0	0.5%/2%	0.5%/2%
Carrier					
Polyester Felt	Fibermat IC-650, 3M (USA)	+	+	+	+

[a]Chemical formulas are given in Table I of Ref. 7.

c. Testing Techniques

Mechanical Tests Tensile lap shear specimens (L.S.S.) were prepared according to ASTM D-1002-72. T-Peel specimens were prepared according to ASTM D-1867. Five specimens were fabricated for each test by compression using a special mold. Bondline thickness for all specimens was 0.10 ± 0.03 mm. Mechanical properties were determined using a 10-ton Instron machine at a crosshead speed of 2 mm/min (L.S.S.) and 200 mm/min (T-peel).

Thermal Analysis Specific heats and extent of cure were determined using the 910 DSC unit of a Du Pont 1090 Thermal Analyzer at a heating rate of 10°C/min.

Microscopy SEM/EDXA analysis of fracture surfaces was obtained using a Jeol SEM, Model JSM-840, equipped with an energy-dispersive analyzer link Model 290. Prior to observation, the specimens were coated with a thin layer (~20 nm) of platinum to obtain a conductive surface and reduce charging.

RESULTS AND DISCUSSION

Mechanical Properties

Table II and Figures 1 and 2 relate the lap shear and T-peel properties of the various formulations (listed in Table I) with temperature. As evident from Table II and Figure 1, formulation 1 (720/510/TETA/ATBN 1300×35) without, or formulation

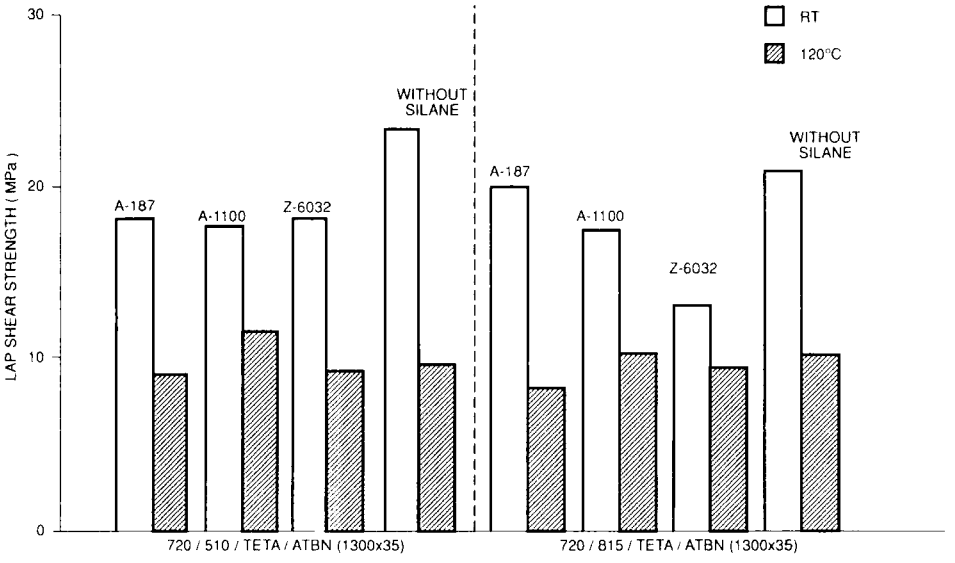


FIGURE 1 Effect of various silanes (0.5%, w/w) on shear strengths.

TABLE II
Adhesion Strength[a] of Epoxy Formulations

	Silane Type	A-187				A-1100				Z-6032				Without Silane	
	Concentration (%)	0.5		2.0		0.5		2.0		0.5		2.0			
	Test Temperature (°C)	RT	120	RT	120	RT	120	RT	120	RT	120	RT	120	RT	120
Lap Shear (MPa)	720/510/TETA/ATBN35 (1)	18.5	9.0	19.4	9.3	17.9	11.4	17.2	9.8	18.4	9.4	19.4	9.4	23.4	9.5
	720/815/TETA/ATBN35 (2)	20.1	8.1	16.3	8.4	17.7	10.2	15.2	8.6	13.3	9.6	15.4	9.1	22.0	9.8
T Peel ($\frac{N}{mm}$)	720/510/TETA/ATBN35 (1)	1.3	0.7	1.3	0.6	1.5	0.5	1.4	0.3	1.2	0.5	1.3	0.5	1.7	0.5
	720/815/TETA/ATBN35 (2)	1.5	0.4	1.5	0.5	1.3	0.6	1.4	0.5	1.0	0.4	1.4	0.6	1.3	0.6

[a]standard deviations ±5%

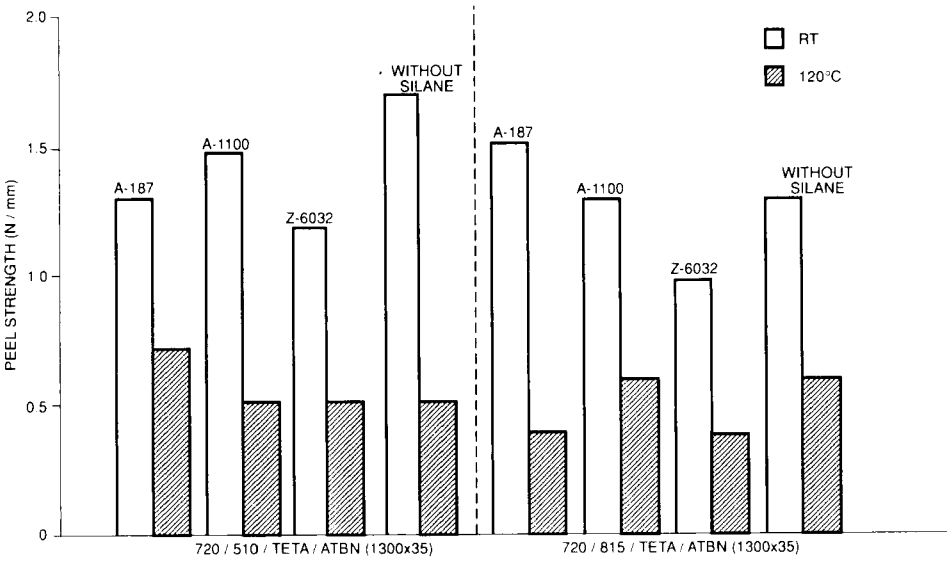


FIGURE 2 Effect of various silanes (0.5%, w/w) on peel strengths.

3 with 0.5% or 2% with, silane coupling agents exhibit, in most cases, at elevated temperature (120°C), shear strengths higher than or equal to those of formulations 2 and 4 (720/815/TETA/ATBN 1300×35).

These results are attributed to a more cross-linked network in the case of formulations 1 and 3 (a blend of tetra- and trifunctional epoxy resins) compared with formulations 2 and 4 (a blend of tetra- and difunctional epoxy resins), as was found also for the neat formulations without silanes.[9] Peel strengths (Figure 2) of both formulations are similar, in most cases, within the standard deviations. It seems that incorporation of any of the three studied silanes into the epoxy formulation causes a reduction in room temperature shear and peel strengths compared with the neat formulations. This may reflect plasticization of the epoxy formulations by a physically bound silane.

To study the effect of silane addition on the environmental endurance of these reduced-temperature-curing formulations, a few bonded specimens were exposed to heat (50°C) and humidity (95% RH) for 90 days. Figure 3 depicts the lap shear strength of formulations with and without silanes, prior to and following hygrothermal exposure. As clearly shown, while the silanes reduce the lap shear strength prior to heat/humidity conditioning, they cause a distinct enhancement of shear strength of these initially strength-degraded formulations following exposure to heat and humidity. The strengthening effect to various levels was demonstrated to depend on the silane types, for both the tetra- and trifunctional epoxy formulation and the tetra- and difunctional blend.

The effect of silane addition on the mechanical properties of the two basic formulations was further investigated in the bulk state for the case of the vinyl-terminated silane (Z-6032).

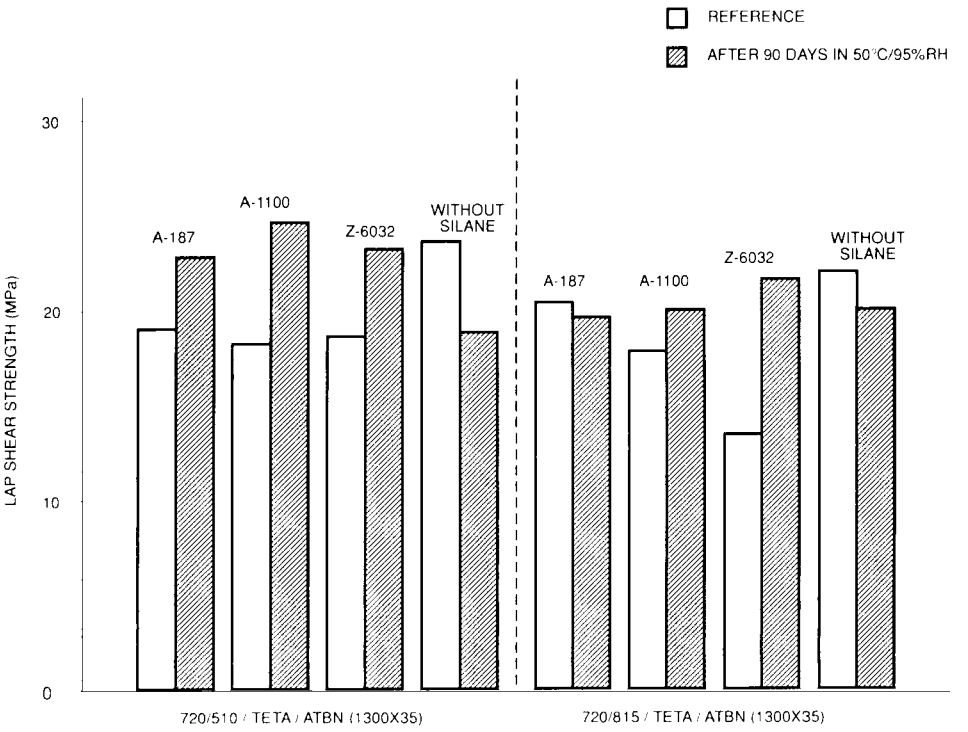


FIGURE 3 Effect of various silanes (0.5%, w/w) on shear strengths prior and after exposure to wet/hot conditions.

Table III indicates that addition of 0.5% of silane to the bulk adhesive reduces, in both formulations, the tensile strength and modulus by a significant level. This may be attributed to plasticization phenomena as reflected also in shear strength reduction of the silane-containing epoxy formulations.

TABLE III
Bulk Tensile Properties of Epoxy Formulations

	Epoxy Resin Formulations	Tensile Properties[a]		
		Strain ϵ (%)	Stress σ_B (MPa)	Young's Modulus E (MPa)
I	720/510/TETA/ATBN 35 (1)	12.8	24.6	1150
	720/510/TETA/ATBN 35 / Z-6032 (0.5%) (3)	9.3	18.9	513
II	720/815/TETA/ATBN 35 (2)	7.6	31.1	1680
	720/815/TETA/ATBN 35 / Z-6032 (0.5%) (4)	8.2	20.5	670

[a]Standard deviations ±5%

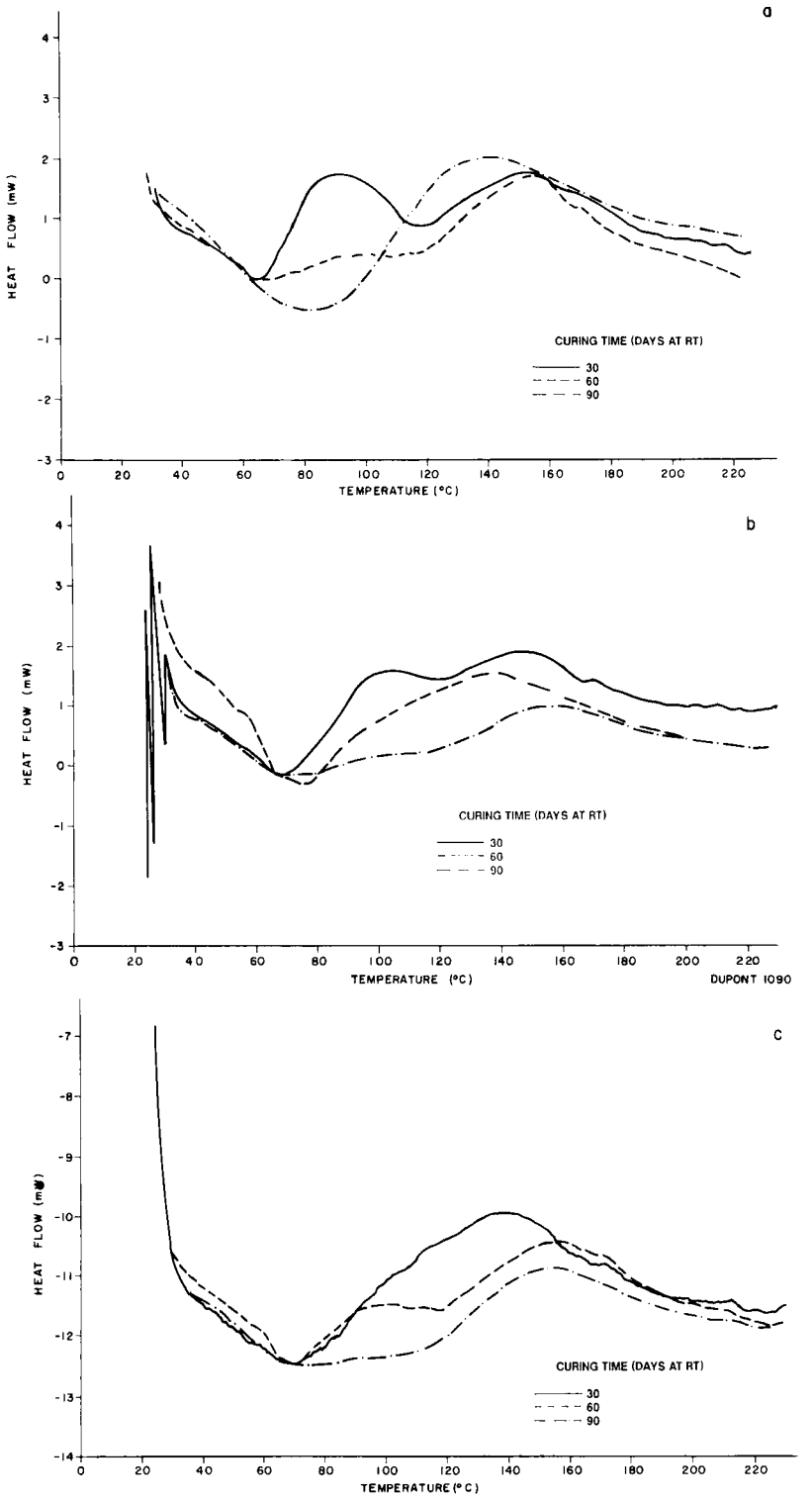


FIGURE 4 DSC scans at various curing times of formulation 3 (720/510/TETA/ATBN 1300×35) containing: a. 0.5%, w/w A-187, b. 0.5%, w/w A-1100, c. 0.5%, w/w Z-6032.

Thermal Analysis

DSC (Differential Scanning Calorimetry) was used to determine the degree of cure, curing temperature and exotherm of the partially-cured polymers.

In Part I of this work[8] the system without silane exhibited a broad cure exotherm peak at 90–100°C, indicating that curing is not complete after 6 days at ambient temperature.[8] Dielectric analysis of this epoxy blend showed that two exotherms appear for the uncured material. That at lower temperature is due to the curing of the epoxy and disappears after longer time curing at ambient conditions.[11]

Figure 4a depicts three thermograms of formulation 3 (720/510/TETA/ATBN 1300 × 35) containing 0.5% of A-187, after 30, 60 and 90 days at room temperature.

The 30-day-cured epoxy exhibits two peak exotherms at 90°C and 140–150°C as found in the dielectric analysis,[11] indicating that curing is not complete after 30 days at ambient temperature. It can be seen that after 60 days the 90°C peak is reduced and after 90 days it disappears, while the peak at 140–150°C remains. Figures 4b and 4c reveal a very similar behavior for the A-1000 and Z-6032 containing formulations.

Based on the above DSC results, it is evident that although curing is incomplete after 6–7 days at RT, it continues with time at ambient temperature as found in previous studies.[8,9,11] Furthermore, it seems that only the lower exotherm (90°C) disappears after longer periods of time at RT indicating that curing continues at RT, leaving the high temperature (140–150°C) exotherm which disappears when a 120°C curing is performed.[9,11]

Figures 5 a–c depict DSC thermograms of formulation 4 (720/815/TETA/ATBN 1300 × 35) containing 0.5% of A-187, A-1100, and Z-6032, respectively. For each composition three runs are shown after 30, 60 and 90 days at ambient temperatures. In this case, it seems that the two exotherms coalesce to one at 120°C. After long curing time the exotherm diminishes indicating that curing continues at ambient temperature.

Microstructure Analysis

The studied relationship between the system composition and the resulting mechanical performance was complemented by a micromorphology analysis.

Figures 6A, B, and C represent typical fractographs of peel loaded formulation 3 (720/510/TETA/ATBN 1300 × 35) specimens, containing 0.5% and 2% of the various silanes at room temperature.

The rubbery particles of less than a micron in size are concentrated in defined circular areas of 5 to 20 μm in diameter. This unique morphology is clearly identified in samples that contain 0.5% silane.[9] The 2% silane exhibits a more ductile morphology.

It seems that the interfacial adhesion between rubber and epoxy is better in the case of the amine-terminated silane (A-1100) compared with the epoxy and vinyl-terminated silanes (A-187, Z-6032, respectively), probably due to improved bonding between the amine and epoxy functional groups as shown in a previous study.[9]

The second composition, formulation 4 (720/815/TETA/ATBN 1300 × 35), (Figures 7A, B, and C), where the trifunctional epoxy was replaced by a difunctional epoxy, showed somewhat different morphology although the appearance of rubbery

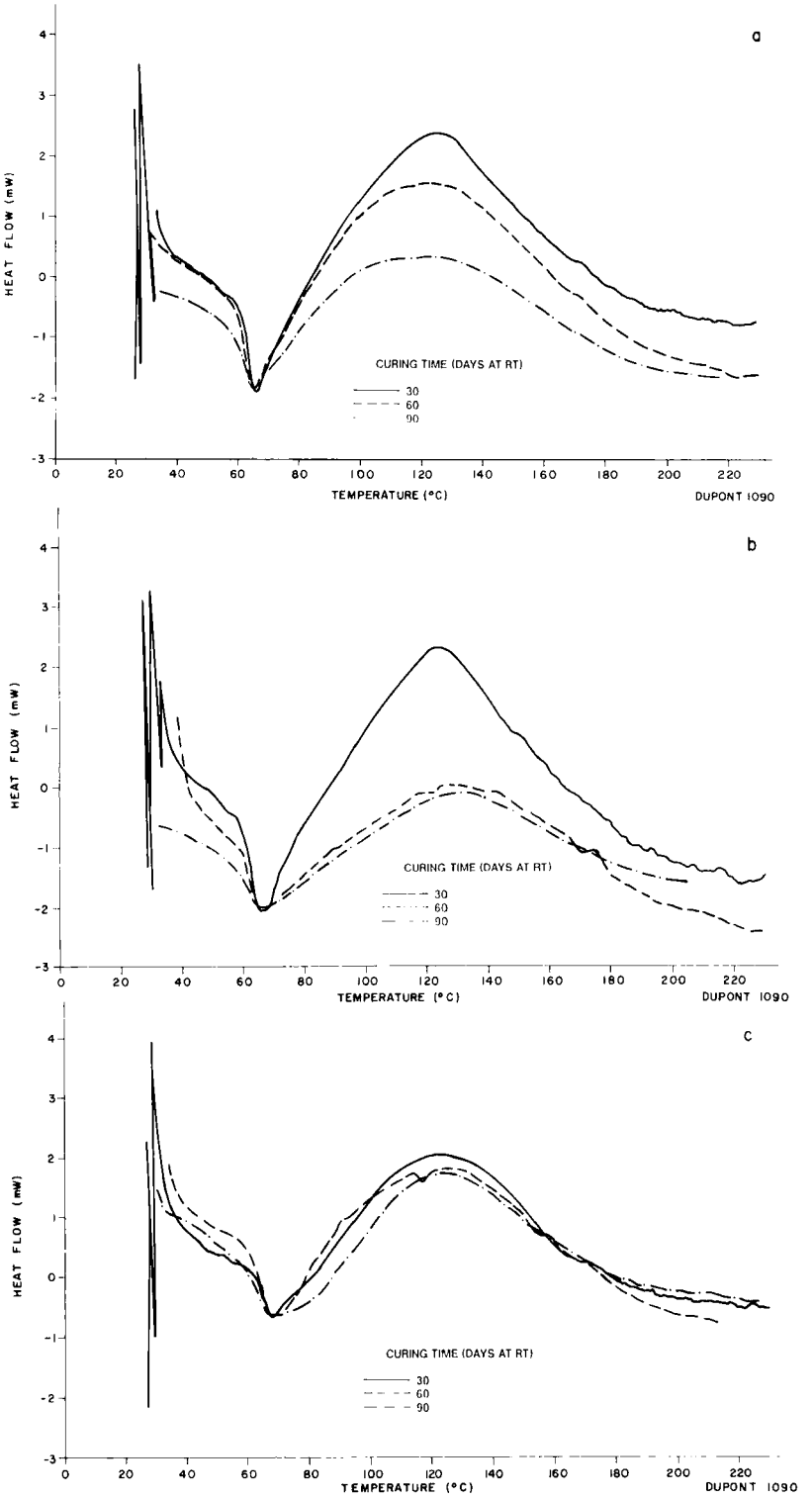


FIGURE 5 DSC scans at various curing times of formulation 4 (720/815/TETA/ATBN 1300×35) containing: a. 0.5%, w/w A-187, b. 0.5%, w/w A-1100, c. 0.5%, w/w Z-6032.

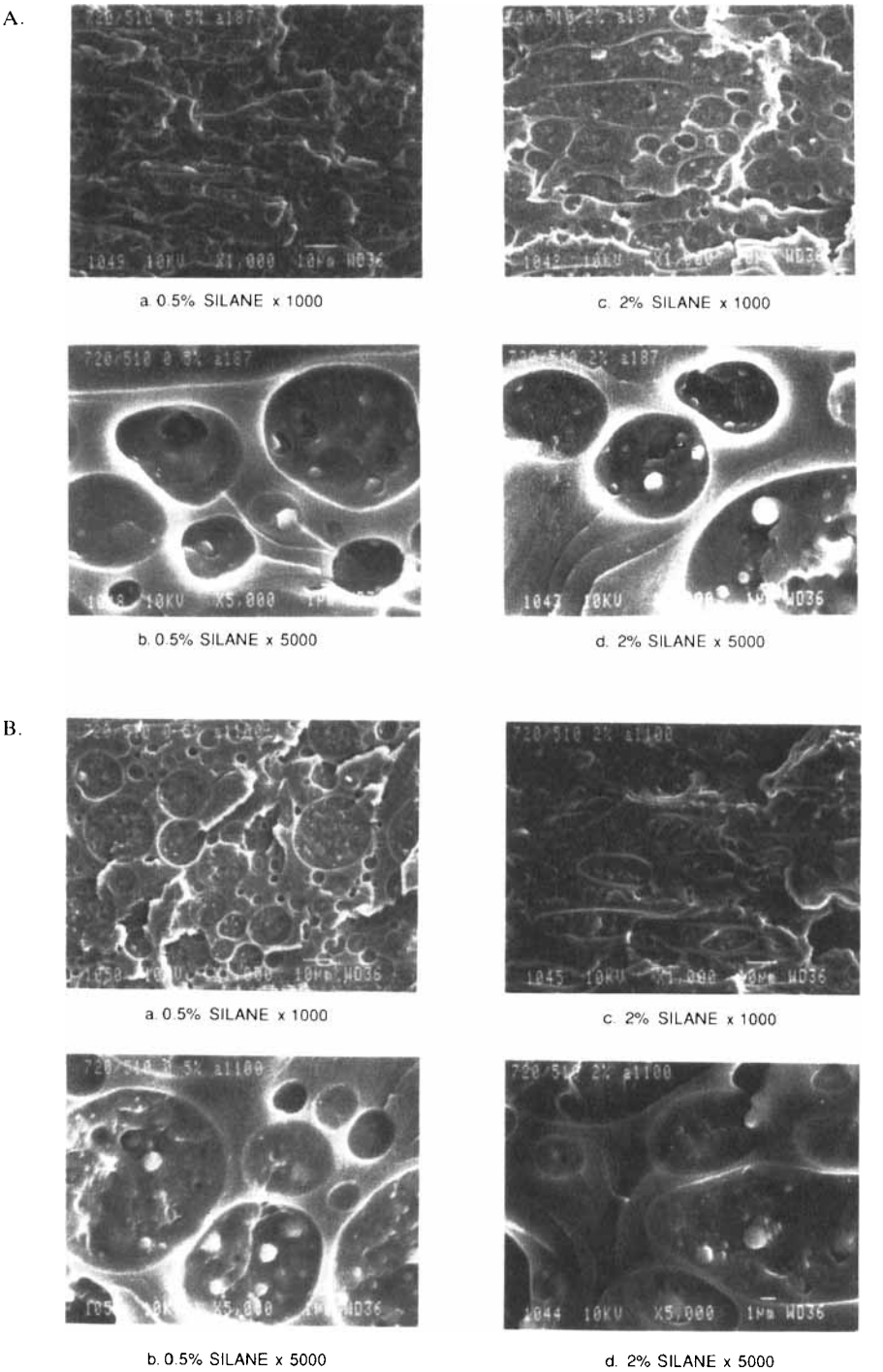
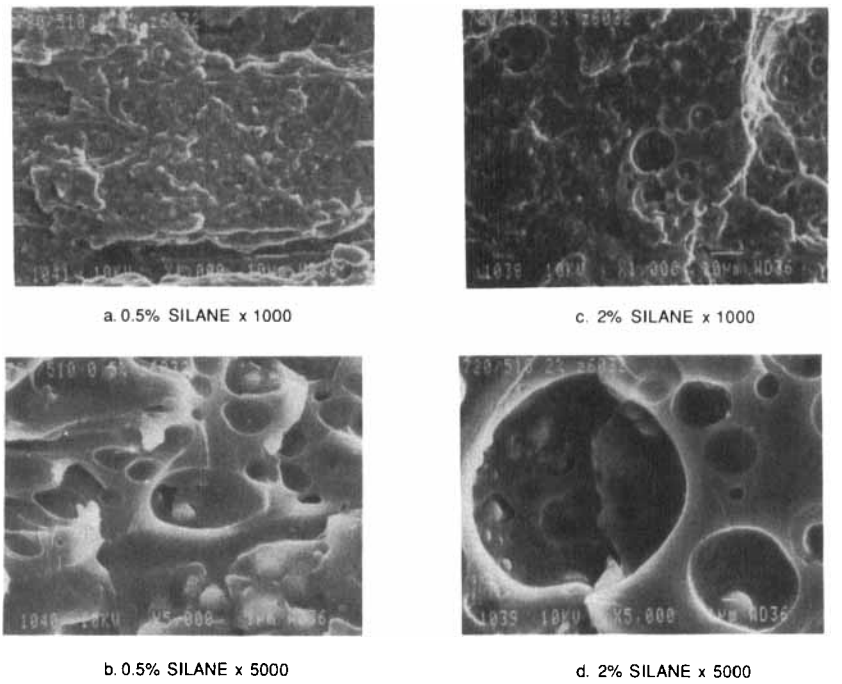


FIGURE 6 Scanning electron micrographs of fracture surfaces of formulation 3 (720/510/TETA ATBN 1300×35) containing 0.5%, w/w and 2%, w/w of various silanes: A. A-187, B. A-1100, C. Z-6032. For a. and c., ⟼ equals 10μ. For b. and d., ⊢ equals 1μ.

C.



a. 0.5% SILANE x 1000

c. 2% SILANE x 1000

b. 0.5% SILANE x 5000

d. 2% SILANE x 5000

FIGURE 6 *Continued.*

particles of 1–10 μm in size is evident. This may be due to the various degrees of compatibility between the silanes and the trifunctional epoxy compared with the difunctional one.

The developing microstructures of these reduced-temperature-curing epoxy formulations containing silanes are somewhat unique, especially in view of the three-phase morphology. The detailed thermodynamic interactions and chemical affinity between the terminated silanes and the system components are probably the cause of this unique microstructure.

CONCLUSIONS

The experimental results presented indicate that the interaction between the various silanes and the blend of epoxy curing agents is complicated. As has been shown, addition of silanes reduces the shear strengths of the adhesives at ambient conditions and elevated temperatures, and improves their durability in a hot/humid environment.

It can be concluded that the resultant properties are related to the specific interaction between a given silane and a given adhesive composition. In some cases, the silane may change the interfacial tension between the blend constituents and form a two- or a three-phase morphology. In other cases, covalent bonds form and interfacial adhesion is thus enhanced between the various adhesive blend components. In the case of exposure to a hot/humid environment, water may hydrolyze

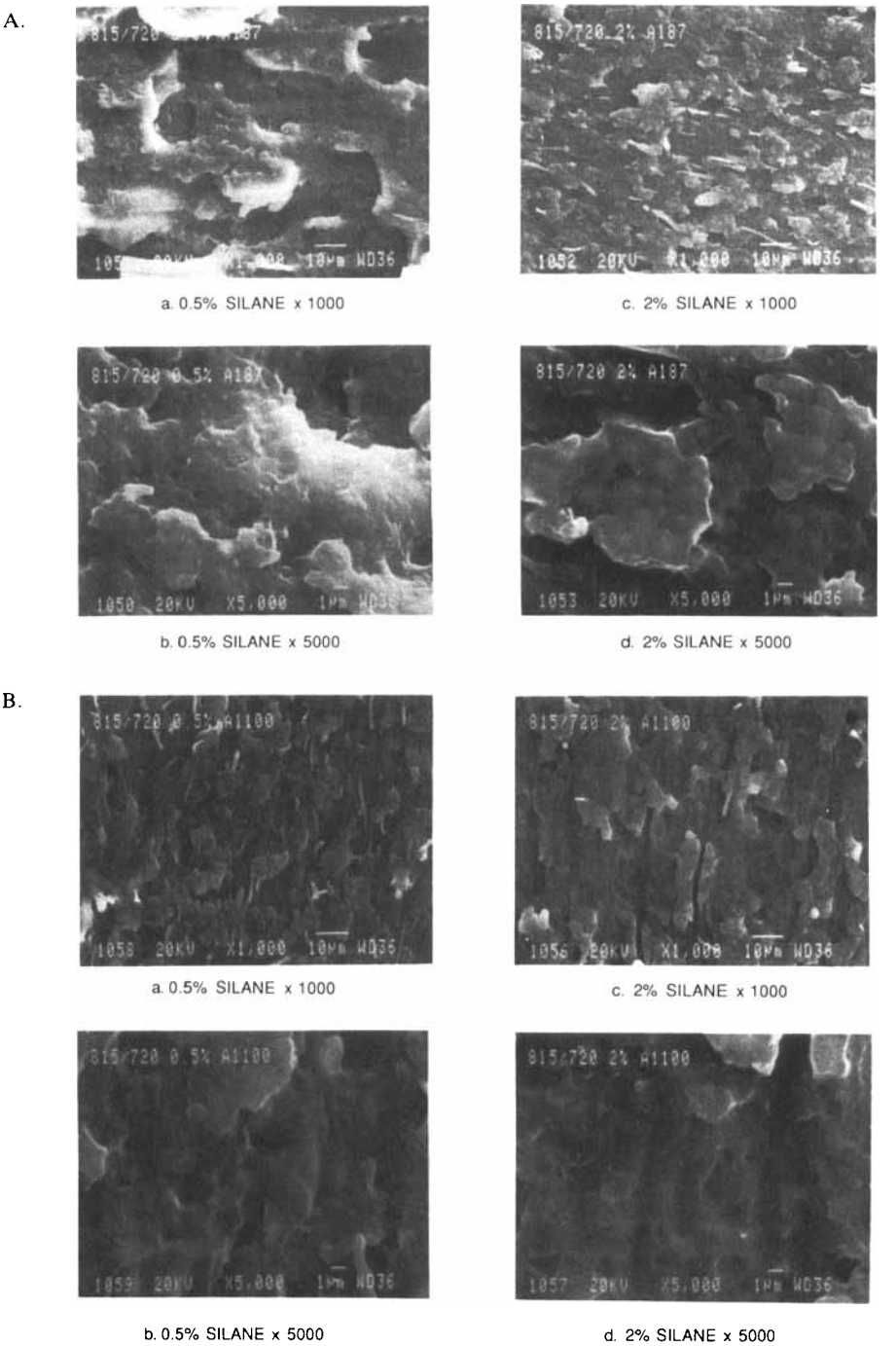


FIGURE 7 Scanning electron micrographs of fracture surfaces of formulation 4 (720/815/TETA/ATBN 1300×35) containing 0.5%, w/w and 2%, w/w of various silanes: A. A-187, B. A-1100, C. Z-6032. For a. and c., ⊢⊣ equals 10µ. For b. and d., ⊢ equals 1µ.

C.

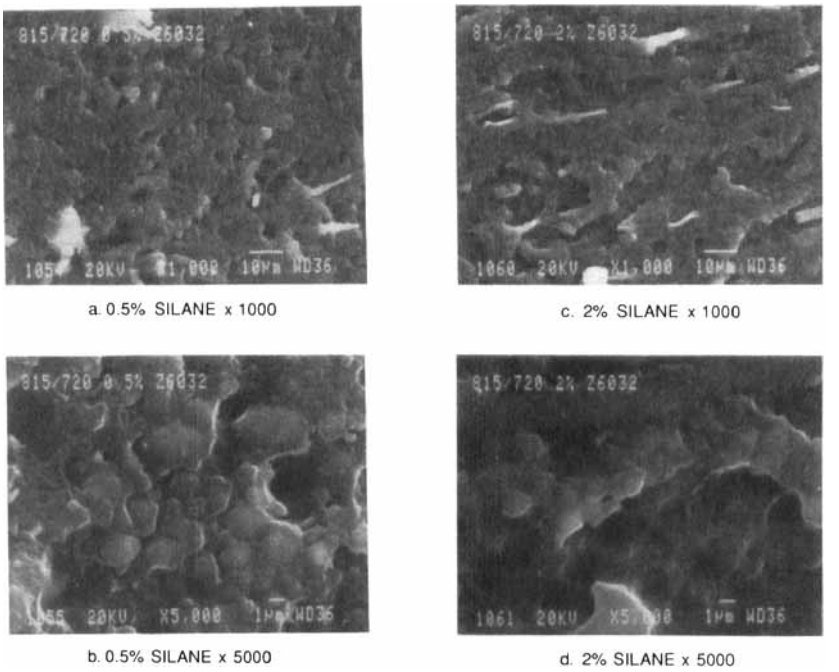


FIGURE 7 *Continued.*

the hydrolyzable end group of the silane to form oligomers and, subsequently, a secondary cross-linked network may form. This may provide a possible explanation for the enhancement of mechanical properties following exposure to a combination of humidity and heat.

A detailed study of the various simultaneous interactions of organosilanes and the various room-temperature-curing adhesive components may provide plausible explanations for the resultant effects seen in the present study.

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