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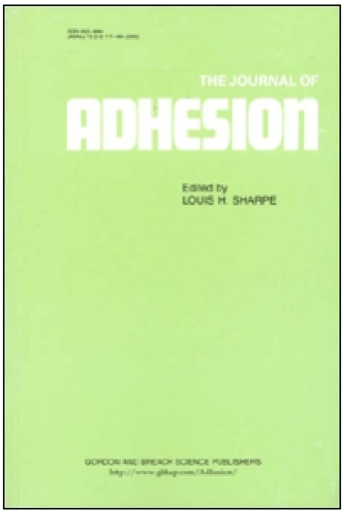

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Room Temperature Curing Epoxy Adhesives for Elevated Temperature Service, Part II: Composition, Properties, Microstructure Relationships

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Room Temperature Curing Epoxy Adhesives for Elevated Temperature Service, Part II: Composition, Properties, Microstructure Relationships

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Low temperature curing epoxy formulations for elevated temperature service have been previously developed and studied (Part I[1]). Balanced performance with respect to shear and peel properties have been obtained for a system composed of a tetra and trifunctional epoxy blend crosslinked by a mixture of multifunctional amine and an amino-terminated elastomer. In continuation of the previous study, the present one is aimed at investigation the effect of substitution of difunctional epoxy resin and curing agent for trifunctional ones on the developing microstructure and resulting mechanical properties. Furthermore, a new type of amino-terminated-acrylonitrile (ATBN) and an epoxy-terminated silane were included in the present investigation. Experimental results show that while reduction in the overall functionality of the reactants results in a lower lap shear strength, it gives rise to enhancement in peel strength. The same effect was observed when the new ATBN was used. Thermal analysis of the polymerization processes, taking place during curing of the various low temperature curing formulations, indicates that the curing activation energies are appreciably lower compared with high temperature curing systems. Addition of silane, ATBN and substitution of the multifunctional amine curing agent by a lower functional one, resulted in a moderate increase in the activation energy. The basic formulation, comprising a tetra- and trifunctional resin blend and a multifunctional amine and ATBN crosslinking mixture, developed a typical two-phase matrix-rubber microstructure. A third phase was observed when the trifunctional epoxy resin or the multifunctional curing agent was substituted by lower functional ones. A similar three-phase morphology was obtained when the epoxy-terminated silane was added to the basic treta- and trifunctional reactant system.

KEY WORDS Elevated temperature service; epoxy adhesives; room temperature curing; thermal analysis; rubber toughening; three phase morphology.

INTRODUCTION

Epoxy resins are increasingly used in the aviation industry and find their application in both structural adhesives and composite systems, where elevated temperature service is required. The combination of TGDDM (tetraglycidyl-4-4′-diamino-phenylmethane) resin and DDS (diaminodiphenyl sulphone) curing agent has been widely accepted to meet the elevated temperature performance requirement. The main drawbacks of the latter epoxy system stems from the elevated curing temperature (>150°C) needed and its relatively low toughness. To overcome these shortcomings, the authors[1] proposed a room temperature curing epoxy system using selected high functionality aromatic epoxy resins (TGDDM and triglycidyl ether of p-aminophenol) combined with a two-component polyamine curing system (TETA—triethylenetetraamine and ATBN—amino-terminated butadiene acrylonitrile). The inherent brittleness of the TGDDM formulation was remedied by a rubbery phase (ATBN), incorporated into the curing system due to its reactive end groups. Though the proposed epoxy system is amenable to cure at room temperature, it exhibits good mechanical properties at elevated temperatures (95–120°C). This combination is now the subject of a patent application.[2] Concurrently, a great deal of effort has been directed towards developing low temperature curing epoxy systems having good high temperature performance, for repair of aircraft components.[3–9]

The present study is a continuation of the authors' previous work,[1] and is aimed at elucidating the relationships between the system's component composition, the resulting mechanical properties and observed microstructure.

METHODOLOGY

As in the previously reported study,[1] the present one includes only commercially-available resins, curing agents and additives. The main objective of the present work was to study the effect of various components on the resulting microstructure and the final lap shear and peel strengths at ambient and elevated temperature and following exposure to heat and humidity (50°C/95% R.H.). The basic formulation introduced in Ref. 1 which was composed of TGDDM, trifunctional epoxy, TETA, ATBN and a polyester carrier, served as a reference. Three components of the latter formulation were changed, one at a time. Difunctional epoxy (DGEBA) substituted the trifunctional one. Diethylene aliphatic amine (DTA) replaced the triethylene aliphatic amine (TETA), and ATBN (1300 × 16) was substituted by a new type ATBN (1300 × 35). The tetra-functional epoxy (TGDDM) was left unchanged due to its basic elevated temperature characteristics. In addition, the effect of an epoxy-terminated silane added to the bulk adhesive, on the resulting durability and morphology, was studied.

Each formulation was evaluated for its adhesion properties in lap shear and peel loading at a wide range of temperatures and after exposure to hot-wet environment for various durations. From thermal analysis the activation energies of the curing reactions were determined. The peel fracture surfaces were analysed for their morphology and microstructure using a Scanning Electron Microscope (SEM).

By systematically varying the adhesive components, evaluating their adhesion properties and studying their micro-morphology, an attempt was made to inter-relate them and provide a better insight regarding the property development of this unique room temperature curing epoxy system.

EXPERIMENTAL

Materials and processes

The compounds used in this work are listed in Table I. In all cases studied, one part was a blend of two epoxy resins and the second part included the amine curing agent which was 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 $\frac{1}{2}$ hour at R.T. and 1 hour at 100°C. The adhesive was applied by brushing. The carrier was impregnated with the adhesive, evacuated for 5 minues 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[1] and found to be of secondary importance.

Sample preparation Typical formulations (Table I) were prepared as described

TABLE I
Epoxy formulations studied

Component (a)		Formulation No. component weight (gr)				
Epoxy resin	Manufacturer	1	2	3	4	5
MY 720	CIBA Geigy (USA)	50	50	50	50	50
ERL 510	CIBA Geigy (USA)	40	—	40	40	40
EPON 815	Miller Stephenson (USA)	—	74	—	—	
Curing agent						
TETA	Miller Stephenson (USA)	18.6	18.6	—	18.6	18.6
DTA	Miller Stephenson (USA)	—	—	18.6	—	—
Toughener						
ATBN (1300 × 16)	B. F. Goodrich (USA)	36	40	40	36	—
ATBN (1300 × 35)	B. F. Goodrich (USA)	—	—	—	—	40
Additive						
A-187 coupling agent	Union Carbide (USA)	—	—	—	0.5%	—
Carrier						
Polyester felt	Fibermat IC-650, 3M (USA)	+	+	+	+	+

[a] Chemical formulae are given in Table I of Ref. 1.

earlier.[1] In the case where the A-187 silane (0.5%) was studied, it was added to the epoxy mixture and remixed to an homogeneous blend.

Testing techniques

Mechanical tests Tensile lap shear specimens 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 2 mm/min (L.S.S.) and 200 mm/min (*T*-peel).

The lap shear and peel specimens were exposed for various durations to hygrothermal conditions, 50°C and 95% R.H., in a humidity chamber.

Thermal anlaysis 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. To obtain kinetic parameters[11] multiple DSC scans were generated at various heating rates (2, 5, 10°C/min). From the variation of the exotherm peak temperature, T_{exo}, with respect to heating rate, ϕ, the activation energy can be determined using the following relationship:

$$\frac{d\ln(\phi)}{d(1/T_{exo})} = \frac{-E_a}{R} - 2T_{exo} \tag{1}$$

where

ϕ = heating rate
T_{exo} = exotherm peak temperature, °K
E_a = kinetic activation energy (Kcal/mole)
R = gas constant (1.987 cal/mole/°K)

Thus, the set of dynamic curves obtained using varying heating rates enables the construction of a plot of $\ln(\phi)$ *versus* $1/T_{exo}$, where the slope is equal to $(-E_a/R)$, and the activation energy can be calculated when $E_a/R \gg 2T_{exo}$.

SEM SEM/EDAX 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

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 Figure 1, formulation 1 (the basic high-aromaticity, high-functionality composition), yields

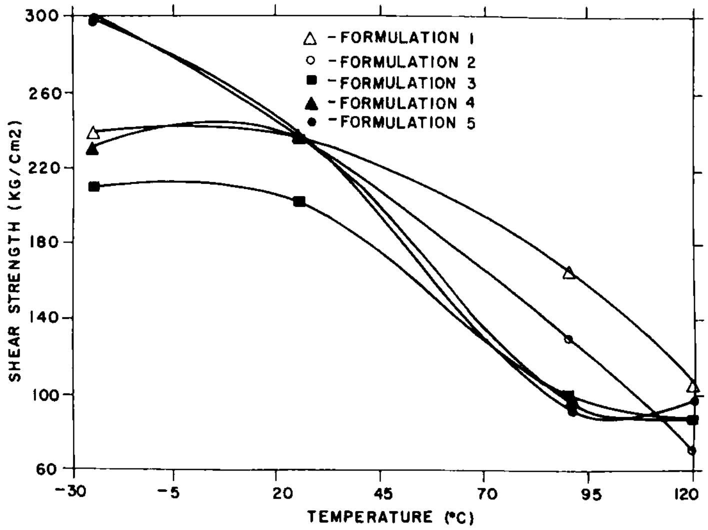


FIGURE 1 Lap shear strengths of various modified epoxy formulations (1–5) as a function of the testing temperatures.

the highest lap shear strength at elevated temperatures. This expected result is accompanied by an outstanding one, related to the case where epoxy-terminated silane was used. Incorporation of silane (formulation 4), results in decreased lap shear strength. Figure 2 indicates that while replacement of the trifunctional epoxy (ERL-510) by a difunctional epoxy (Epon 815) and, similarly, the high-functionality curing agent (TETA) by one of lower functionality (DTA),

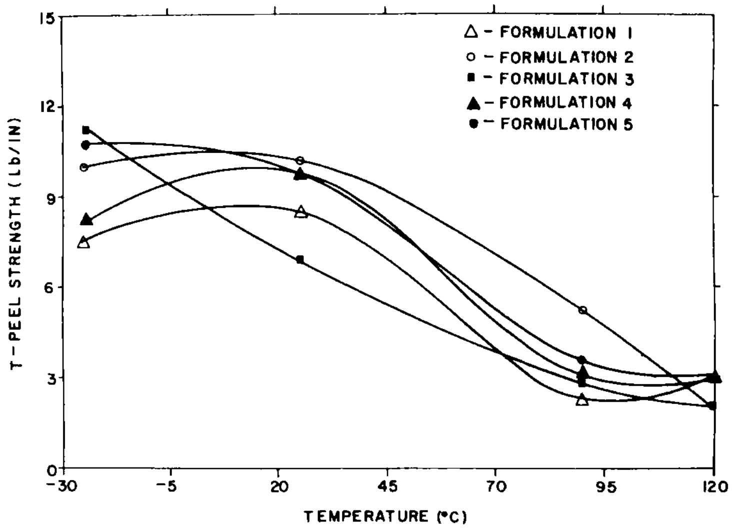


FIGURE 2 *T*-peel strengths of various modified epoxy formulations (1–5) as a function of the testing temperatures.

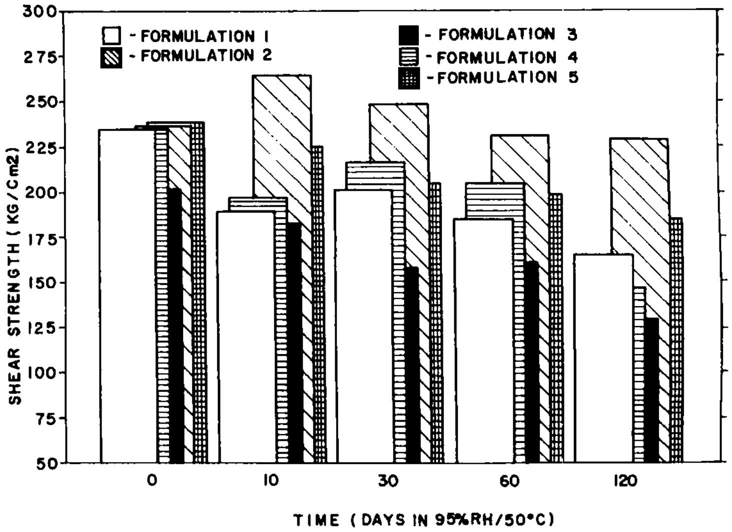


FIGURE 3 Lap shear strengths of various modified epoxy formulations (1–5) prior to and after exposure to a combination of heat/humidity (50°C, 95% R.H.) for various periods of time.

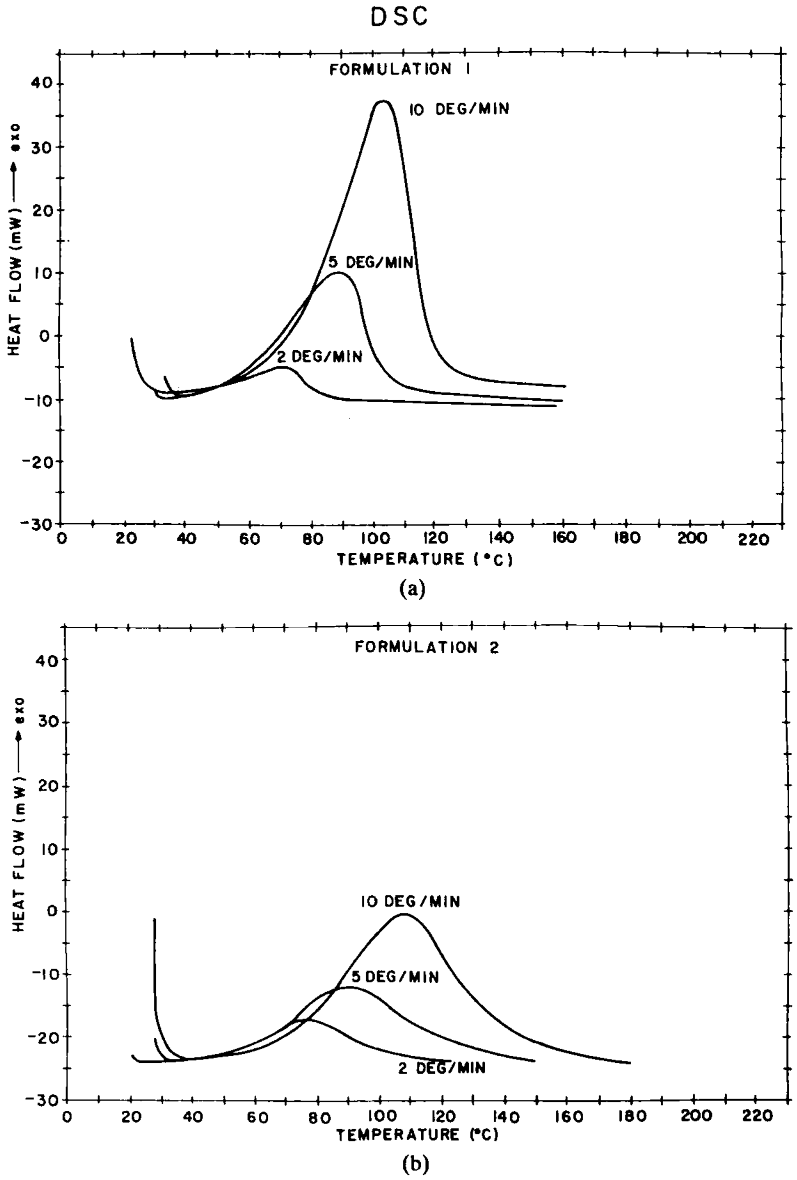
caused a reduction in lap shear strength, there was a beneficial effect with respect to peel strength. This may be attributed to the lower average functionality in the substituted formulation and consequently to its lower cross-linking density. It should be emphasized that this phenomenon is manifested especially at elevated temperatures.

Substitution of the toughening and curing agent (ATBN 1300 × 16) with (ATBN 1300 × 35), formulation 5, affects the lap shear and peel properties in the same direction, as in the cases of formulations 2 and 3.

The effect of hot-wet environment on the five epoxy formulations is given in Figure 3. As can be observed, a 30% degradation in lap shear strength takes place in most cases. However, the residual properties are satisfactory for most requirements (~150 kg/cm^2).

Thermal analysis

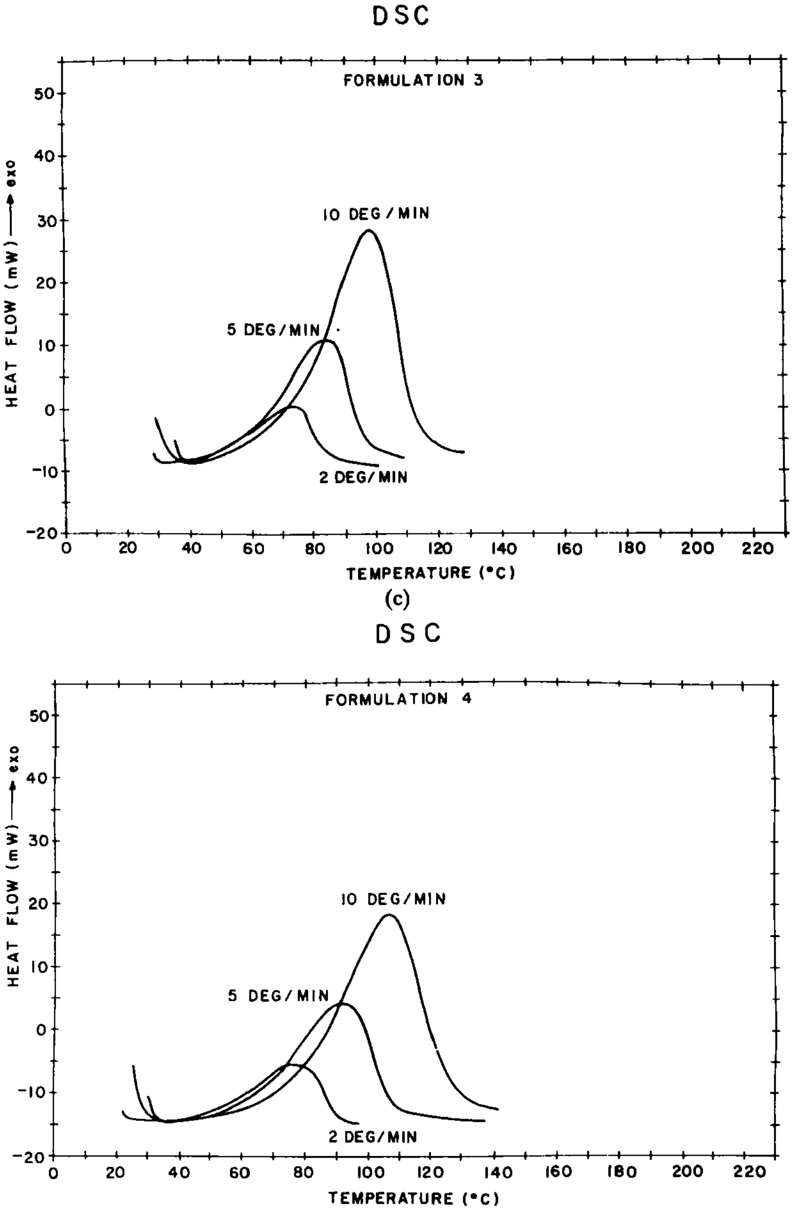
As shown previously,[1] the curing reactions of the original formulations and the modified ones were incomplete following 6 days at ambient temperature. Progressively, after 3 and 6 months the curing process continued, accompanied by decrease of the residual exotherm. Furthermore, thermal analysis results indicated that curing at moderate temperatures (~50°C) for a short period of time (~1 hour) resulted in complete curing. The activation energy of the curing reaction was determined using Kissinger's approach,[11] where the exotherm peak temperature is related to the change in heating rates as shown in Figure 4. Figure 5 describes the relationship between the logarithm of the heating rate, ϕ, and the reciprocal of the exotherm peak temperature, T_{exo}. As distinguished in Figure 5 and summarized in Table II, the activation energies of the studied formulations are characterized by two levels, the lower one belonging to the basic formulation 1 and formulation 2 (10–11 Kcal/mole) and the upper one to formulations 3, 4 and 5 (16–17 Kcal/mole). For typical high temperature curing epoxy systems composed of TGDDM and DDS,[12] the activation energies reported are in the range of 18 to 25 Kcal/mole. It could be concluded from Table II that substitution



(a)

(b)

FIGURE 4 DSC scan of formulations 1–5 at various heating rates (a–e, respectively).

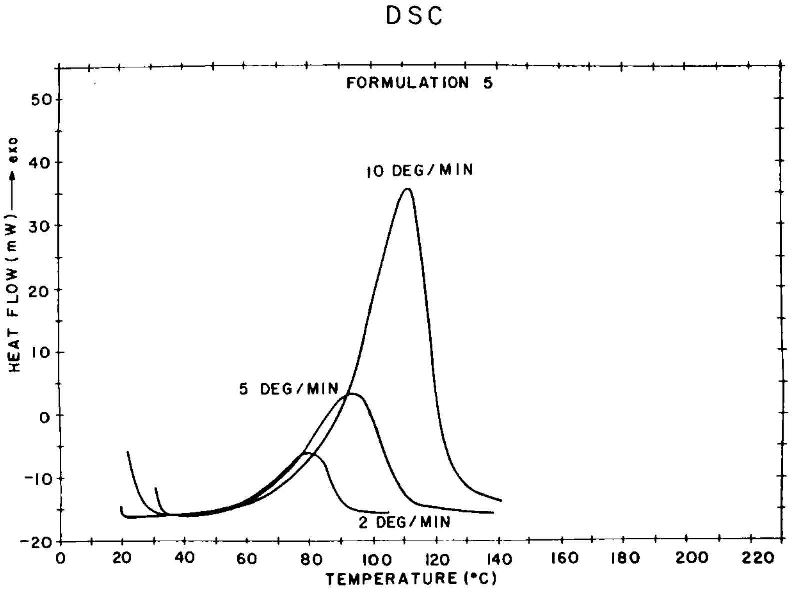


(c)

(d)

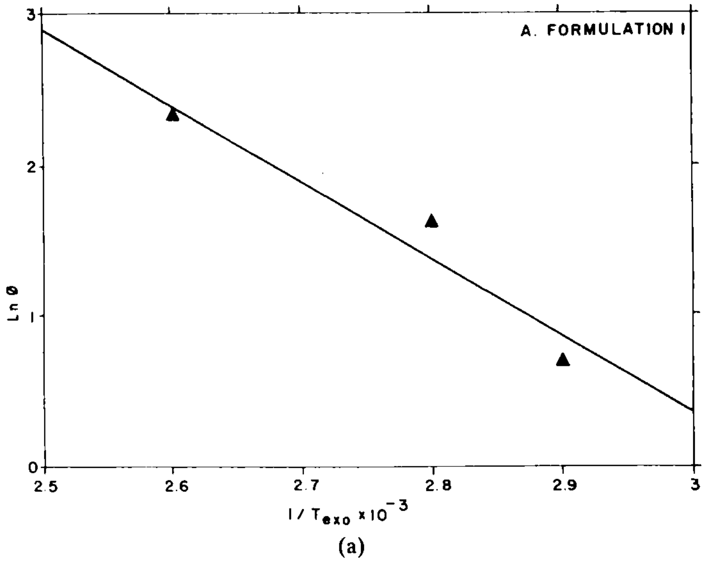
FIGURE 4 (*continued*)

of the trifunctional epoxy (ERL-510) by the difunctional one (Epon 815) did not change the basic curing kinetics. Distinctively, addition of the epoxy-terminated silane (A-187) and replacement of the curing agent TETA by DTA and the ATBN (1300 × 16) by the ATBN (1300 × 35) resulted in a moderate increase in the activation energy. The relatively low activation energies of the present



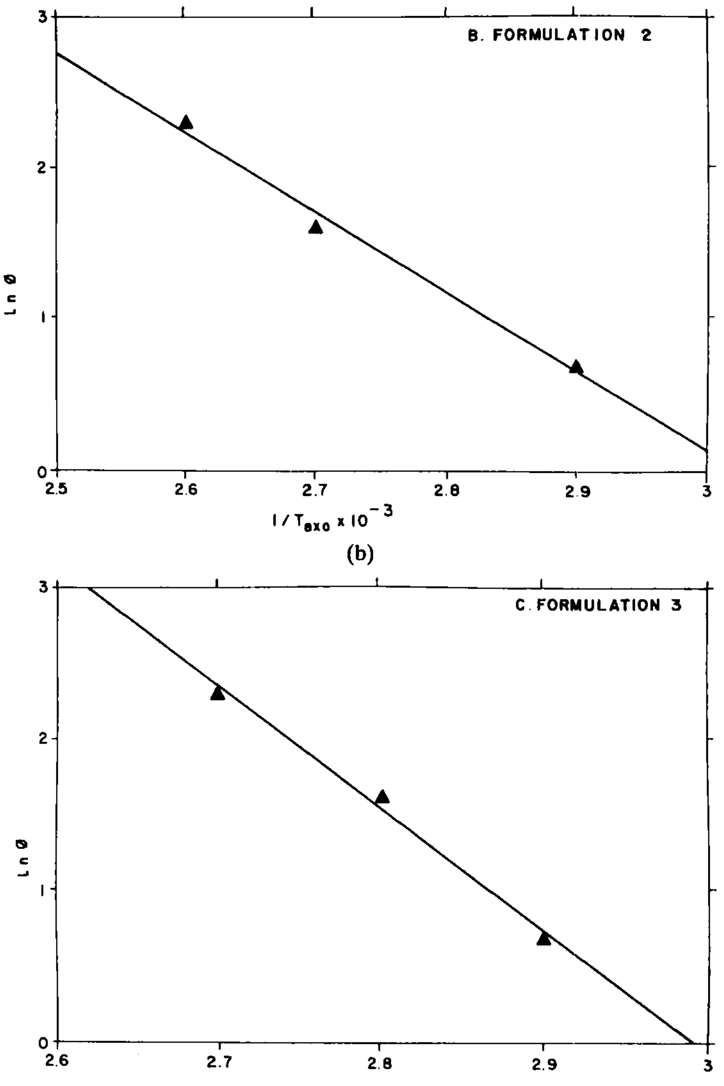
(e)

FIGURE 4 (*continued*)



(a)

FIGURE 5 A plot of ln ϕ *versus* $1/T_{eox}$ for formulations 1-5 (a-e, respectively).



(b)

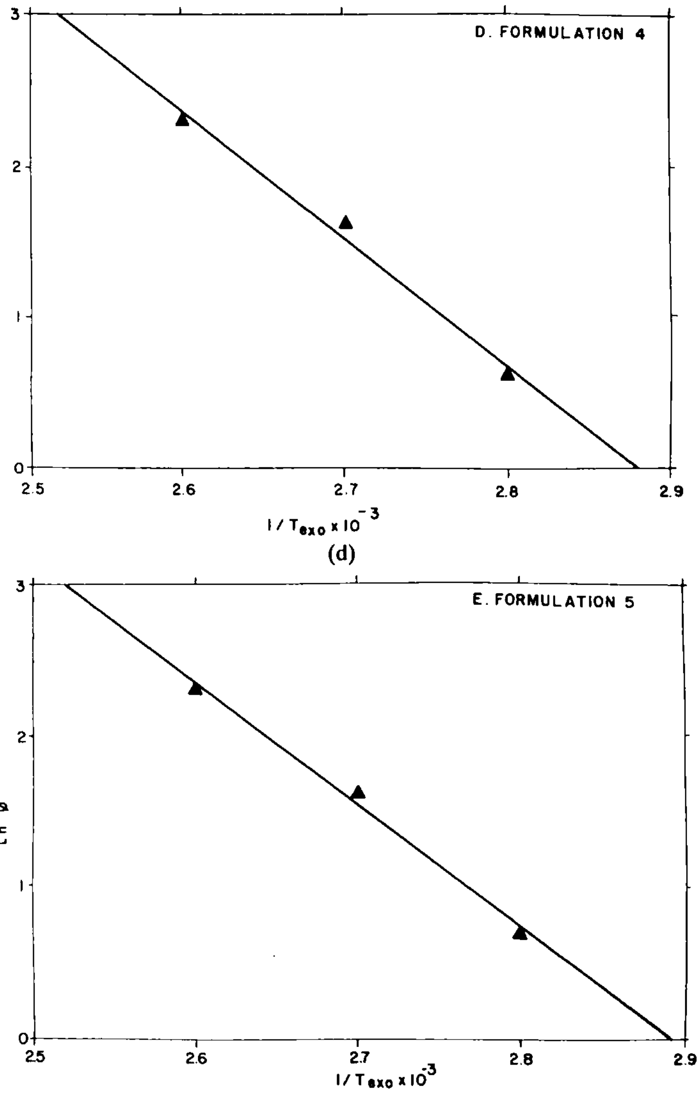
(c)

FIGURE 5 (*continued*)

compositions is a manifestation of the low curing temperatures required for these systems compared with the higher temperatures required to cure the conventional TGDDM/DDS system.

Microstructure analysis

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



(d)

(e)

FIGURE 5 (*continued*)

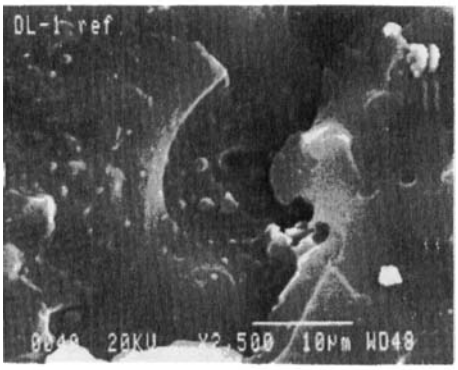
TABLE II
Activation Energies of Various Epoxy Formulations

Formulation	Activation energy E_a (Kcal/mole)	Fig. 5	Fig. 4
1	10.2	a	a
2	10.9	b	b
3	16.1	c	c
4	16.8	d	d
5	16.1	e	e
5208 resin (LMSC)	(a) 18.1-21.2	—	—
5208 resin (JPL)	(a) 24.7	—	—

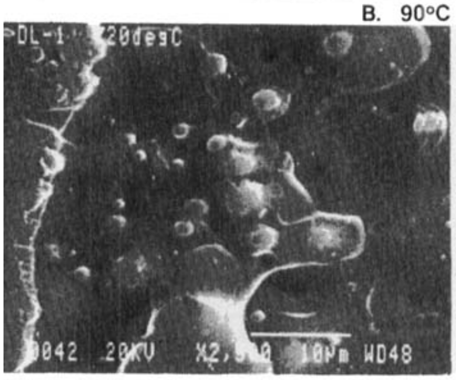
[a] Taken from Ref. 12, Table 8, page 1134.

FORMULATION 1

A. REF.



B. 90°C



C. 50°C / 95% RH
FOR 60 DAYS

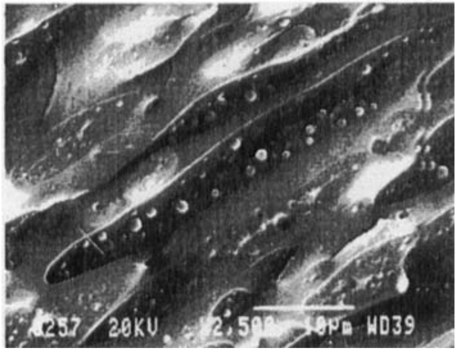
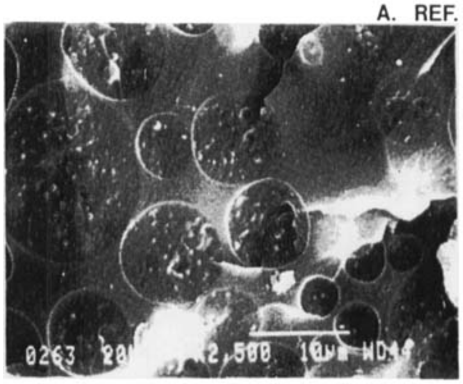


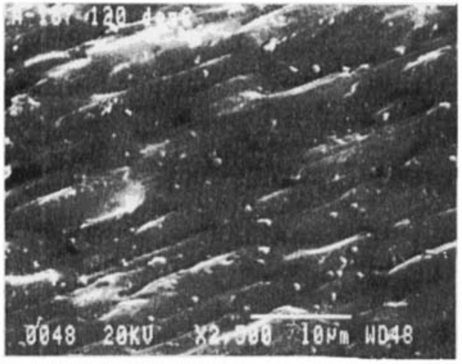
FIGURE 6 Scanning electron micrographs of fracture surfaces of formulation 1 peeled at various conditions (×2500): a: Fractured at RT, b: Fractured at 90°C, c: Fractured after exposure for 60 days at 50°C/95% R.H.

FORMULATION 4

A. REF.



B. 120°C



C. 50°C / 95% RH
FOR 60 DAYS

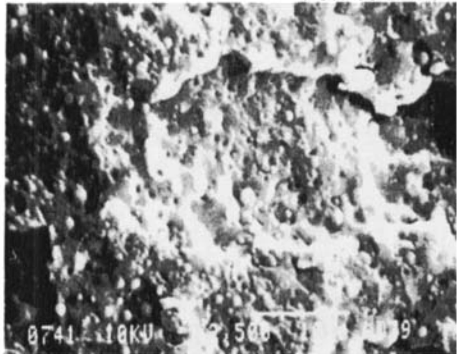


FIGURE 7 Scanning electron micrographs of fracture surfaces of formulation 4 peeled at various conditions (×2500): a: Fractured of RT, b: Fractured at 120°C, c: Fractured after exposure to 60 days at 50°C/95% R.H.

Figure 6 represents a typical fractograph of a peel loaded specimen at room temperature, at 120°C and following exposure for 60 days to heat and humidity. The basic morphology is a typical two-phase one observed in ATBN-toughened compositions, showing the segregated rubbery phase of 1 to 4 μm in size.[10] While loading at room temperature and 120°C results in a cohesive semi-ductile fracture, loading of the moisture-conditioned specimens yields a partial interfacial brittle failure.

The formulations containing the silane (No. 4) exhibit a unique morphology, as could be observed in Figure 7(a,b,c). The rubbery particles of less than a micron in size are concentrated in defined circular areas of 5 to almost 20 μm in diameter. This unique morphology is clearly identified in samples that have been loaded at room temperature (Figure 7a). In cases where the loading takes place at elevated temperatures the circular morphology is somewhat diffused (Figure 7b). When loading took place after moisture conditioning (Figure 7c), the fracture surfaces did not exhibit the circular morphology but rather a morphology typical of brittle-type failure.

The third composition (formulation 3), where the multifunctional amine was replaced by a lower functional amine curing agent, showed the same basic islands of more than 10 μm in size. In these regions the rubbery particles of less than 1 μm in diameter are located (Figure 8a). Upon loading at 90°C the fracture tends to be ductile in nature, with somewhat diffused circular boundaries (Figure 8b).

Formulation 2 again demonstrates the basic moon-like circular cavities in which the elastomeric particles are nested, (Figure 9a). In this case, where the trifunctional epoxy was substituted by the difunctional one, the fracture surfaces showed the circular morphology even after moisture conditioning prior to loading (Figure 9c).

In the fifth epoxy composition, in which the ATBN (1300 × 35) was used, the resulting fracture morphology is similar to the original formulation (Fig. 10a). It seems that the rubbery phase is larger in size compared with the case where the ATBN (1300 × 16) was used (Figure 6a).

The developing microstructures of these reduced temperature curing epoxy systems are somewhat unique, especially in the cases of the three-phase morphology. As reported earlier,[13] the resulting microstructure of rubber-toughened epoxy formulations depends upon the detailed polymerization chemistry of the reactants: resin, hardener and elastomer. The fact that the present low temperature curing systems contain a blend of two resins and two curing agents causes them to be very complicated with regard to the consequential microstructure. The two-phase, matrix-elastomer morphology, resulting from formulation 1 is typical of rubber-toughened epoxy, even though it contains a blend ot tetra- and trifunctional resins. This may be due to the apparent compatibility of the blend constituents, both in the liquid and solid states. Distinctively, when the trifunctional resin or the multi-functional curing agents were replaced by lower functional ones the specific polymerization kinetics, in addition to the thermodynamic interactions of the various reactants, resulted in a unique three-phase microstructure. As shown, the rubbery phase was concentrated in defined

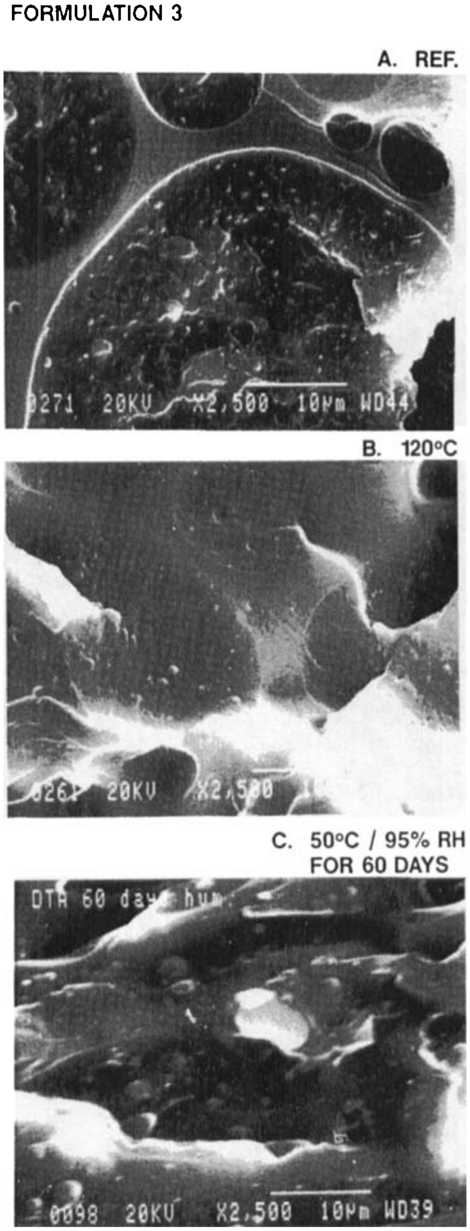
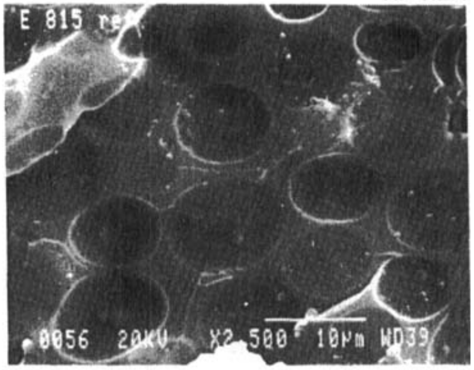
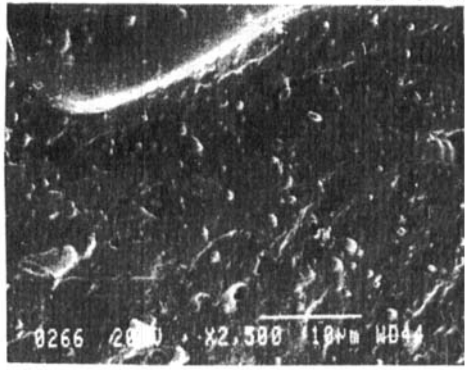


FIGURE 8 Scanning electron micrographs of fracture surfaces of formulation 3 peeled at various conditions (×2500): a: Fractured at RT, b: Fractured at 120°C, c: Fractured after exposure to 60 days at 50°C/95% R.H.

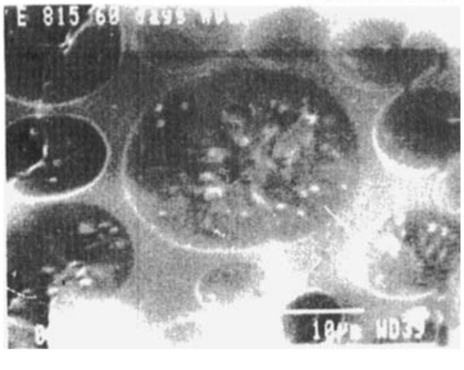
FORMULATION 2



A. REF.



B. 90°C

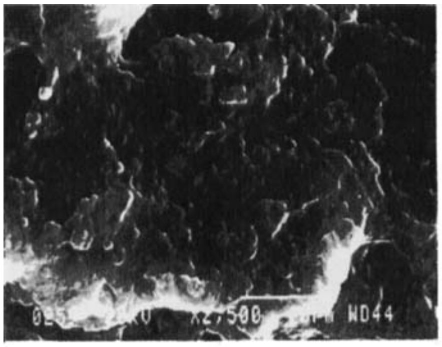


C. 50°C / 95% RH
FOR 60 DAYS

FIGURE 9 Scanning electron micrographs of fracture surfaces of formulation 2 peeled at various conditions (×2500): a: Fractured at RT, b: Fractured at 90°C, c: Fractured after exposure to 60 days at 50°C/95% R.H.

FORMULATION 5

A. REF



B. 120°C

C. 50°C / 95% RH
FOR 60 DAYS

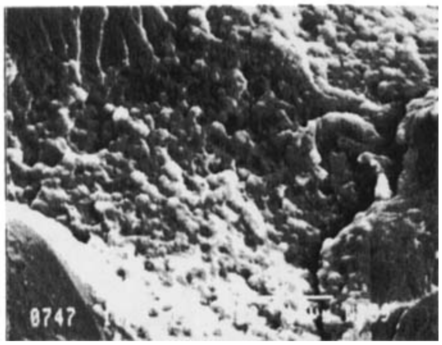


FIGURE 10 Scanning electron micrographs of fracture surfaces of formulation 5 peeled at various conditions (×2500): a: Fracture of RT, b: Fracture at 120°C, c: Fracture after exposure to 60 days at 50°C/95% R.H.

circular regions and a rubber-free zone comprised the matrix regions. When a small amount of silane was introduced into the tetra- and trifunctional system (formulation 4) a similar three-phase morphology developed. The detailed thermodynamic interactions and chemical affinity between the epoxy-terminated silane and the system components are the cause for this unique microstructure.

A clear relationship between these special two- and three-phase systems and the respective mechanical properties could not be established from the present data. A more detailed and systematically designed study is required.

CONCLUSIONS

A series of room temperature curing epoxy systems that exhibit practical elevated temperature properties have been developed and studied with respect to their final mechanical and thermal properties and the resulting microstructure.

When the highest possible functionality of both resins and curing agents, which are amenable to room temperature curing, was used, the highest lap shear properties at elevated temperatures were realized. Upon substituting the trifunctional reactants by a difunctional resin and lower functional curing agent, a reduction in lap shear properties was observed accompanied by a simultaneous increase in peel strength, especially in the intermediate temperature range. A detailed thermal analysis has indicated that the curing activation energies of the studied systems are lower than for high temperature curing compositions. The developing microstructure of the low temprature curing formulations are unique, exhibiting two- and three-phase morphologies depending on the specific constituents employed. A conventional two-phase morphology of matrix and rubber was observed when the basic composition comprising the tetra- and trifunctional reactants were used. However, when the trifunctional resin and high functional curing agent were substituted by lower functional ones, or a silane was added to the basic system, a three-phase microstructure developed. In this case the precipitated elastomeric phase was concentrated in defined regions. This unique microstructure is presumed to be the result of the specific polymerization kinetics and thermodynamic interactions between the system reactants. A conclusive relationship between the composition employed, the resulting properties and the developing microstructure, of this unique system requires a more detailed study. This will be the subject of a forthcoming investigation.

Acknowledgment

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