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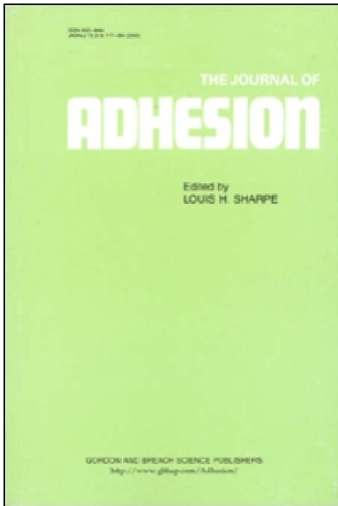

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Room Temperature Curing Epoxy Adhesives for Elevated Temperature Service†

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Room Temperature curing compositions of epoxy resins with high temperature service capability (95–120°C) were formulated and evaluated. The compositions were based on selected high functionality atomatic epoxy polymers and multicomponent polyamine curing agent systems. Toughening was achieved by addition of a rubbery phase either by prereaction of the epoxy resin with carboxyl terminated (CTBN) or by amine terminated (ATBN) poly butadiene acrylonitrile. The latter elastomeric component served as a part of the polyamine curing agent.

Best results were achieved with an adhesive formulation comprising tetra glycidyl-4-4′-diaminodiphenylmethane (TGDDM) and triglycidyl ether of p-aminophenol with triethylenetetramine and addition of ATBN with a felt carrier.

Lap shear strengths of aluminum/aluminum specimens primed by silane coupling agent in the order of 22 MPa at 25°C and 11 MPa at 120°C with T-Peel strengths of 1.6 N/mm at 25°C and 0.52 N/mm at 120°C, were obtained.

The thermal behaviour and transitions, the chemical and mechanical properties, the microstructure and morphology of the selected adhesive formulation were studied, using DSC, Gehman, FTIR, mechanical testing and SEM analysis, respectively.

Experimental results showed that the selected compositions could develop good high temperature (120°C) properties while cured at room temperature. Furthermore, their high temperature performance compares favorably or even exceeds that of commercially available room-temperature-curing adhesive compounds, and are competitive with elevated temperature cured film adhesives.

KEY WORDS epoxy; mechanical properties; morphology; room temperature curing; rubber toughening; DSC.

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INTRODUCTION

High temperature service is a common requirement for adhesives and fiber-reinforced composites, especially for aerospace applications. Epoxy resins with their high strength properties, toughness, corrosion resistance, excellent electrical properties and processing characteristics, have emerged as the most important adhesive and matrix materials for high-performance fiber reinforced structures. However, in order for epoxy to develop its optimal properties at elevated temperatures, heat has to be applied during curing. In most cases the maximum curing temperature has to exceed the expected service temperatures.

Perhaps the most outstanding characteristic of epoxy resins is their versatility,[1,2] depending upon their physical and chemical nature, the type and amount of the curing agents, fillers and other additives used as well as the curing conditions employed. By proper selection it is possible to obtain cured materials with a wide range of highly-reproducible, tailor-made properties.

Recently the possibility of employing room temperature curing resins with high temperature service characteristics has aroused considerable interest, especially for structural adhesives and fiber-reinforced composites. Room-temperature-curing resin systems could lower manufacturing cost of the composites and adhesives and simplify their processing, especially under field repair conditions.

The formulation of room-temperature-curing epoxy with high temperature service capability has been attempted by a number of approaches using specific types of polyfunctional epoxies and various curing agents comprising modified highly functional amines and aromatic dianhydrides.[3,4]

The primary objective of the present study has been aimed at developing a two-part paste adhesive for field repair that can be cured at ambient temperature with final properties equivalent to high-temperature-cured epoxy film adhesives.

Elevated-temperature-curing adhesive formulations and synthesis of new polymers for field repair of damaged structures was not within the scope of this study, although there were some successful efforts in these directions during the last years.[5–13]

In the course of the present investigation an extensive screening of commercially available epoxy resins and curing agents has been

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carried out and, consequently, a few multi-component room temperature curing epoxy compositions were developed. The selected formulations exhibited remarkably high service temperature capabilities. Results obtained were evaluated and compared to various commercially available structural adhesives.

EXPERIMENTAL

Materials and processes

The compounds used in this work are listed in Table I. In all cases the adhesive comprised a multi-component formulation. Two principal cases were studied.

In the first case, one part of the composition was the product of a carboxyl-terminated liquid rubber prereacted with a blend of two epoxy resins. In this way linear epoxy rubber chains were obtained. The second part of the adhesive was an amine curing agent (Procedure A).

In the second case, 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 (Procedure B). Details are given in the next section and the list of the adhesive formulations are given in Tables II and III.

Adhesives compositions were first characterized by determining their shear and peel properties. Testing specimens were prepared from aluminum (A1-2024-T351) that has 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 TF-35 solution (manufactured by DuPont) 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. When a felt carrier was used, it was impregnated with the adhesive, evacuated for 5 minutes at 5 mm/Hg (absolute pressure) and excess resin was squeezed out. The felt used was FIBERMAT IC-650 (3M, U.S.A.).

The test specimens were permitted to cure at ambient temperature for 6 days, prior to testing. The 95°C and 120°C test data are reported after 10 min soak at testing temperature. In order to

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TABLE I
Chemical formula

Materials	Chemical formula	Trademark
Epoxy Resin EE[a] = 183 gr/eq	O—CH_2—CH—CH_2 (O) ; [O—CH_2—CH—CH_2 (O)] ; O—CH_2—CH—CH_2 (O) ; —CH_2— ; —CH_2—	EPN1138 CIBA GEIGY
Epoxy Resin EE = 128 gr/eq	R_2N—C_6H_4—CH_2—C_6H_4—NR_2 R = CH_2—CH—CH_2 (O)	MY720 CIBA GEIGY
Epoxy Resin EE = 107 gr/eq	CH_2—$CHCH_2$ (O) ; CH_2—CH—CH_2 (O) ; N—C_6H_4—OCH_2CH—CH_2 (O)	ERL510 CIBA GEIGY

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Epoxy Resin EE = 190 ± 20 gr/eq	$\sim CH_2-\overset{O}{CH}-R-\overset{O}{CH}-CH_2\sim$ $R = CH_2O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-$	EPON828 Miller Stephenson Chem. Co
Epoxy Resin EE = 200 ÷ 260 gr/eq	Tetra functional, unknown chemical formula.	ER0163 CIBA GEIGY
Curing Agent AE[b] – 40 ± 3 gr/eq	$_2HN(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	TETA Miller Stephenson Chem. Co.
Curing Agent AE – 111 gr/eq	$H_2N-(S)-CH_2-(S)-NH_2$	PACM20 DuPont
Curing Agent	(BTDA structure)	BTDA Gulf Advanced Materials

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TABLE I (*continued*)

Materials	Chemical formula	Trademark
Curing Agent	Hexahydrophthalic anhydride: ring of four CH_2 groups and two CH carbons, each CH bonded to a $C(=O)$, the two C=O groups joined through O	HHPA Miller Stephenson Chem. Co.
Rubber ATBN AE − 1160 gr/eq	$HN\langle S \rangle N(CH_2)_2-NH-C(=O)(CH_2CH=CHCH)_x-(CH_2-CH(CN))_y-C(=O)-NH-N(CH_2)_2-N\langle S \rangle NH$	Hycar ATBN 1300 × 16 BF GOODRICH Chem. Co.
Rubber CTBN COOH No. = 2000 ± 150	$HOOC[-(CH_2CH=CHCH)_x-(CH_2CH(CN))_y]_zCOOH$ $x = 5,\ y = 1,\ z = 10$	Hycar CTBN 1300 × 8 BF GOODRICH Chem. Co.

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Catalyst	$P-(C_6H_5)_3$	T.P.P. (Tri Phenyl Phosphine) Aldrich
Curing Agent	CH_3 / N / CH_2CH_3 (ring structure)	EMI (2-Ethyl-4-Methyl-Imidazole) Aldrich
Primer	Unknown	EA9203 HYSOL Division
Coupling Agent γ-Glycidoxypropyl-trimehtoxy-silane	$_2HNCH_2CH_2CH_2-Si-(OCH_2)_3$	A-187 UNION CARBIDE

[a] EE – Epoxy Equivalent.
[b] AE – Amine Equivalent.

TABLE II
Lap shear strengths of room temperature curing high functionality epoxy resin systems

Epoxy resin formulation	Lap shear strength,[b] MPa.	
	25°C	120°C
1. Epoxy Resin 0163/EPON828/TETA 60/40/18	7.2 ± 1[a]	inconvenient
2. EPN 1138/EPON828/TETA 60/40/13	8.8 ± 2.5[a]	10.9 ± 0.5[a]
3. MY 720/EPON828/TETA 60/40/16.4	9.6 ± 4.9[a]	9.6 ± 0.3[a]
4. ERL510/EPON 828/TETA 72/40/12	9.3 ± 1.5[a]	2.2 ± 0.2[a]
5. ERL510/HHPA/BTDA 49/29/20	2.6 ± 0.6[a]	9.6 ± 1.4[a]
6. MY720/ERL510/PACM20 50/40/45	5.4 ± 0.4[a]	15.6 ± 1.4[a]
7. MY720/ERL510/HHPA/BTDA 50/40/53/36	9.9 ± 0.8[a]	14.6 ± 1.4[a]
8. MY720/ERL510/TETA 50/40/20	14.7 ± 1.6[a]	10.2 ± 4.8[a]

[a] Adhesive failure.
[b] Average of 5 test specimens ± standard deviation.

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evaluate the influence of soaking at testing temperature on the shear strength, tests were conducted after 2 minutes, 5 minutes and 10 minutes at 120°C. It should be noted that the test specimen reached the 120°C after 2 minutes soaking at that temperature. Results (shown in Table III, footnote e) indicated that the shear strength did not change markedly during the soaking period. Similar behaviour was found for the other formulations, within the experimental error.

Sample preparation

Epoxy and CTBN prepolymers were prereacted to ensure the formation of an epoxy rubber intermediate. The mechanisms of this

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TABLE III
Lap shear and T-Peel strengths of high functional room temperature curing epoxy compositions formulated in the present study, and selected commercial adhesives

Adhesive composition	Adhesive type	Manufacturer	Lap shear strength (MPa)[b]			T-Peel Strength (N/mm)[b]		
			25°C	85–95°C	120°C	25°C	95°C	120°C
9. MY720/ERL510/TETA/CTBN[d] 50/40/20/14.9	R. T. Cure Epoxy	M.O.D.	22 ± 3.5[a]	—	8.5 ± 1.4[a]	0.29[a]	—	0.5[c]
10. MY720/ERL510/TETA/CTBN/EMI[d] 50/40/20/14.9/4	R. T. Cure Epoxy	M.O.D.	28.3 ± 5.9[a]	—	11.7 ± 0.9[a]	—	—	—
11. MY720/ERL510/TETA/ATBN 50/40/18.6/36	R. T. Cure Epoxy	M.O.D.	23.0 ± 2.3[c]	16.2 ± 3.2[c]	9.3 ± 0.9[c]	1.1 ± 0.1[c]	0.2 ± 0.03[c]	0.2 ± 0.02[c]
12. MY720/ERL510/TETA/ATBN/EMI 50/40/18.6/36/4	R. T. Cure Epoxy	M.O.D.	27.3 ± 3.5[c]	15.8 ± 1.5[c]	15.0 ± 1.7[c]	0.30 ± 0.03[c]	0.19 ± 0.03[c]	0.12 ± 0.02[c]
13. MY720/ERL510/TETA/ATBN + felt 50/40/18.6/36	R. T. Cure Epoxy	M.O.D.	21.5 ± 1.2[c]	—	10.6 ± 1.2[e,c]	1.6 ± 0.09[c]	—	0.52 ± 0.05[c]
14. EA9321	R. T. Cure Epoxy	HYSOL	29.4 ± 0.98[a]	7.6 ± 0.49[a]	2.94 ± 0.69[a]	0.5 ± 0.1[c]	0.3 ± 0.03[c,a]	0.12 ± 0.03[c,a]
15. EA9309	R. T. Cure Epoxy	HYSOL	24.5 ± 0.9[a]	3.0 ± 0.7[a]	2.5 ± 0.3[a]	5.3 ± 0.6[c]	0.3 ± 0.1[c,a]	0.07 ± 0.02[c,a]
16. EA9330	R. T. Cure Epoxy	HYSOL	22.1 ± 1.2[a]	3.9 ± 0.3[a]	2.5 ± 0.2[a]	3.6 ± 0.5[c]	0.12 ± 0.04[c,a]	0.05 ± 0.01[c,a]
17. FM300K	177°C/35 psi Cure Epoxy	American Cyanamid	27.9 ± 1.9[c]	—	19.6 ± 2[c]	1.4 ± 1.5[c]	—	—
18. Versilok 204/Ac4	RT Cure Acrylic	Hughson	24.2 ± 2.7[a]					

[a] Adhesive failure.
[b] Average of 5 test specimens ± standard deviation.
[c] Cohesive failure
[d] Without primer 187
[e] After 2 minutes soaking at 120°C—8.1 ± 1.1 MPa.
After 5 minutes soaking at 120°C—9.0 ± 0.9 MPa.
After 10 minutes soaking at 120°C—9.4 ± 0.6 MPa.

reaction has been discussed by Siebert and Riew.[15] The epoxy-rubber prepolymer was prepared at 150°C, with mechanical stirring under nitrogen flow, using triphenyl phosphite (0.15 percent) as catalyst. The reaction advancement was monitored by titration of the carboxyl groups with 0.1 N KOH/ETOH. Reaction continued to 1 percent of the initial EPHR. Following preparation, the intermediate prepolymer was stored at 0°C and used in appropriate amount as described in Procedure A (see below).

Since ATBN reacts directly with the epoxy end groups (it was used as one of the curing agents[16]), it was added directly to the epoxy as described in Procedure B (see below).

Two typical formulations (Tables II and III), were prepared as described by the following procedures:

Procedure A: MY720/ERL510/TETA/CTBN (50/40/20/3.3).
10 grams of prereacted mixture of MY720/ERL510/CTBN (95/76/72 W/W) was added to 41.2 grams of MY720 and 33.0 grams of ERL510 and was mixed to a homogeneous mixture which contained 3.7% CTBN (epoxy resin basis). Then, 18 grams of the TETA curing agent was mixed with the combination of the epoxy resins. This formulation has a low enough viscosity to be easily mixed and applied.

Procedure B; MY720/ERL510/TETA/ATBN (50/40/19.3/13.5).
To a resin mixture of 50 grams MY720 and 40 grams of ERL510, a curing agent mixture of 19.3 grams of TETA and 13.5 grams of ATBN was added. This formulation (which contains 15% ATBN on the epoxy resin basis) was mixed to a homogeneous mixture.

In some cases, preheating of some components was needed to lower their viscosity and promote mixing.

Testing techniques

Tensile lap shear specimens (L.S.S) were prepared according to ASTM D1002-72. T-Peel specimens were prepared according to ASTM D1867. 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—crosshead speed 2 mm/

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min (L.S.S.) and 200 mm/min (T-peel) at 25°C, 95°C and 120°C. The mode of failure (adhesive or cohesive) was evaluated by visual inspection.

The selected compositions were characterized in bulk using tensile samples that were cut from cast specimens and loaded at an extension rate of 5 mm/min. In this way, Young's modulus and maximum stress and strain to failure were obtained.

Densities of the cast cured epoxy specimens were measured at ambient temperature, according to ASTM D3800-79.

Specific heats and extent of cure were determined using a 910 DSC unit of DuPont 1090 Thermal Analyzer at a heating rate of 10°C/min. The Tg was determined from the plot of 10-sec flexural modulus *versus* temperature, using a modified Gehman apparatus according to ASTM D1043-58 (rate of heating 1°C/min).

Infrared spectra of the aluminum adherend surfaces after fracture were obtained in a FTIR Nicolet 5DX. The External Specular Reflectance mode was used. In addition, it was equipped with a horizontal stage in a near-to-normal incidence, with gold mirror for reference.

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 sputter-coated with a thin layer (~20 nm) of platinum to obtain a conductive surface and reduce charging.

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RESULTS AND DISCUSSION

Methodology

The special combination of room-temperature curing with elevated-temperature service performance places a few restrictions on the potential use of certain constituents and calls for special considerations.

The primary demand for high temperature preformance and thermal stability dictates that the selected epoxy resins should be capable of creating a high cross-linking density. This, in turn, limits one to the use of polyfunctional epoxy resins and curing agents.

Preferably, all of the components should consist of aromatic rings for enhanced thermal stability.

The use of polyfunctional epoxy resins with high aromaticity results in brittle solids with low toughness. To remedy this consequence, reactive elastomers and a thermoplastic carrier have to be incorporated in the formulation, preferably without sacrifice of the high temperature performance.

The other most important requirement of room temperature curing capability demands the use of reactive room temperature curing agents and low viscosity resins and other components.

In this study another restriction was imposed, namely, all resins, curing agents and additives should be commercially available. On the basis of these considerations all of the materials used in the present study were selected.

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Optimization of adhesive compositions

As previously described, the basic approach in the present study was the use of high functionality and high aromaticity epoxy resins and hardeners to yield a high level of cross-linking and consequently improved stability.

The selected epoxy resins, as described in Table I, were:

- MY720—This resin is a tetra functional epoxy with high aromaticity.
- ERL510—A very low viscosity trifunctional epoxy. It was added to MY720 to reduce its viscosity and to allow easy mixing.
- EPON828—A general purpose difunctional epoxy.
- EPN1138 and ER0163—Are high functionality epoxies. However, they are less convenient since they are solids at RT.

In this investigation, two curing agent types were used. One initiated reaction at a moderate temperature, the other provided high temperature stability.

High functionality aromatic amine curing agents have been selected as they have high reactivity and introduce good thermal stability.[5] PACM-20 has been selected because it has fast cure times with epoxy resins and gives products with good thermal stability.[10,11] Being a low viscosity liquid, it could be readily mixed with the resin.

BTDA and HHPA are tetrafunctional anhydrides which result in products with good thermal stability.[3] A list of the evaluated formulations is presented in Tables II and III.

Table II summarizes the initial lap shear results at both ambient and elevated temperature (120°C). Results indicated that high functionality epoxy resins such as EPN1138/EPON828, MY720/EPON828 and MY720/ERL510 can be incorporated with a curing agent such as TETA to produce room-temperature-curing compositions having a respectable high temperature shear strength. More specifically, formulations 2, 5, 6, 7 of Table II were not completely cured at room temperature during 7 days, as shown by the bond strength enhancement at 120°C. Lap shear strengths values of formulations 1 and 4 (Table II) decreased markedly at 120°C. However, those of formulations 3 and 8 are particularly interesting with regard to both the initial and 120°C values obtained, with some advantage of formulation 8 at 25°C. Consequently, at that stage, the high functionality epoxy resin with the TETA curing agent was selected for further investigation. However, as expected, it was brittle and its T-Peel strength was very low (~0.12 N/mm), as shown in Figure 1.

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In the next step, the fracture toughness as manifested by the peel strength had to be improved in order to engineer an adhesive which not only would possess high shear strength but also substantial resistance to peel stresses.

Extensive work has been carried out and reported on the mechanical properties of rubber-modified epoxy resins, usually heat cure formulations. It has been shown that a substantial increase in fracture toughness can be achieved by using carboxyl terminated acrylonitrile-co-butadiene rubbers (CTBN).[14–27] Furthermore, it has been shown that similar results can be obtained with amine-terminated rubbers (ATBN).[16,27]

Figure 1 demonstrates the effect of ATBN and CTBN content on the shear and peel strengths in the various epoxy formulations. As shown, T-Peel strength at 25°C increases with increasing rubber content until some optimal limit is obtained (~40% ATBN and ~12% CTBN). Moreover, at higher temperatures (95°C, 120°C) the general behaviour is different for ATBN and CTBN. Generally, lap shear strength decreases while T-Peel increases for CTBN-containing formulations, while for ATBN both shear and peel strengths decrease. It is evident from Figure 1 that the ATBN

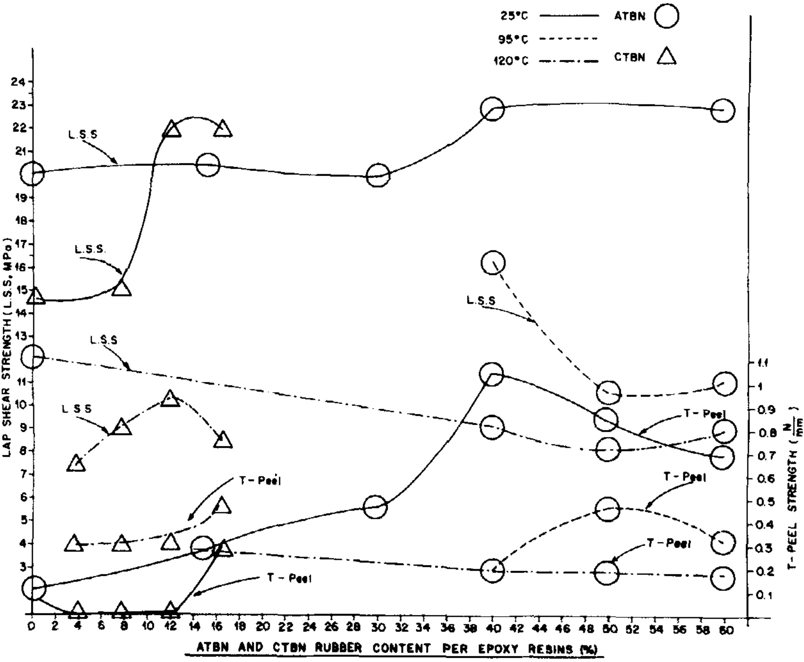

FIGURE 1 Lap shear and T-Peel strengths as a function of ATBN and CTBN rubber concentration in epoxy (%).

formulations exhibit somewhat higher elongation than the CTBN ones. These property differences may be attributed to a greater degree of chemical bonding between the ATBN and epoxy compared to CTBN and the expoxy. At 40% ATBN, the material exhibits the best combination of shear and T-Peel strengths. Moreover, epoxy resin systems, toughened by ATBN that serves also as a curing agent, demonstrate good adhesive strength at elevated temperatures.

Thorough experimental work[12] has confirmed that the presence of imidazole species in the curing agent could substantially enhance the high temperature preformance of epoxy resin compositions while ATBN could contribute to toughness. Data are shown in Table III that substantiate the effect of imidazole addition to these epoxy resin systems. Results indicate that the inclusion of the 2-ethyl-4-methyl imidazole has enhanced the 120°C lap shear

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performance but has degraded the T-Peel preformance. Though the role of imidazole as an effective curing agent for epoxy has long been recognized,[12] the beneficial effects of such a compound as shown in this investigation are not fully understood. Hence, formulation 11 (without imidazole) was selected for further investigation, as an adhesive.

To improve the durability of aluminum-epoxy and avoid interfacial failure, a silane coupling agent was used. As can be seen in Figure 2, the coupling agent has caused a dramatic change in the failure mode which becomes cohesive. To study the environmental durability of the selected epoxy formulation, a number of specimens were exposed to a combination of heat and humidity (50°C/95% RH) for 15 days and their shear and T-Peel strengths were measured. As depicted in Figure 2, significant improvement in bond strength has been achieved. In both cases, (with and without the

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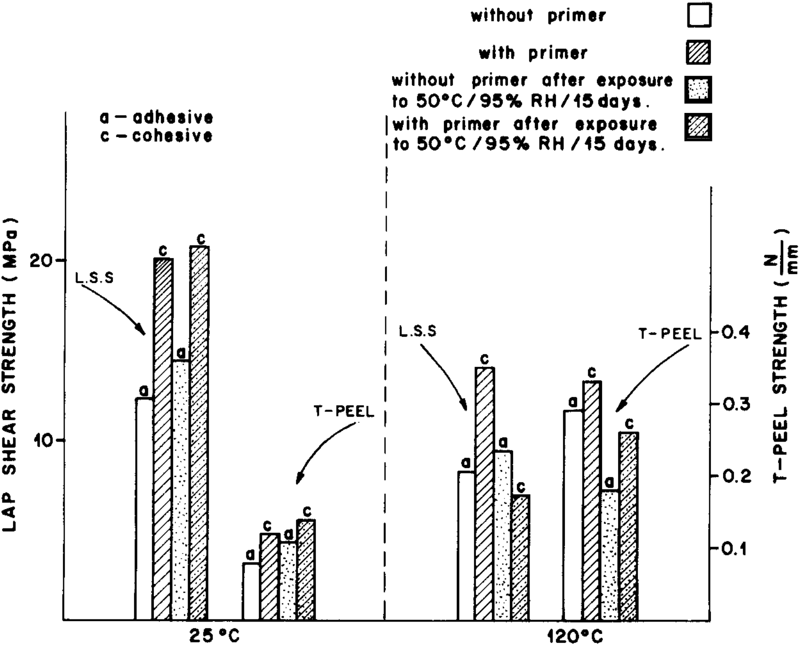

FIGURE 2 The effect of primer on the lap shear and T-Peel strengths of the MY720/ERL510/TETA/CTBN (50/40/20/10.8) formulation in ambient and 50°C/95% RH/15 days conditions.

silane primer) bond strength slightly increased after exposure to humidity and heat at 25°C, while at 120°C a pronounced reduction was observed. These results indicate that at elevated temperature the adhesive joint is more sensitive to environmental conditions as the effect of water/humidity is accelerated.

In the last phase of the investigation, the effect of a carrier on the toughness and bond line thickness was studied. Generally, shear and T-Peel strengths showed an improvement of 10 to 50% (Table III). It seemed that the addition of the thermoplastic carrier had increased the toughness and the resistance to crack propagation. Figure 3 shows the failure surfaces of the T-Peel specimen. The mode of failure is cohesive and both surfaces are covered completely with the adhesive and felt.

The results obtained in this study are impressive when compared to typical commercially available room-temperature-curing adhesive systems. Table III compares the lap shear and T-Peel strength properties, at various temperatures, of a number of such commercial structural adhesives with the present room-temperature-curing resin systems. The commercial adhesives included epoxy and acrylic types. For information purposes, lap shear and T-Peel strengths of a commercial structural autoclave curing adhesive are also shown. The five compositions (9–13) exhibited superior properties, especially at 120°C. Formulation 13 demonstrated the best combination of properties compared to the various room-temperature-cured commercial adhesives, but somewhat inferior to FM-300K.

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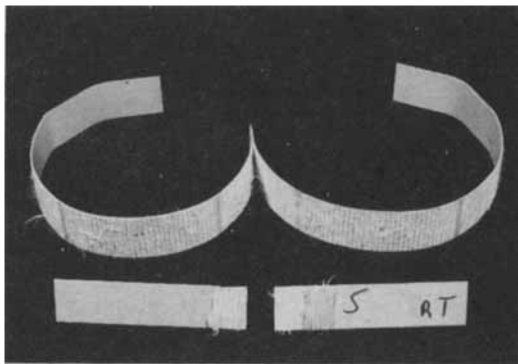

FIGURE 3 Failure surfaces of formulation 13 including carrier.

The improved performance of these high functionality epoxy resin compositions at elevated temperature, *e.g.*, 120°C, should be regarded as most noteworthy and certainly promising for further development and optimization.

Adhesive characterization

Following the adhesive compositional optimization, formulation 13 was further characterized and evaluated as to its thermal properties and transitions, chemical structure, mechanical behavior and microstructure.

(1) *Thermal behavior and transitions* DSC (Differential Scanning Calorimetry) was used to determine the degree of cure, curing temperature, and exotherm of the partially cured polymers. Figure 4 depicts the first and second run thermograms of the cured epoxy resin. The first run, (a), shows that the resin system has a peak cure exotherm at 90–100°C, indicating that curing is not complete after 6

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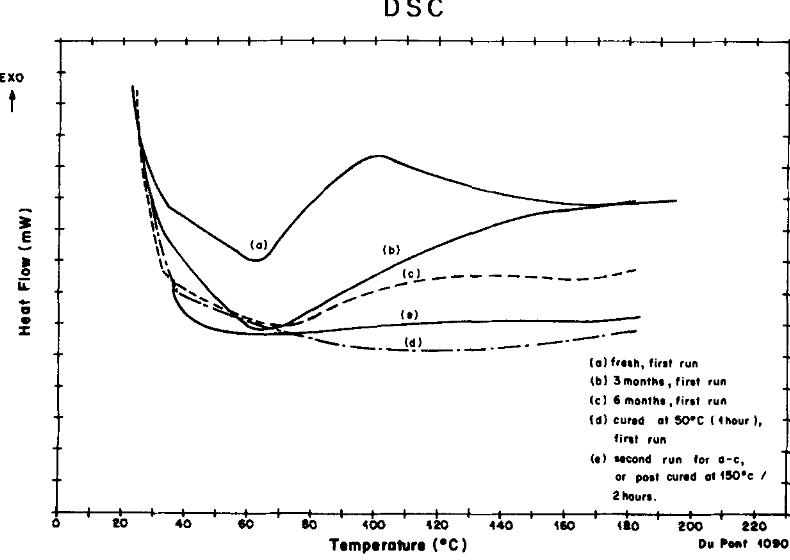

FIGURE 4 DSC scans of MY720/ERL510/TETA/ATBN (50/40/18.6/36) formulation, cured at various conditions.

days at ambient temperature. It can be seen that after 3 and 6 months at ambient temperature, the curing process continues, and the exotherm decreases (Figure 4, b,c). When cured at 50°C for 1 hour (Figure 4, d) or post cured at 150°C/2 hr, (e), no exotherm was observed, which indicates in turn that curing has been completed. The second runs (e) confirm that the epoxy matrix is in a fully-cured state following the first heat treatment of the first run.

Based on the above DSC results, it is evident that even if curing is incomplete after 6 days at RT, it could be completed either by 50°C/1-hour curing or after longer periods of time at RT. Furthermore, as can be concluded from the ambient temperature and moderate temperature (50°C) cure, the selected formulation is highly reactive. Hence, the thermal history that the adhesive is exposed to during thermal characterization changes its degree of cure and consequently the glass transition temperature.

Determination of the glass transition temperature was carried out by means of a modified Gehman apparatus. As can be seen in Figure 5, typical curves of log G (10) *vs.* T indicated that the Tg is

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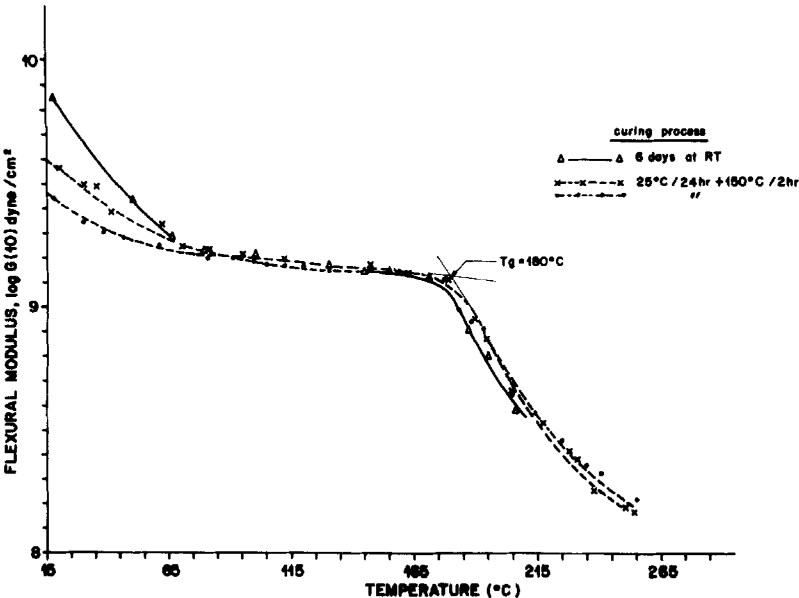

FIGURE 5 Log G(10) *vs.* Temperature for MY720/ERL510/TETA/ATBN (50/40/18.6/36) formulation, cured at various conditions.

close to 180°C for both samples; *i.e.*, cured 6 days at ambient temperature, and postcured for 2 hours at 150°C. The flexural modulus at low temperatures (15–35°C) was surprisingly higher by 25% for the RT-cured epoxy formulation compared to the elevated temperature (150°C/2 hr) cured resin. Similar results were observed when tensile properties of bulk specimens were determined, as will be discussed in the following section. It should be emphasized that the selected adhesive formulation exhibited a relatively high Tg compared to other epoxy adhesives, especially to those cured at low and medium curing temperatures (25–60°C).

(2) *Chemical structure.* FTIR (Fourier Transform Infra-Red) was used to monitor the rate at which reactive molecular species such as epoxide group disappear during cure.[21] Figure 6 shows, for example, the fracture surface FTIR spectrum of the selected epoxy formulation. The spectrum does not have a noticeable epoxide band (at 906 cm^{-1}) which indicates that curing is almost complete. In addition to hydroxyl and ether bands in the region of 3400 cm^{-1} and

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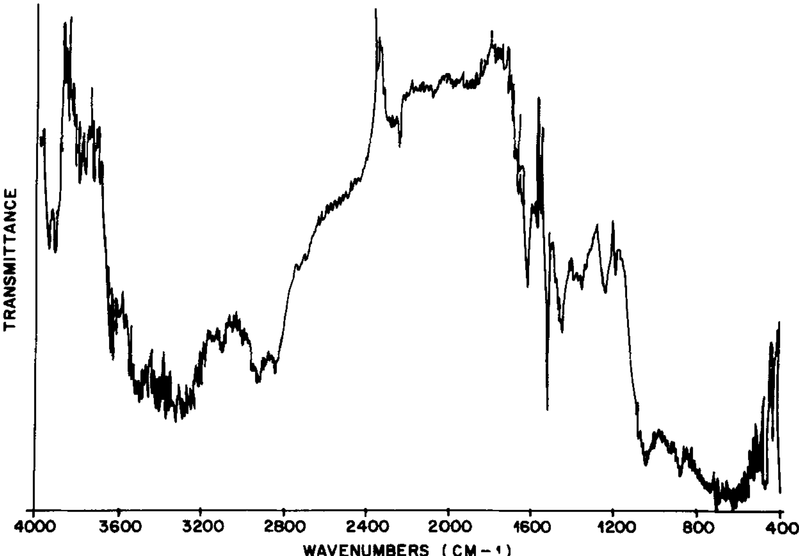

FIGURE 6 FTIR spectrum of Al/Al fracture surface of specimens bonded with MY720/ERL510/TETA/ATBN (50/40/18.6/36) formulation.

at 1040 cm^{-1} respectively, phenyl bands at 830, 1187, 1238, 1363, 1448 and 1517 cm^{-1} are present and remain constant regardless of epoxide reactions. The absorption at 2235–2242 cm^{-1} is due to the presence of ATBN's cyano-functional group.

(3) *Mechanical behaviour* The high functionality resin systems look promising as adhesives that cure at ambient temperatures. The degree of curing of this formulation at RT was verified by lap shear and bulk testing. As can be seen in Table IV, lap shear and T-Peel strengths were not improved after post-cure at 150°C for 2 hours.

Mechanical properties of the bulk adhesive showed significant differences under various cure conditions, as shown in Table IV, Figure 5 and Figure 7. In general, it could be observed that the epoxy formulation showed highest mechanical properties and lower density following cure at 25°C for 6 days. The mechanical properties obtained after post-cure at 150°C or two months at ambient temperature were similar to RT cure but had higher density.

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TABLE IV
Effect of cure conditions on mechanical properties of epoxy formulation (MY720/ERL510/TETA/ATBN, 50/40/18.6/36)

Mechanical property \ Curing process	25°C/24 hr + 150°C/2 hr	25°C 6 days	25°C 2 months
ρ(g/ml) Density	1.1507 ± 0.0007	1.1441 ± 0.0020	—
σ_B (MPa) Stress at break	17.5 ± 1.9	30.5 ± 3.9	18.1 ± 3.5
Σ_B (%) Strain at break	1.21 ± 0.1	1.80 ± 0.2	0.83 ± 0.2
E (MPa) Young's Modulus	1631 ± 48	1792 ± 98	1551 ± 1.25
Lap Shear Strength (MPa)	14.7 ± 0.8[c]	20.1 ± 2.8[c]	—
T-Peel Strength $\left(\frac{N}{mm}\right)$	0.21 ± 0.02[c]	0.22 ± 0.04[c]	—

[c] Cohesive failure.

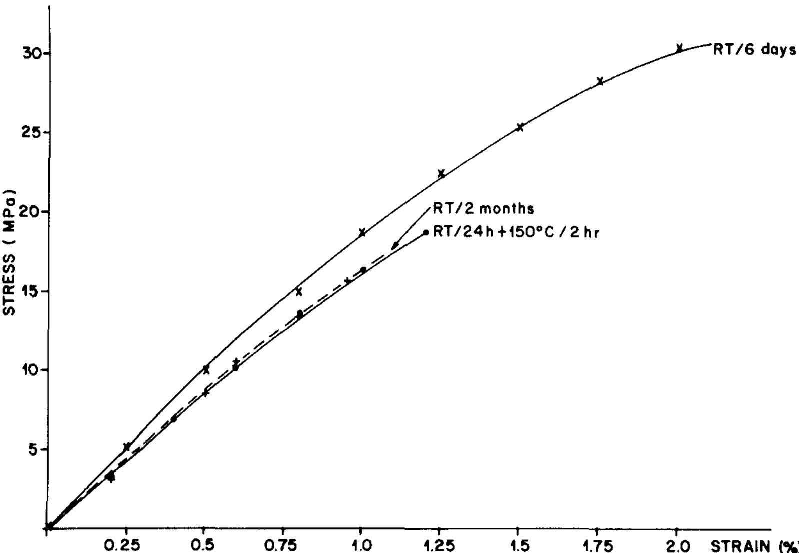

FIGURE 7 Stress-strain plot of MY720/ERL510/TETA/ATBN composition following various curing procedures.

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Curing conditions are expected to influence the mechanical properties such as Young's modulus, stress and strain at break and density. However, the direction of the changes were unexpected.[28] It seems that the additional post-curing or ambient-temperature-curing for longer periods (two months) does not improve and even reduces the bulk and the adhesive mechanical properties.

The effect of curing conditions on the mechanical properties and densities of epoxy resins were studied by Gillman *et al.*[17b] The results of this latter investigation do not agree with the present ones. While Gillham[17b] reported high Young's modulus accompanied by high density at low temperature curing, the present investigation indicated that ambient temperature cure resulted in lower densities and higher moduli compared to elevated temperature cure.

(4) *Microstructure and Morphology.* SEM (Scanning Electron Microscope) micrographs of fracture surfaces from specimens cured at ambient temperature for 6 days are given in Figure 8. The

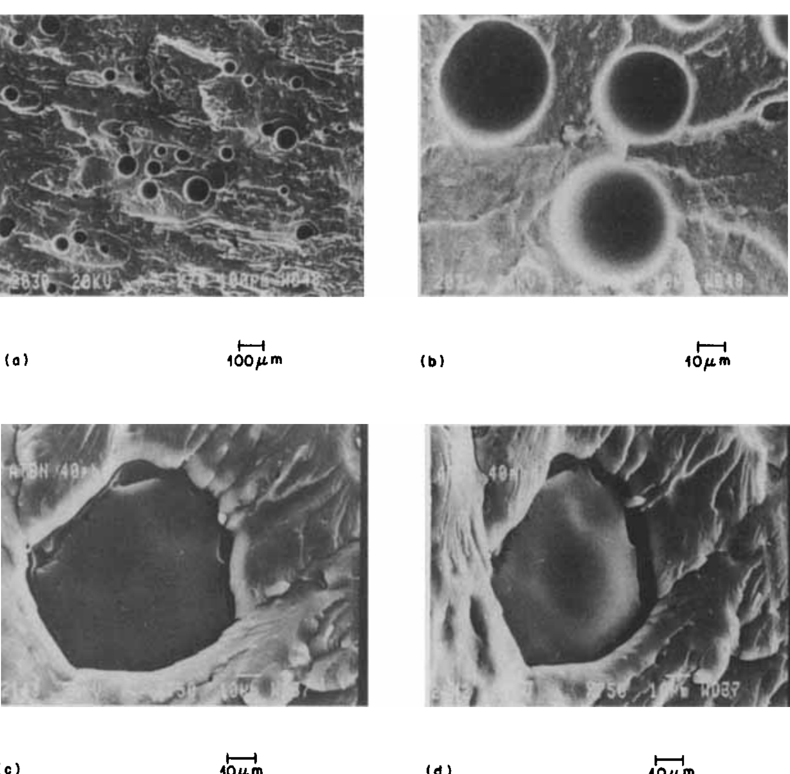

FIGURE 8 Scanning electron photomicrographs taken from fracture surfaces of 40% ATBN modified epoxy resin at various magnifications (a—×70, b—×400, c—×750 $\theta = 0°$, d—×750 $\theta = 43°$).

outstanding observation is that the particle diameters are very large—up to 100 μm. The properties of the ATBN/epoxy formulations are strongly dependent on the relative amounts of the two components. This is manifested in the marked increase of the number of large particles as the rubber content increases and uneven distribution of small particles (Figure 8, a,b). ATBN particles show highly irregular contours which often appear as agglomerated islands of smaller particles. As can be seen from Figure 8, c and d, the relatively giant rubber spheres create a discontinuous phase. There is a bimodal distribution of rubber particles; 80–100 μm and 15–30 μm. Both spheres are much bigger

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in size than the CTBN and ATBN rubber spheres reported earlier[14–18, 22–23], except those reported by H. N. Nae[17c], A. J. Kinloch *et al.*[19] and Z. Nir *et al.*[20]

In general the morphology develops during the cure cycle and depends on the rubber-epoxy compatibility, the temperature and time of cure, and elastomer concentration. A possible mechanism for morphology development was suggested by Nae.[17c] At the beginning of polymerization the system behaves like a compatible solution. As the network grows, the rubbery segments are segregated from the main chain, and agglomerates are formed.

Such agglomerates were also observed in other trifunctional systems.[17c] In these systems containing CTBN, rubber particles as large as 80–120 μm were observed, similar to the present system containing tri- and tetra-functional epoxy resin.

Results point out that ATBN in large quantities is a better toughening agent than CTBN rubber.[16] In addition, most of the studies reported show well-bonded particles as a consequence of the chemical reactivity of the rubber. Poor interfacial bonding was observed in the ATBN/epoxy formulation, as evident in the fracture surface shown in Figure 8, d. Similar description was given by Kinloch.[19] In the latter case (contrary to the present study) it has been specifically designed by using an unreactive system.

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CONCLUSIONS

Room-temperature-curing epoxy formulations for elevated temperature use have been developed. Results have shown that the fundamental lap-shear and peel strengths at ambient and high temperature of the proposed composition are superior to commercially-available, room-temperature-cure adhesive systems. Moreover, they are only marginally inferior to high-temperature-cured film adhesives.

The thermal, mechanical and chemical characterizations that accompanied the composition development have shown that, although curing has not come to completion after six days at room temperature, the resulting properties are satisfactory and termination of cross-linking is achieved after 3–6 months cure at ambient temperature or 1 hour at 50°C.

Toughening of the room-temperature-curing formulations has been enhanced by cross-linking with ATBN and addition of thermoplastic carrier. Under these curing conditions the morphology that develops is rather unique comprising large elastomeric inclusions (100 μm). Furthermore, room temperature hardening results in higher modulus of elasticity compared to elevated temperature curing, of the same adhesive composition.

The improved performance characteristics of the high-functionality and aromaticity epoxy composition at high temperatures are very promising and call for further investigation. The relationship between the morphological microstructure and the consequential viscoelastic behaviour and toughening mechanism are among the issues that require further study.

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