Liquid-Rubber-Modified Epoxy Adhesives Cured with Dicyandiamide. II.—Morphology and Adhesion Strengths

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Synopsis

The lap shear and T-peel strengths of n-butylacrylate/acrylic acid (nBA/AA)-copolymer-modified DGEBA adhesive were evaluated. Adherends used in this study included carbon-fiber-reinforced plastics (CFRP), glass-fiber-reinforced plastics (GFRP), and aluminum. It was found that the adhesive strengths could be improved by incorporating nBA/AA copolymer in the DGEBA matrix. An optimum functionality of the copolymer existed for maximum lap shear strength. Morphological studies revealed that the adhesive strength was also influenced by the compatibility between the copolymer and the matrix, the property of the adherend as well as the addition of the bisphenol A.

INTRODUCTION

Since it was shown by McGarry and Willner[1] that the carboxy-terminated copolymer of butadiene and acrylonitrile (CTBN) can improve the fracture toughness of epoxy resins, liquid-rubber-modified epoxy resins have been studied by many workers.[2-16] Factors which influence the fracture resistance of the epoxy resin include the liquid rubber concentration,[2,4] the types and concentration of the curing agents,[3,5,6,] the curing temperature,[3] and the solubility parameter, the initial molecular weight, and the functionality of the liquid rubber.[2,3,14] In these researches, different conclusions with respect to the effects of rubber particle size and the toughening mechanism were obtained because the controlling variables and the compositions in each system were hardly the same.

In a previous study,[17] we have reported the preparation and characterization of nBA/AA copolymer modified DGEBA adhesives cured with DICY. In this paper, we continue to present the adhesive strengths and fracture surface morphologies of these adhesives. The adherends used include carbon-fiber-reinforced plastics (CFRP), glass-fiber-reinforced plastics (GFRP), and aluminum.

EXPERIMENTAL

Materials

Formulations of nBA/AA-copolymer-modified epoxy (diglycidyl ether of bisphenol A, DGEBA) adhesives are listed in Table I. The preparation and

TABLE I
Epoxy Adhesive Formulations[a] (by Parts)

Sample no.	DGEBA	DICY	Liquid rubber	Functionality of rubber	Bisphenol A
2	100	6	0	—	0
7	100	6	10 (CTBN)	—	0
8	100	6	10 (LR 1)	1.62	0
9	100	6	10 (LR 2)	4.31	0
10	100	6	10 (LR 3)	7.16	0
11	100	6	10 (LR 4)	9.93	0
12	100	6	0	—	15
13	100	6	10 (LR 2)	4.31	15
14	100	6	10 (CTBN)	—	15

[a] Each formulation contained 3 phr fumed silica and 2 phr glass beads.

characterization of these formulations have been described previously.[17] Adherends CFRP and GFRP were supplied by the Chung Shan Institute of Science and Technology. Both of them were epoxy-based solvent-type prepregs. The surfaces of glass fiber in GRFP were treated with silane type coupling agent while carbon fibers were used without any treatment of the surface. The curing cycle for CFRP was at 110°C for 1 h 10 min and 171°C for 2 h. The average thickness of the CFRP laminates was 2.0 mm with fiber content of 68% by weight. The curing cycle for the GFRP was at 80°C for 1 h, 110°C for 1 h, and 150°C for 2 h. The average thickness of the GFRP laminates was 2.5 mm with fiber content of 75% by weight. Adherend aluminum was a product of Taiwan Aluminum Co.

Treatments of the Adherend Surface

CFRP and GFRP

The surfaces of the CFRP and GFRP specimen were washed with acetone and dried at 60°C. The surface portion which would be adhered was then polished with 600 Grade Sci-C sand paper and washed again with acetone and dried in an air-forced oven at 120°C for 2 h. Specimens thus treated should be used within 6 h.

Aluminum

The procedures for the surface treatment of aluminum adherend included four steps:

1. The aluminum adherend was washed with acetone thoroughly; then it was put in an air-forced oven in a vertical position and dried at 60%C for 2 h.
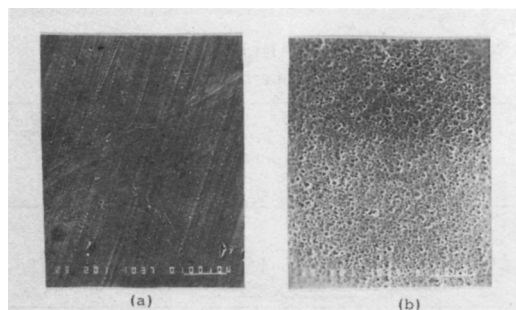
Fig. 1. Surfaces of the aluminum adherend: (a) before surface treatment, magnification 200 × ; (b) after surface treatment, magnification: 200 × .

2. The acetone-cleaned aluminum adherend was dipped in fresh distilled chloroform for 24 h; then it was dried in an air-forced oven in a vertical position at 60°C for 30 min. Any contact of the surface portion which would be adhered should be avoided.

3. The chloroform cleaned aluminum adherend was dipped in a $Na_2Cr_2O_7/H_2SO_4$ solution at $67 \pm 1°C$ for 30 min. The composition of the $Na_2Cr_2O_7/H_2SO_4$ solution was $Na_2Cr_2O_7 : H_2SO_4 : H_2O = 1 : 10 : 30$ by weight. After the dipping, the aluminum adherend was washed with cold water for 3–5 min. A well-treated aluminum adherend should have a continuous uniform water film attached to the·surface. Otherwise the treatments should be repeated again until a satisfactory result was obtained.

4. The water washed aluminum adherend was finally dried in an air-forced oven in a vertical position at 60°C for 1 h. The portion which would be adherend should be in the upper direction. The specimen thus treated should be used within 6 h. The surfaces of the aluminum adherend before and after the treatments are shown in Figure 1.

Preparation of the Testing Sample

The nBA/AA copolymer modified DGEBA was coated evenly on both the surface portions of the adherend which would be adhered with a glass rod. The coating length was about half an inch longer than the adhering length. Samples for lap shear test were adhered in aluminum bonding jig; then the bonding jig was sandwiched by two steel plates with Teflon surface. The whole heating platen arrangement was pressed in a compression molding machine at preset curing temperature and curing time (177°C, 1 h). The compression pressure was kept at 50 psi. Samples for T-peel test were adhered directly without the bonding jig; then the procedures described above were followed.

Measurements

Lap shear strength and T-peel strength were measured in accordance with ASTM D1002-72 and D1876-72, respectively. The cross head speed was 2 mm/min for the former test and 200 mm/min for the latter test. The morphology of the fracture surface was observed by using the scanning electron microscope (SEM). The fracture surfaces were coated with a layer of

<div align="center">TABLE II</div>
<div align="center">Mechanical Properties of Adherends</div>

Adherend	Tensile strength ($\times 10^3$ psi)	Tensile modulus ($\times 10^6$ psi)	Yield strength ($\times 10^3$ psi)
Al	24.4 ± 2.9	1.90 ± 0.2	17.6 ± 0.9
GFRP	84.8 ± 4.5	5.40 ± 0.3	—
CFRP	65.5 ± 1.1	7.90 ± 0.7	—

gold about 200 Å thick. T_g of the cured nBA/AA-copolymer-modified DGEBA adhesive was measured by DSC at a heating rate of 10°C/min.

Tensile Strength and Tensile Modulus of the Adherends

The tensile strength and tensile modulus of the aluminum adherend were measured in accordance with ASTM E2819 while those of the CFRP and GFRP adherends were measured by the procedures described in ASTM D3039-76. The ends of the CFRP and GFRP adherends were reinforced with aluminum plates of 1.6 mm thickness to keep the clips from slippage. The cross head speed was 2 mm/min. Mechanical properties of the adherends are listed in Table II.

RESULTS AND DISCUSSION

Lap Shear Strength and Morphology of Fracture Surface

Table III shows that the lap shear strength of nBA/AA-copolymer-modified DGEBA adhesives between an Al–Al joint increases with the increasing functionality of the nBA/AA copolymer until a maximum value is reached where the functionality of the copolymer is about 7. The improvement of the lap shear strength cannot be attributed to the increasing interactions between the matrix and the copolymer particles alone. The flexibilization of the matrix may have a significant effect as well. As shown in Figure 2, no phase separation is observed in both the control (no rubber) and the DGEBA matrix modified with nBA/AA copolymer of high functionality (samples 10 and 11). This observation that the copolymer phase with high functionality does not separate from the matrix is inconsistent with Gazit and Bell's founding.[12] In

<div align="center">TABLE III</div>
<div align="center">Lap Shear Strengths and T-Peel Strengths of Unmodified and Liquid Rubber</div>
<div align="center">Modified Epoxy Adhesives between Al–Al Joints</div>

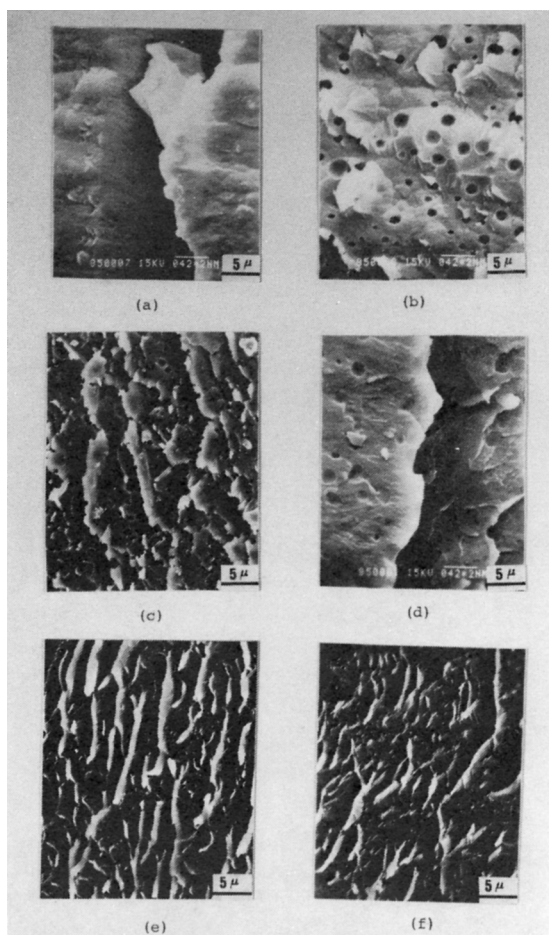| Sample no.	Functionality of rubber	Lap shear strength (psi)	Improvement (%)	T-peel strength (psi)	Improvement (%)	T_g (°C)
2	—	2150 ± 100	—	11.7 ± 0.9	–	134
7	(CTBN)	2510 ± 130	17.0	19.6 ± 1.1	67.5	102
8	1.62	2280 ± 130	5.8	15.7 ± 1.1	34.2	124
9	4.31	2450 ± 79	14.0	14.1 ± 2.0	20.5	114
10	7.16	2850 ± 90	32.6	16.0 ± 2.0	36.8	102
11	9.93	2520 ± 50	16.7	15.2 ± 1.5	29.9	95

Fig. 2. Lap shear fracture surfaces of unmodified and liquid-rubber-modified epoxy adhesives between Al–Al joint: (a) sample 2, unmodified; (b) sample 7, CTBN-modified; (c) sample 8, LR 1 modified (functionality = 1.62); (d) sample 9, LR 2 modified (functionality = 4.31); (e) sample 10, LR 3 modified (functionality = 7.16); (f) sample 11, LR 4 modified (functionality = 9.93).

this case, the improvement of the lap shear strength is probably due to the flexibilization of the matrix by the copolymer.

Another interesting observation shown in Figure 2 and more clearly in Figure 3 is that the fracture surfaces of all rubber-modified DGEBA are fish-skin-like [Figs. 2(b), 2(c), 2(d), 2(e), 2(f), and 3(b)] while those of the control [Figs. 2(a) and 3(a)] illustrate deep ditches in direction perpendicular to the shear force. This phenomenon can be explained by the mixing mode fractural mechanism.[14] If the matrix has crack resistance, such as a rubber-modified epoxy, it will form many microcracks before the main cracks grow to the fracture region.

T-Peel Strength and Morphology of Fracture Surface

The T-peel strength of nBA/AA-copolymer-modified DGEBA adhesive between the Al–Al joint is listed in Table III also. The improvements of the T-peel strength are between 20 and 40% in comparison to the control;
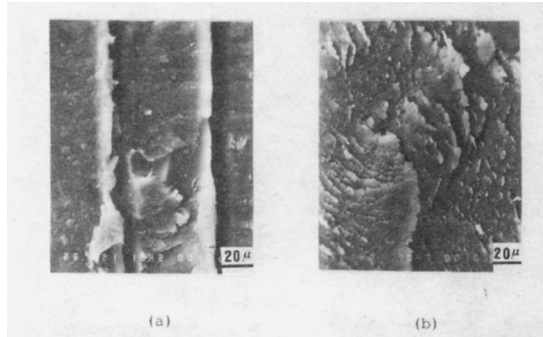
Fig. 3. Lap shear fracture surfaces of unmodified and CTBN-modified epoxy adhesives between Al–Al joint: (a) sample 2, unmodified; (b) sample 7, CTBN-modified.
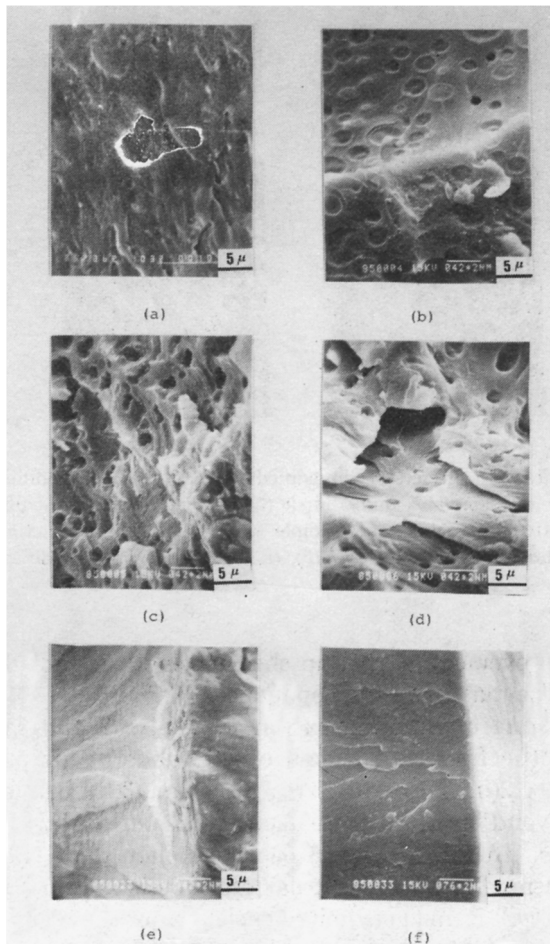

Fig. 4. T-peel fracture surfaces of unmodified and liquid-rubber-modified epoxy adhesives between Al–Al joint: (a) sample 2, unmodified; (b) sample 7, CTBN-modified; (c) sample 8, LR 1 modified (functionality = 1.62); (d) sample 9, LR 2 modified (functionality = 4.31); (e) sample 10, LR 3 modified (functionality = 7.16); (f) sample 11, LR 4 modified (functionality = 9.93).

however, a clear trend cannot be found. The tremendous increasing of the T-peel strength (near 70%) of the CTBN-modified adhesive indicates that the chemical structure of the liquid rubber is probably more important than the interaction between the rubber and the matrix with respect to the toughening effect of the T-peel strength.

Figure 4 shows the fracture surfaces of the T-peel test. Serious plastic deformation of the matrix is observed. Traces also appear of the shear yielding band in the fracture surfaces of the DGEBA adhesives modified by nBA/AA copolymer of high functionality [Figs. 4(c) and 4(f)].

The Bisphenol A Effect

As shown in Table IV, the addition of bisphenol A in the formulation of DGEBA adhesive will increase both the lap shear and T-peel strengths. However, it also decreases the T_g of the cured DGEBA significantly. The explanation is that bisphenol A acting as a chain extender will decrease the crosslinking density and therefore increase the free volume of the cured DGEBA. Figure 5 illustrates the T-peel fracture surfaces of unmodified and modified DGEBA containing bisphenol A. Both the surfaces of DGEBA modified with LR 2 and CTBN show the existence of two size particle distributions. This phenomenon was observed by Riew et al.[6] and Gazit and Bell[12] as well.

In our previous report,[17] we have shown that bisphenol A would reduce the gel time of DGEBA. Since bisphenol A is a weak acid which has a catalyst effect on the reaction between the epoxy group and the amine group. Furthermore, the chain extension reaction of bisphenol A will increase the molecular weight of DGEBA rapidly and therefore reduce the gel time. The limitation of adding bisphenol A to improve the toughness of epoxy adhesive is that it will decrease the pot life of the system, which is very unfavorable particularly when hardner is DICY.

TABLE IV
Effect of Bisphenol A on the Lap Shear and T-Peel Strengthsof Unmodified and
Liquid Rubber Modified Epoxy Adhesives between Al–Al Joints

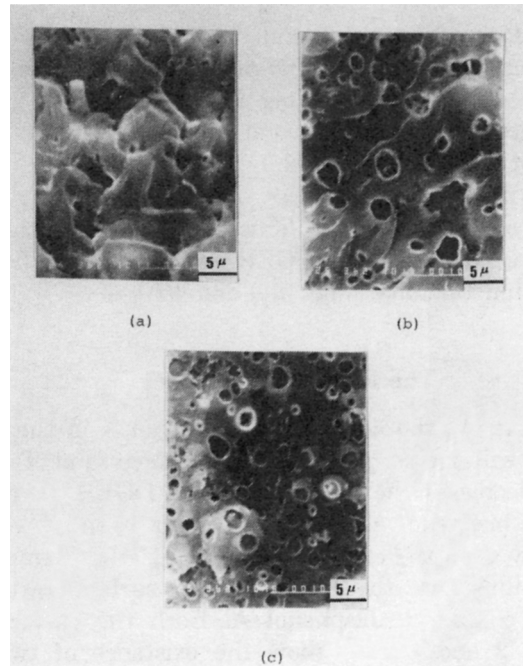| Sample no.	Bisphenol A (phr)	Liquid rubber (phr)	Lap shear strength (psi)	T-peel strength (pli)	T_g (°C)
2	0	0	2150 ± 100	11.7 ± 0.9	134
12	15	0	2700 ± 200	15.7 ± 0.9	105
9	0	10 (LR 2)	2450 ± 80	14.1 ± 2.0	114
13	15	10 (LR 2)	2770 ± 90	14.9 ± 9.8	105
7	0	10 (CTEN)	2520 ± 130	19.6 ± 1.1	102
14	15	10 (CTEN)	2940 ± 90	20.4 ± 2.4	92

Fig. 5. T-peel fracture surfaces of epoxy adhesives containing bisphenol A between Al–Al joint: (a) sample 12, unmodified; (b) sample 13, LR2-modified; (c) sample 14, CTBN-modified.

Lap Shear Strength of Composite Adherends

Table V compares the lap shear strengths of CFRP–CFRP, GFRP–GFRP, GFRP–Al, and GFRP–Al joints. The improvement of the modified DGEBA adhesive is apparent. The low value of the lap shear strength between the CFRP and Al joint can be explained in Figure 6, which shows the fracture surfaces on the Al side. Figure 6(a) shows that carbon fibers are pulled out from the CFRP matrix and remain in the adhesive. The surfaces of the pulled-out carbon fiber are rather smooth, indicating poor bonding between the carbon fiber and the resin. In comparison, Figure 6(b) shows that the fiber pulled-out phenomenon is much less serious in GFRP and large quantity of the resin is attached to the pulled-out glass fiber surface, which means the bonding between the glass fiber and the resin is better and higher lap shear strength is obtained.

TABLE V
Comparison of the Lap Shear Strengths of Unmodified and Liquid
Modified Epoxy Adhesives between CFRP–CFRP,
GFRP–GFRP, CFRP–Al, and GFRP–Al Joints

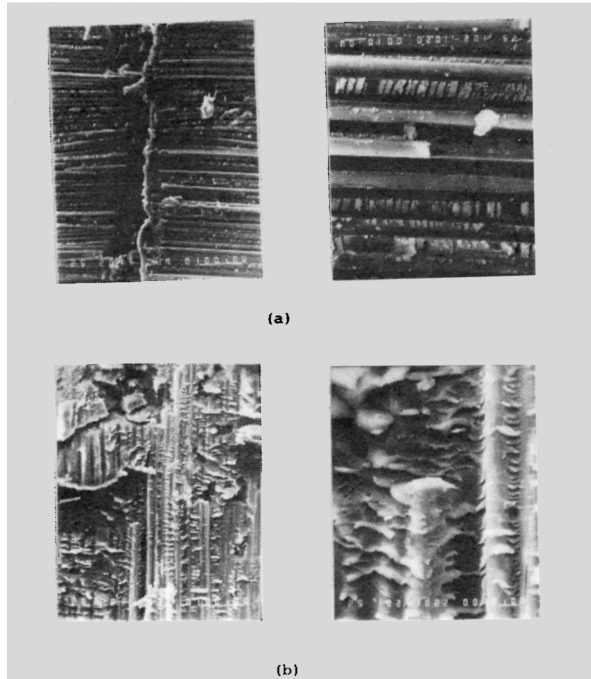| Sample no.	Liquid rubber (phr)	CFRP–CFRP (psi)	GFRP–GFRP (psi)	CFRP–Al (psi)	GFRP–Al (psi)
2	0	1800 ± 380	1780 ± 130	1620 ± 250	2110 ± 90
7	10 (CTBN)	2250 ± 240	2000 ± 230	2040 ± 290	2630 ± 90

Fig. 6.   Lap shear fracture surfaces of CTBN-modified epoxy adhesive between CFRP–Al and GFRP–Al joints (magnification 200 ×): (a) CFRP–Al joint; (b) GFRP–Al joint.
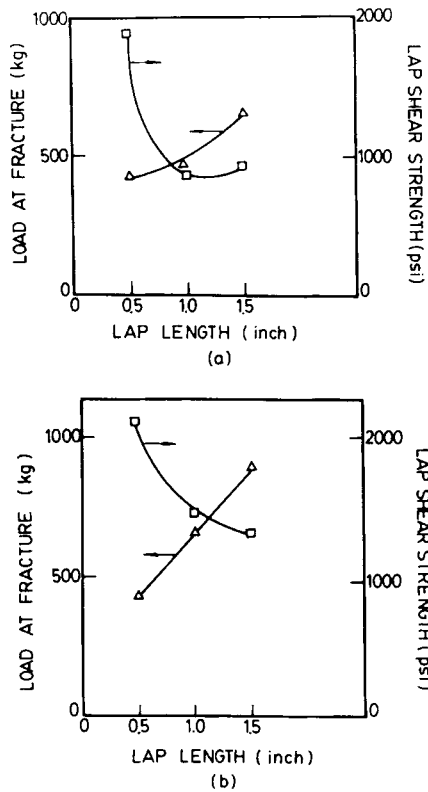

Fig. 7.   Effect of lap length on the load at fracture and lap shear strength of unmodified epoxy adhesive (sample 2): (a) CFRP–CFRP joint; (b) GFRP–GFRP joint.

Effect of the Lap Joint Length

Figure 7 shows the effect of the lap joint length on the load at fracture and the lap shear strength of nBA/AA-copolymer-modified EDBGA adhesive. The adherends were GFRP and CFRP, respectively. In both cases the load at fracture decreases and lap shear strength increases with increasing lap joint length, which indicates that the stress concentration is more serious when the lap joint length is long.

CONCLUSIONS

The adhesion strengths of nBA/AA copolymer modified DGEBA adhesive were evaluated via lap shear and T-peel tests. Our results showed that improvement of the adhesion strength could be achieved by incorporating nBA/AA copolymer in the DGEBA matrix. It also depended on the functionality of the copolymer, the type of the adherend, and the length of the lap joint. Morphological studies revealed that nBA/AA copolymer of high functionality was compatible with DGEBA while two size particle distributions were observed when phase separation occurred. The addition of bisphenol A would increase the adhesion strength of DGEBA but reduce its pot life.

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