

Liquid-Rubber-Modified Epoxy Adhesives Cured with Dicyandiamide. I. Preparation and Characterization

YU-DER LEE, SHI-KWUN WANG, and WEI-KUO CHIN, *Institute of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China*

Synopsis

n-Butylacrylate/acrylic acid (nBA/AA) copolymers were synthesized and used to modify epoxy resin (DGEBA) cured with dicyandiamide (DICY). The precuring reaction between nBA/AA copolymer and DGEBA, the curing cycle of DGEBA, and the effects of DICY and aluminum powder upon the adhesive strengths of modified DGEBA were studied. It was found that the optimum DICY/DGEBA ratio was 6 g/100 g, and lap shear strength and T-peel strength increased with increasing amount of aluminum powder. The curing cycle for modified DGEBA was determined to be 1 h at 177°C.

INTRODUCTION

Epoxy resins have been used as adhesives since the 1950s due to their better wetting ability, superb mechanical properties, and chemical resistance. However, when cured with stoichiometric amounts of polyfunctional amines, the high degree of crosslinking makes epoxy resin a very brittle material. It weakens epoxy's peeling and impact strengths and therefore limits its applications. Much work has been done to try to improve the toughness of epoxy resin, including (i) using flexible long chain hardner, such as polyimide and polysulfide,¹ (ii) introducing long aliphatic epoxy chain, and (iii) blending with other polymer and forming two polymer adhesive, for example, the epoxy-nylon or epoxy-phenolic system.² Since the early 1970s, the elastomer toughened epoxy resins, especially the nitrile-epoxy³ and CTBN-epoxy⁴⁻¹³ systems, were being viewed as potential high performance adhesives because they have unusual crack and creep resistances. The theory¹⁴ is that reactive liquid rubber having functional ends will react with epoxy or chain extender. During the initial stage, the reactive liquid rubber is compatible with the epoxy-hardner mixture if the composition is properly controlled. As the curing process proceeds, molecular weight increases, and phase separation occurs.¹⁵ The elastomer becomes dispersed particles in the epoxy matrix. Such a two-phase system has unique crack resistance without significantly sacrificing other mechanical properties.¹⁴

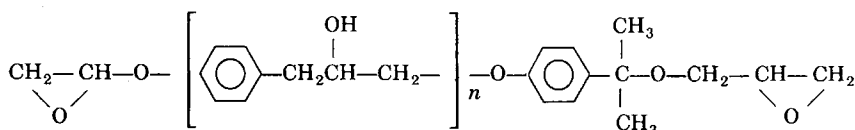
Recently, Bell et al.¹⁶⁻¹⁸ showed that both carboxy-terminated poly(*n*-butylacrylate) liquid rubber and *n*-butylacrylate/acrylic acid copolymer having carboxyl groups (nBA/AA copolymer) are effective modifiers for improving the impact resistance of amine cured epoxy resins. In this study, nBA/AA copolymer was chosen as the modifier for dicyandiamide (DICY)-

cured epoxy resin (DGEBA), and its behavior as adhesive was investigated as well. Four subjects, namely the synthesis and characterization of nBA/AA copolymer, the epoxy formulation, the filler effects, and the determination of the curing cycle, were included in this report. Other subjects, such as adhesive properties and morphology of fractured surface, will be presented in a later paper.

EXPERIMENTAL

Materials

The epoxy resin (diglycidyl ether of bisphenol A, DGEBA) used was liquid type (Ciba-Geigy, Araldite LY 556) with an equivalent weight per epoxide group of 195 ± 5 . The structure is shown below, where n is between 0.14 and 0.18:



Dicyandiamide (DICY) was used as the curing agent. Monomers *n*-butyl acrylate (nBA) and acrylic acid (AA) were reagent grade and products of Merck, West Germany. 4,4'-Azobis(*n*-cyanovaleric acid) (ABCVA) and dithiodiglycolic acid (DTDGA) were used as the initiator and chain transfer agent, respectively. A commercial available carboxy-terminated copolymer of butadiene and acrylonitrile (Hycar CTBN 1300 \times 8) was obtained from B. F. Goodrich Co. for the purpose of comparison.

Synthesis of nBA / AA Copolymer

nBA/AA copolymers were bulk-polymerized following procedures described by Gait and Bell.¹⁶ The nBA/AA volumetric ratio was varied from 50/0 to 50/6. Initiator (ABCVA) and chain transfer agent (DTDGA) were used at concentrations of 5 and 10 mol% of the total monomers, respectively. After the polymerization, products were purified by washing with acetone and distilled water.¹⁸

Precuring of Epoxy Resin

Ten parts by weight of nBA/AA copolymer were added to 90 parts of DGEBA in a three-neck flask blanketed with nitrogen, and the mixture was placed in an oil bath for 2.5 h at 150°C. Every 15 min, a small amount of the mixture was taken out for carboxyl content analysis. After the reaction, products were still liquid. Viscosity and IR spectrum of samples before and after the precuring process were measured.

Preparation of Epoxy Adhesives

Curing agent DICY, thixotropic agent fumed silica and glass beads (160–180) in proper weight ratio were added in pure or nBA/AA-modified DGEBA and were mixed with a mechanical stirrer for 2 h. Some selected formula also contained 200-mesh aluminum powder or bisphenol A. The well-blended

TABLE I
Epoxy Adhesive Formulations^a (by Parts)

Sample no.	DGERA	DICY	Al Powder (200 mesh)	Liquid rubber	Bisphenol A
1	100	4	0	0	0
2	100	6	0	0	0
3	100	8	0	0	0
4	100	10	0	0	0
5	100	6	50	0	0
6	100	6	100	0	0
7	100	6	0	10 (CTBN)	0
8	100	6	0	10 (LR 1)	0
9	100	6	0	10 (LR 2)	0
10	100	6	0	10 (LR 3)	0
11	100	6	0	10 (LR 4)	0
12	100	6	0	0	15
13	100	6	0	10 (LR 2)	15
14	100	6	0	10 (CTBN)	15

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

mixture was then degassed in a vacuum oven for 48 h at 70°C and stored in a freezer for later use. Formulations of all samples were listed in Table I.

Measurements

The carboxyl content of the carboxyl-terminated nBA/AA copolymers was determined by a titration method.¹⁶ The molecular weight of nBA/AA copolymers were measured by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). Curing cycle of DGEBA was determined by DSC. Gel point and cloudy point were measured by the procedures described in ASTM D2471-71. Lap shear strength and T-peel strength were measured in accordance with ASTM D1002-72 and D1876-72, respectively. The crosshead speeds were 2 mm/min for the former method and 200 mm/min for the latter method. Fractured surfaces were observed with a JEOL Super Probe 733 scanning electron microscopy.

RESULTS AND DISCUSSION

Characterization of nBA / AA Copolymer

Table II lists some characteristic properties of nBA/AA copolymers. It appears that the molecular weight distributions (\bar{M}_w/\bar{M}_n) are rather large. This might be due to the high reaction rate of bulk polymerization, and the reaction heat could not be evolved fast enough. By choosing solution poly-

TABLE II
Characteristic Properties of Synthetic Liquid Rubbers

Sample	nBA/AA (v/v)	\bar{M}_n^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	Conc of COOH (mol/kg)	Functionality (eg/mol)	Yield (%)
LR 1	50/0	5100	2180	8.79	0.3179	1.62	85
LR 2	50/2	5140	2090	10.59	0.8378	4.31	83
LR 3	50/4	4830	1840	9.08	1.4819	7.16	87
LR 4	50/6	6020	2140	18.50	1.5015	9.93	78

^a Measured by VPO.

^b Measured by GPC.

merization, a narrow molecular weight distribution should be able to be obtained; however, the solvent would probably participate the chain transfer reaction and affect the functionality of the copolymer. The number average molecular weights measured by VPO are approximately twice as much as those measured by GPC. Since the existence of carboxyl group increases the polarity of the molecule, the interaction between the polymer molecules and the packing material within the GPC column prolongs the retention time. Element analysis showed that the nitrogen content of every sample was below 0.03% by weight, which corresponded to one nitrogen atom per 10–30 molecules. This fact indicates that the propagation of the polymer chain is mainly due to the chain transfer reaction. As shown in Table II, the functionality of pure poly(*n*-butyl acrylate) is only 1.62 instead of a theoretical value of 2. It is probably due to the fact that some polymer chains are terminated by monomer chain transfer reaction or disproportionation.

Precuring Reaction of Epoxy Resin

Four nBA/AA copolymers and CTBN 1300 × 8 were reacted with excess DGEBA without catalyst at 150°C for 2.5 h. The large excess of DGEBA made it possible for each carboxyl group to react with an unreacted DGEBA molecule. Table III shows that the remaining carboxyl groups of all five samples are negligible after the precuring reaction. IR spectrum (Fig. 1) also

TABLE III
Carboxyl Group Concentration and Viscosity of 10% Liquid
Rubber Modified Epoxy before and after Precuring

Sample	Conc of COOH (eq/kg)		Viscosity ^a (cps)	
	Before precuring	After precuring	Before precuring	After precuring
CTBN/DGEBA	0.0451	None	22300	47600
LR 1/DGEBA	0.0436	None	19800	35200
LR 2/DGEBA	0.0867	None	24500	53600
LR 3/DGEBA	0.1047	0.0075	31200	97000
LR 4/DGEBA	0.1063	0.0098	39200	114000

^a Measured by Brookfield viscometry.

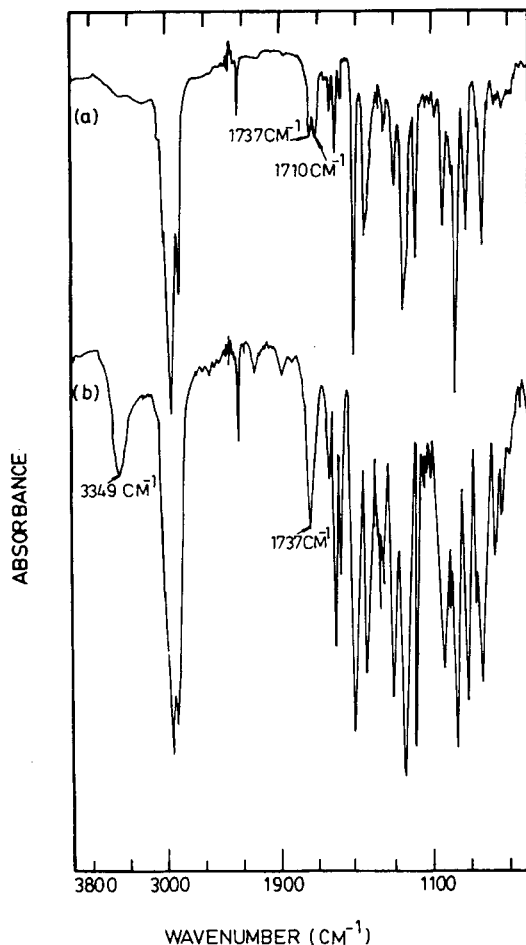


Fig. 1. IR spectrum of 10% CTBN-modified DGEBA: (a) before precuring; (b) after precuring.

shows the disappearance of the —COOH characteristic peak at 1710 cm^{-1} , the appearance of the —OH characteristic peak at 3499 cm^{-1} , and the increasing intensity of the —COOR characteristic peak at 1737 cm^{-1} of 10% CTBN-modified DGEBA after the precuring reaction. The viscosity changes of nBA/AA copolymer and CTBN-modified DGEBA are listed in Table III as well. Generally, viscosities increase 2–3 times after the precuring reaction.

Determination of the Epoxy Curing Cycle

Curing cycle of a thermosetting material includes curing temperature, pressure, time, and heating rate, etc. A better curing cycle should be able to complete the reaction between the resin and the hardener without producing residual stress or degradation. Figure 2 is the thermogram of unmodified DGEBA with 6 wt% DICY. It shows that no exothermic reaction is observed below 160°C . In other words, the curing temperature of DGEBA/DICY should be higher than 160°C . The isothermal DSC trace of DGEBA/DICY is shown in Figure 3. The exothermic peak appears at about 4 min curing time;

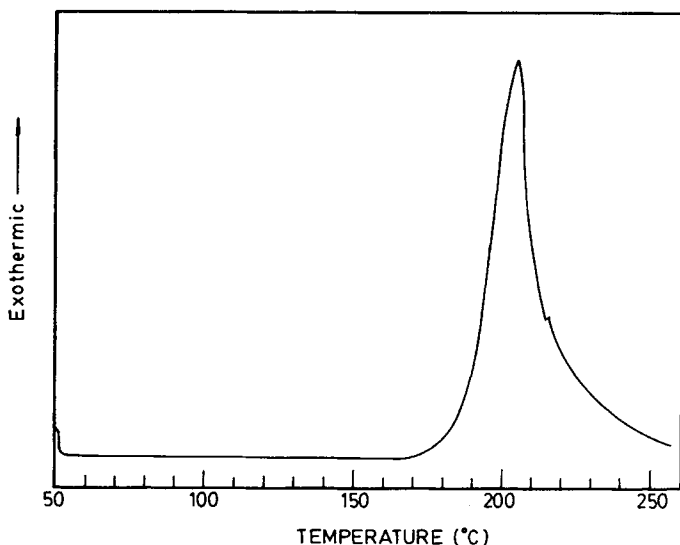


Fig. 2. Dynamic DSC thermogram of unmodified DGEBA (DICY/DGEBA ratio: 6 g/100 g; heating rate: 10°C/min).

no exothermic heat is detected after 27 min curing time. Heat evolved during the curing reaction is often used to estimate the reaction rate and conversion.¹⁹⁻²¹ Although the residual reaction heat near the completion of the curing cannot be measured accurately by DSC,²² the amount of heat evolved measured by DSC is still a valuable reference in determination of the curing cycle. The gel point is the other parameter used frequently to decide the curing cycle. Table IV lists the gel points and cloud points of some selected formula at 177°C. It shows that gel points of nBA/AA-copolymer-modified

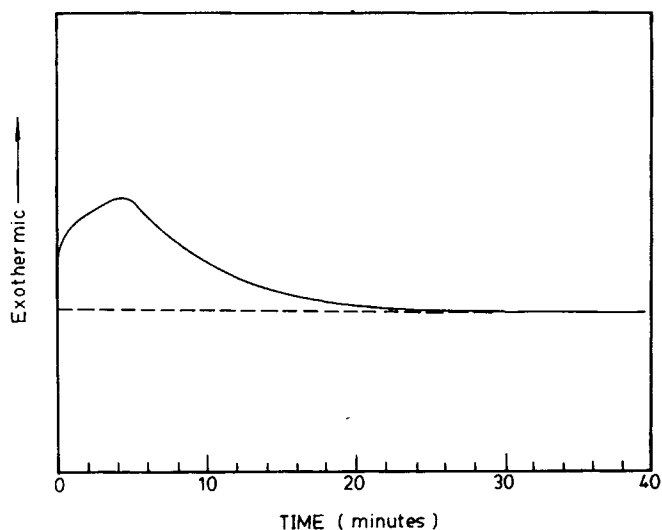
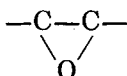


Fig. 3. Isothermal DSC thermogram of unmodified DGEBA (DICY/DGEBA ratio: 6 g/100 g; at 177°C).

TABLE IV
Gel Point and Cloud Point of Selected Samples at 177°C

Sample	Gel point	Cloud point
2	None	8 min 25 s
7	11 min 57 s	16 min 51 s
8	6 min 20 s	16 min 50 s
9	9 min 52 s	16 min 37 s
10	None	15 min 42 s
11	None	13 min 51 s
12	None	7 min 23 s
13	4 min 20 s	7 min 06 s
14	3 min 40 s	8 min 17 s

DGEBA are longer than that of unmodified DGEBA; hence modified DGEBA requires longer curing time. Considering above factors, all samples were cured at 177°C for 1 h. Figure 4 shows the IR spectrum of DGEBA/DICY system before and after the curing reaction. It is observed that the characteristic peak of



group at 910 cm^{-1} disappears completely after curing. Another interesting observation is that the doublet peak of $\text{---C}\equiv\text{N}$ at 2200 cm^{-1} becomes a single peak, which indicates that the $\text{---C}\equiv\text{N}$ group has probably participated the curing reaction.

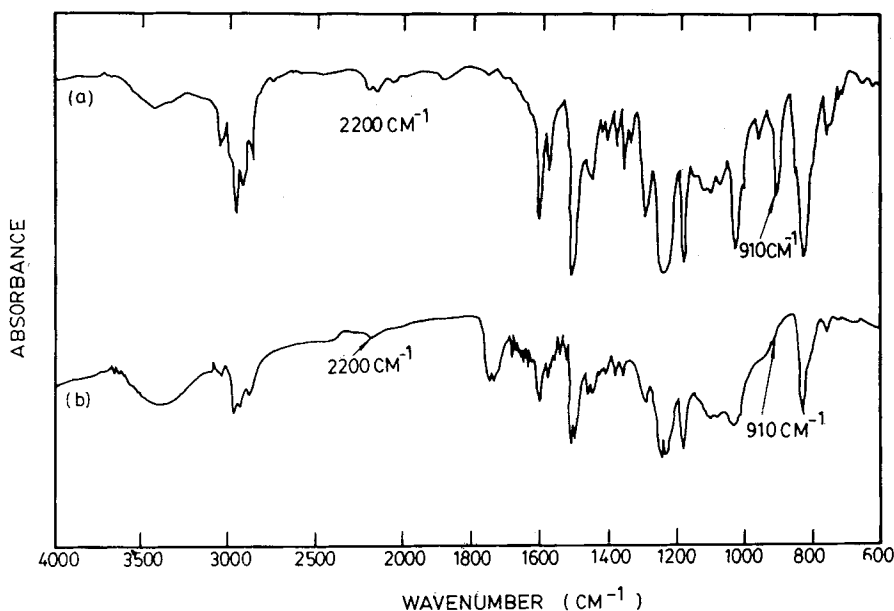


Fig. 4. IR spectrum of DICY/DGEBA at ratio of 6 g/100 g: (a) before curing; (b) after curing at 177°C for 1 h.

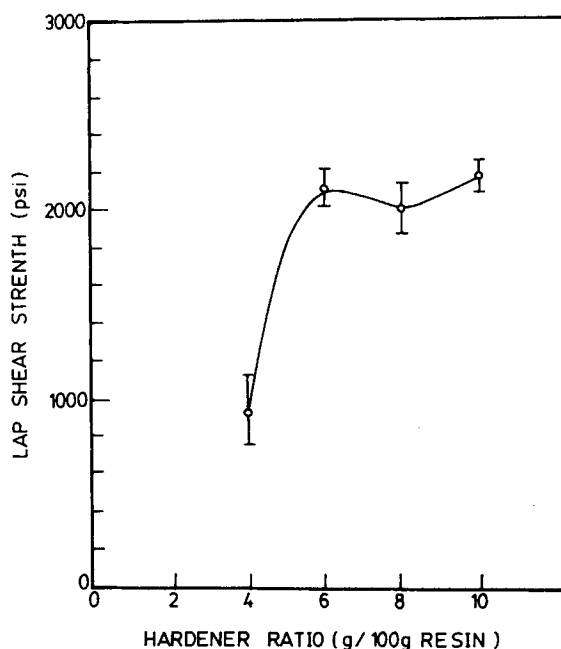


Fig. 5. Effect of hardener ratio (DICY/DGEBA) on the lap shear strength of Al-Al joints.

Effect of Curing Agent on the Adhesive Property of Epoxy Resin

The curing agent DICY has four active hydrogen atoms; therefore, the stoichiometric ratio of DICY/DGEBA is approximately 11 g/100 g. However, the mechanism of DICY curing process is very complex. In addition to the hydrogen atom, etherification could happen, and the $-C\equiv N$ group of DICY might enter the reaction as well.^{23,24} In this report, four DICY/DGEBA ratios were chosen, and their effects on the lap shear and T-peel strengths of DGEBA adhesive were studied. Figure 5 shows that the lap shear strength of an Al-Al joint increases with DICY/DGEBA ratio and then levels off as the DICY/DGEBA ratio is over 6 g/100 g. Since as the DICY/DGEBA ratio is small, DGEBA would be undercured in a fixed curing cycle (177°C, 1 h). On the other hand, a higher DICY/DGEBA ratio could increase the degree of crosslinking only. Because the glass transition temperature of cured DGEBA is much higher than the testing temperature (room temperature), the lap shear strength is not affected significantly by a high degree of crosslinking due to a large DICY/DGEBA ratio. Figure 6 shows that the T-peel strength of DGEBA exhibits a miximum at DICY/DGEBA ratio of 6 g/100 g. Excess crosslinking resulting from a high DICY/DGEBA ratio would cause stress concentration, increase flaws, and consequently reduce the T-peel strength.

Effect of Aluminum Powder on the Adhesive Property of Epoxy Resin

Aluminum powder is the most frequently used filler in epoxy adhesives. It plays two important roles: (1) to prevent the happening of cracking in a high temperature curing system; (2) to reinforce the adhesive strength.²⁵ Figure 7

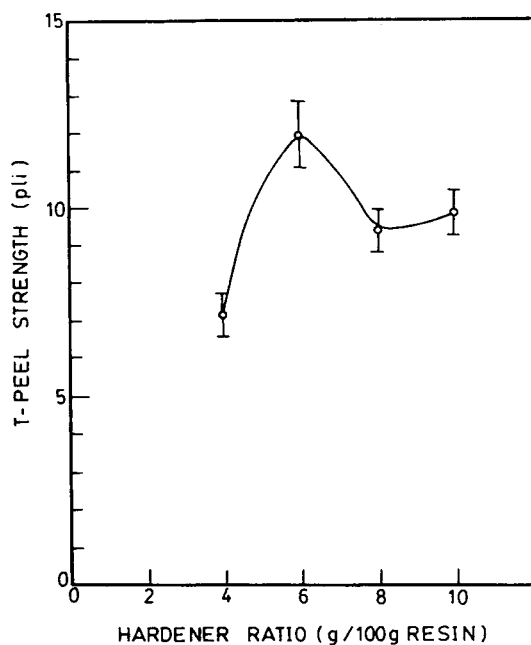


Fig. 6. Effect of hardener ratio (DICY/DGEBA) on the T-peel strength of Al-Al joints.

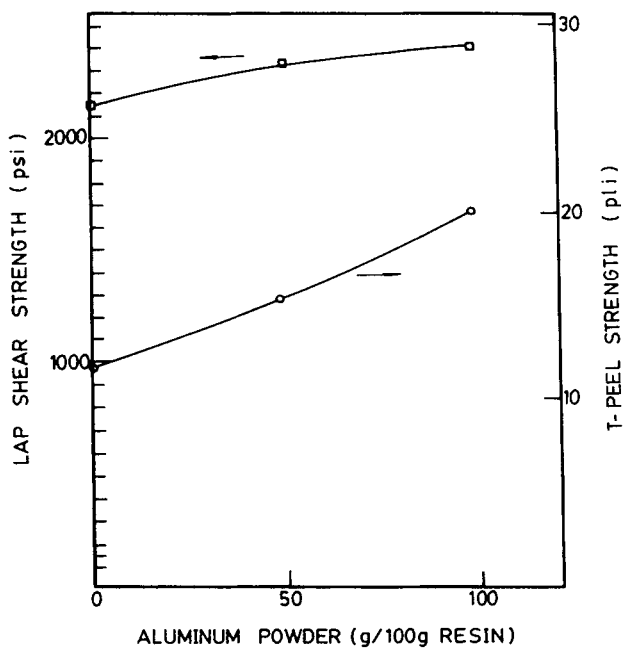


Fig. 7. Effect of aluminum powder on the lap shear and T-peel strengths of Al-Al joints.

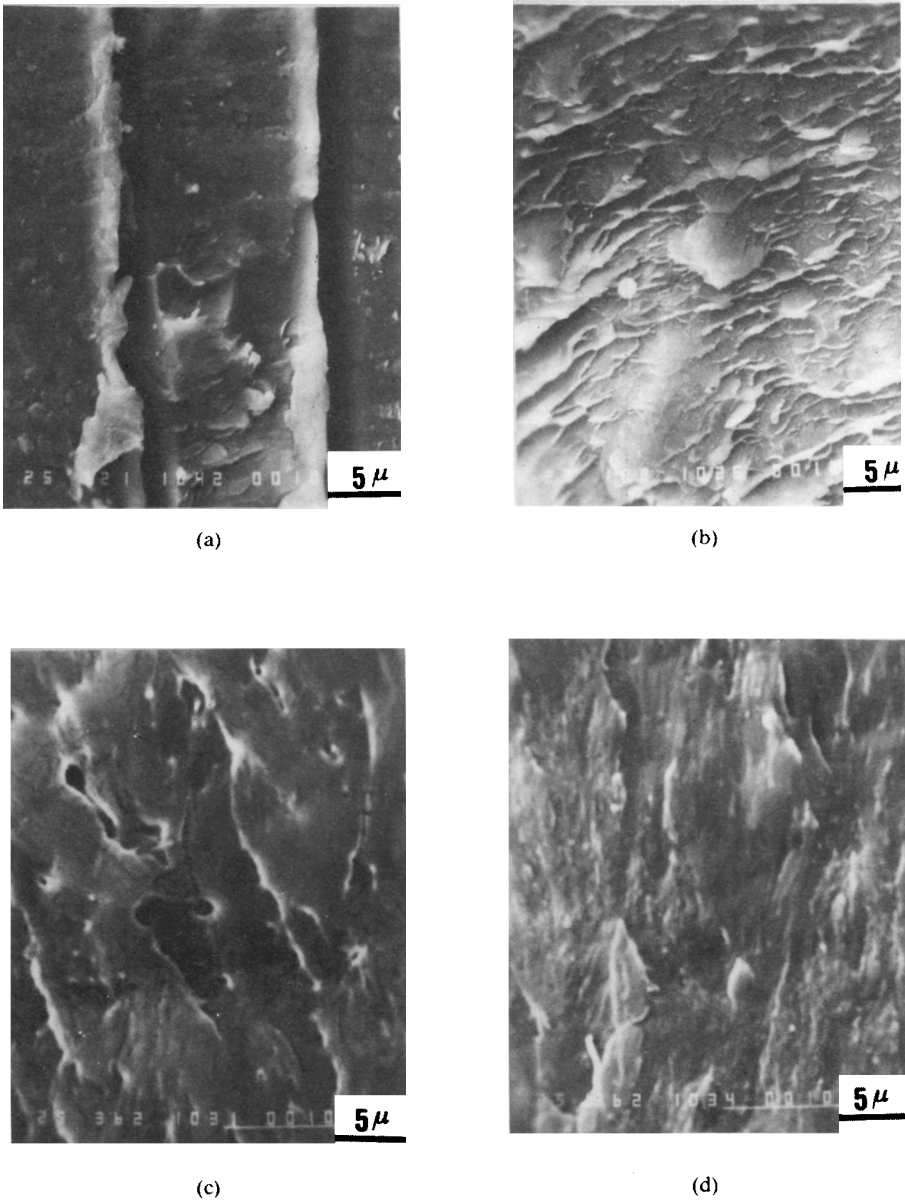


Fig. 8. Single lap shear and T-peel fractural surfaces of Al-Al joints: (a) single lap shear; without aluminum powder (sample 2); (b) single lap shear; with aluminum powder (sample 5); (c) T-peel; without aluminum powder (sample 2); (d) T-peel; with aluminum powder (sample 5).

shows the effects of aluminum powder on the lap strength and T-peel strength of the Al-Al joint. It is observed that both lap shear strength and T-peel strength increase with increasing amount of aluminum powder. Figure 8 compares the lap shear and T-peel fractured surfaces of the Al-Al joint with and without aluminum powder. It shows that the fractured surfaces of DGEBA having aluminum powder have less voids and cracks. The limitation

of using aluminum powder in epoxy adhesive is that it will increase the viscosity of the formulation tremendously, especially for the liquid-rubber-modified epoxy systems. Therefore, effective compounding equipment is required to mix aluminum powder in liquid-rubber-modified epoxy.

CONCLUSIONS

A family of nBA/AA copolymers with functionality of 1.62–9.93 was synthesized and characterized. These copolymers were used to modify an epoxy-type adhesive (DGEBA) cured with dicyandiamide (DICY). Studies of the precuring reaction indicated that the reaction between the copolymer and DGEBA could proceed without catalyst. The curing cycle of DGEBA determined through the thermal analysis was at curing temperature of 177°C for 1 h. In relation to the lap shear strength, the optimum DICY/DGEBA ratio was found to be 6 g/100 g. It was also shown that the addition of aluminum powder would increase both the lap shear and T-peel strengths of the copolymer-modified DGEBA adhesive.

References

1. R. A. Peters and T. J. Logan, *Adhesive Age*, (Apr.), 17 (1975).
2. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 21.
3. C. E. M. Morris, P. J. Pearce, and R. G. Davidson, *J. Adhesion*, **15**, 1 (1982).
4. F. J. McGarry and A. M. Willner, Toughening of an Epoxy Resin by an Elastomeric Second Phase, R68-8, MIT, March 1968.
5. E. H. Rowe, A. R. Siebert, and R. S. Drake, *Mod. Plast.*, **47**, 110 (1970).
6. C. K. Riew, E. H. Rowe, and A. R. Siebert, *Advances in Chemistry Series, No. 154*, Am. Chem. Soc., Washington, DC, 1976, p. 326.
7. W. D. Bascom, R. L. Cottingham, R. L. Jones, and P. Peyser, *J. Appl. Polym. Sci.*, **19**, 2545 (1975).
8. A. C. Meeks, *Polymer*, **15**, 675 (1974).
9. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York, 1976.
10. L. T. Manzione, J. K. Gillham, and C. A. Mcpherson, *J. Appl. Polym. Sci.*, **26**, 889 (1981).
11. L. T. Manzione, J. K. Gillham, and C. A. Mcpherson, *J. Appl. Polym. Sci.*, **26**, 907 (1981).
12. B. L. Lee, C. M. Lizak, C. K. Riew, and R. J. Moulton, *Natl. SAMPE Tech. Conf.*, **12**, 1116 (1980).
13. S. D. Hong, S. Y. Chung, G. Neilson, and R. F. Fedors, *Am. Chem. Soc. Symp. Ser.*, **243**, 91 (1984).
14. J. L. Bitner, J. L. Rushford, W. S. Rose, D. L. Hunston, and C. K. Riew, *J. Adhesion*, **13**, 3 (1981).
15. P. R. Scarito and L. H. Sperling, *Polym. Eng. Sci.*, **19**(4), 297 (1979).
16. S. Gazit and J. P. Bell, *Am. Chem. Soc., Org. Coatings Plast. Chem.*, **46**, 401 (1982).
17. S. Gazit and J. P. Bell, *Am. Chem. Soc., Org. Coatings Plast. Chem.*, **46**, 406 (1982).
18. M. Ochi and J. P. Bell, *J. Appl. Polym. Sci.*, **39**, 1381 (1984).
19. J. M. Barton, *J. Macromol. Sci. Chem.*, **A8**(1), 25 (1974).
20. L. W. Crane, P. J. Dynes, and D. H. Kaebler, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 533 (1973).
21. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci.*, **A1**(8), 1357 (1970).
22. C. L. Brett, *J. Appl. Polym. Sci.*, **20**, 1431 (1976).
23. T. F. Saunders, M. F. Levy, and J. F. Serino, *J. Polym. Sci.*, **A1**(5), 1607 (1967).
24. N. S. Schnieder, J. F. Sprouse, and G. L. Hagnaner, *Polym. Eng. Sci.*, **19**(4), 304 (1979).
25. A. C. DeLeon and D. L. Paradis, *26th Natl. SAMPE Symp.*, (Apr.), 1431 (1981).

Received December 19, 1985

Accepted April 9, 1986