

Diluted Epoxy Adhesives. I. Physical Properties and Lap Shear Strengths

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Synopsis

A series of epoxy adhesives were prepared from a commercial bisphenol A-epichlorohydrin epoxy resin by diluting it with varying amounts of either phenyl glycidyl ether or 1,4-butanediol diglycidyl ether and curing with either diethylenetriamine (DTA) or diethylaminopropylamine (DPA). The initial physical properties (density, viscosity, and surface tension) of the epoxy solutions were determined both with and without curing agents. It was found that the surface tensions of adhesives catalyzed with DPA are initially very low (31–32 dynes/cm), and within several hours these solutions attain an equilibrium surface tension of 40–46 dynes/cm. When the steel-to-steel lap shear strengths of these adhesives were measured, a correlation was not observed between the initial properties and the strengths of these materials.

INTRODUCTION

Background

The formation of a strong adhesive bond is dependent upon a great many factors, namely, the preparation of the surfaces to be bonded, the formulation of the adhesive, the curing conditions of the adhesive, the geometry of the adhesive bond, and the environmental conditions to which the bond will be subjected. The identification of those variables that most strongly contribute to the properties of an adhesive joint has been the subject of investigations for many years. Some of the research has been along strictly theoretical lines such as the determination of the surface energy of solids^{1–3} and the identification of the polar and dispersion force contributions associated with the surface tension of different materials.^{4–6} There have been some attempts to correlate adhesive strengths to theory. Levine et al.⁷ reported a relationship of bond strength to the critical surface tension for wetting (γ_c) of a series of polymer films, while Schonhorn and Sharpe^{8,9} investigated the bonding of chlorotrifluoroethylene copolymers with epoxy adhesives that had different initial surface tensions (γ_{LV}). Kitazaki¹⁰ correlated Levine's work with some that Schonhorn had reported and showed that epoxy adhesives cured with diethylenetriamine (DTA) or diethylaminopropylamine (DPA) exhibited the highest adhesive strengths with polymers having a γ_c value between 40 and 42 dynes/cm.

The majority of the work reported in the literature concerning the adhesive strength of various systems has been deficient in data concerning the physical properties of the adhesives both before and after curing. Thus it would be of interest to systematically alter the physical properties of an epoxy adhesive and to determine the effect that these changes have on its adhesive performance. Therefore, the physical properties of a common bisphenol A-epichlorohydrin epoxy resin and its mixtures with either a monofunctional diluent, phenyl glycidyl

ether (PGE), or a difunctional diluent, 1,4-butanediol diglycidyl ether (BDE), were investigated in detail.

The use of diluents in formulating epoxy adhesives is very common.¹¹ The major reason for mixing diluents into an adhesive formulation is to reduce viscosity, thereby giving faster wetting and allowing the addition of a higher percentage of fillers. In general, the greater the percentage of diluents in an epoxy resin, the lower will be the deflection temperature, the viscosity, the hardness, and the modulus. The water adsorption, time to peak exotherm, and peak exothermic temperature all increase at high diluent levels. Flexural or tensile strengths may remain the same at low percentages of diluent before decreasing quite rapidly as higher amounts of diluent are added. Very little information is available on the effect of diluents on bond strength and adhesion phenomena.

Objectives

The changes in physical properties of a commercial epoxy resin, such as viscosity and surface tension, were measured as a function of diluent level. Further changes that occur in these properties upon the addition of either diethylenetriamine or diethylaminopropylamine curing agents were then measured. These adhesive systems were used to prepare steel-to-steel lap shear specimens, and a comparison of the lap shear strengths to the observed changes in viscosity and/or surface tension was made. These data comprise the text of this paper.

The same adhesive formulations were used in the lap shear bonding of polymeric films such as polystyrene, mylar, and poly(vinyl chloride). The wetting behavior of the adhesives on the films was also measured using contact angles, which yielded some insight into the effect of diluents on this property. The critical surface tension for wetting (γ_c) was determined with uncatalyzed diluted epoxy resin for the polymer films, and the γ_c values were found to differ somewhat from published literature values. The data from this portion of the research program will be the subject of a subsequent paper.

Since the reason for this work is to determine what property of either the uncured adhesive or the cured adhesive most strongly influences its performance, it was necessary to measure some selected bulk properties of the cured adhesives. Therefore, the shrinkage of these adhesive systems were measured and compared to their lap shear strengths. These results are published in an accompanying paper.

EXPERIMENTAL

Materials

All the chemicals used in this research were obtained from commercial sources and, unless otherwise stated, were used without further purification. The diluents and amine curing agents were rebottled into small amber glass bottles in order to minimize their contamination.

Preparation of Epoxy Solutions

Two series of epoxy resin solutions were prepared using a bisphenol A-epi-chlorohydrin epoxy resin, DER 330 [equivalent weight = 182–189, viscosity at 25°C = 7–10 Pascal seconds (Pa-s)], diluted with either phenyl glycidyl ether (PGE) or 1,4-butanediol diglycidyl ether (BDE). Each series of epoxy solutions consisted of 100 g epoxy resin diluted with 5, 20, and 50 g diluent. When diethylenetriamine (DTA) was used as the curing agent, its concentration was adjusted in order to maintain a stoichiometric balance of amine hydrogens to epoxide groups. In the case of diethylaminopropylamine (DPA), its level was maintained at 6 parts per 100 parts epoxy solution (phr).

A coded referral numbering system for the various mixtures of epoxy resin and diluents, with and without curing agents, will be used in this discussion. This number may have as many as three sections depending on the number of components in the formulation. The resin (abbreviated as 330) is always assumed to be 100 parts by weight, and the level of diluent is given in conjunction with its proper designation. The third section of the referral number denotes the amount of curing agent per 100 g of the epoxy resin-diluent solution. For example, 330-50 BDE-DPA6 indicates that 100 g of a mixture initially prepared from 100 g DER 330 and 50 g BDE was catalyzed with 6 g DPA.

Viscosity

The viscosity measurements on uncatalyzed samples were taken using Ostwald viscometers in a constant-temperature water bath maintained at $30.00 \pm 0.01^\circ\text{C}$. The viscometers were calibrated with standards obtained from the Cannon Laboratories, and, when feasible, the calibration for a given viscometer was crosschecked with two different standards.

For catalyzed samples, the plate-and-cone attachment of a Rheotest rotating viscometer was employed. The sample temperature was maintained at $30.00 \pm 0.01^\circ\text{C}$, and a complete determination required less than 5 min after the addition of the curing agent to the epoxy resin.

Surface Tension

Surface tensions were determined at room temperature using the duNouy tensiometer. The calibration of the equipment was periodically checked using a 500-mg weight according to a standard procedure outlined in the manual. Prior to the addition of the liquid sample to either 15×55 mm or 20×90 mm glass culture dishes, the dishes were cleaned with a standard chromate cleaning solution followed by rinsing with copious amounts of distilled water, an acetone rinse, and oven drying at 60 – 70°C . A 60-mm platinum-iridium ring was cleaned by treatment in dilute nitric acid, followed by distilled water and acetone rinsing, and then flaming to a dull red color with a Bunsen burner. The calibration of the ring was checked periodically with spectro-grade benzene.

Multiple readings were taken on each sample. They were normally found to be reproducible to 0.1 dyne/cm. As a result of the high viscosities of some of the epoxy resin samples, a special procedure was required for the determination of their surface tension. The ring was allowed to equilibrate near the expected value of surface tension while the excess resin drained from it. After several

minutes the ring was slowly pulled from the sample to yield the surface tension.

All surface tension readings were corrected from room temperature to 30°C using a temperature coefficient of -0.1 dyne/cm for each °C increase in temperature. The accuracy of the temperature coefficient was determined by measuring the change in surface tension with increasing temperature for pure DER 330 and for an epoxy solution containing 100 parts DER 330 and 50 parts BDE (330-50 BDE). These measurements were taken on an Instron testing machine using the A cell (load range 10–50 g), environmental box, and strip chart recorder. The recorder, set for 2 g full-scale deflection, was calibrated with nitromethane, carbon tetrachloride, benzene, and DER 330 epoxy resin so that the readings in grams could be converted to dynes/cm. The sample temperature was monitored using a potentiometer with the thermocouple taped to the outside of the glass sample dish. The platinum-iridium ring was connected to the load cell with a 17-gauge drill rod which had small hooks attached to either end. All surface tension readings were corrected¹² for the nonvertical pull of the liquid on the ring.

Density

The densities of the uncatalyzed epoxy solutions and the catalyzed epoxy solutions prior to curing were obtained in a water bath at $30.00^\circ \pm 0.01^\circ\text{C}$ using 10-cc specific gravity bottles. The volumes of the different bottles were determined with distilled water and were precise to $\pm 5.0 \times 10^{-4}$ cc.

Lap Shear Tests

Steel coupons ($101 \times 25.4 \times 0.94$ mm) were cut to size from cold-rolled steel panels ($305 \times 101 \times 0.94$ mm). An acid etching technique,¹³ as outlined below, was used for cleaning the coupons. The initial cleaning steps were a vapor degreasing in trichloroethylene followed by rinsing in methyl ethyl ketone. The coupons were then immersed for 7 min in an 85 °C acid solution that was prepared by dissolving 50 g potassium iodide in 1 l. of 1:1 concentrated phosphoric acid:water by volume. After the acid etch, the specimens were rinsed with copious quantities of distilled water and acetone and air dried.

The lap shear samples were prepared in a bonding fixture under 110 kPa pressure. A small piece of 0.127-mm copper wire was placed in the bond line to prevent the possible problem of squeezing out an excessive amount of adhesive. The strengths were determined on an Instron test machine with a cross-head speed of 1.27 mm/min. A minimum of five replicates were run for each adhesive system.

RESULTS AND DISCUSSION

Physical Properties

The densities at 30°C of the catalyzed and uncatalyzed epoxy resin, diluted with either PGE or BDE, are tabulated in Table I. The densities of the individual components (Table Ia) were used to calculate the theoretical densities of the epoxy solutions using the following equation:

TABLE I
Density at 30°C of Uncatalyzed and Catalyzed Epoxy Solutions
(a) Individual Components

Material	Density, g/cc
Epoxy resin (DER 330)	1.1593
Phenyl glycidyl ether (PGE)	1.1007
1,4-Butanediol diglycidyl ether (BDE)	1.1038
Diethylenetriamine (DTA)	0.9434
Diethylaminopropylamine (DPA)	0.8194

(b) Uncatalyzed Systems

Formulation	Density, g/cc		Difference
	Measured	Calculated	
330-5PGE	1.1557	1.1564	+0.0007
330-20PGE	1.1489	1.1491	+0.0002
330-50PGE	1.1390	1.1391	+0.0001
330-5BDE	1.1564	1.1565	+0.0001
330-20BDE	1.1495	1.1497	+0.0002
330-50BDE	1.1408	1.1402	-0.0006

(c) Catalyzed Systems

Formulation	Density with DTA, g/cc			Density with DPA, g/cc		
	Measured	Calculated	Difference	Measured	Calculated	Difference
330	1.1340	1.1336	-0.0004	1.1361	1.1327	-0.0034
330-5PGE	1.1310	1.1311	+0.0001	1.1318	1.1301	-0.0017
330-20PGE	1.1228	1.1229	+0.0001	1.1266	1.1235	-0.0031
330-50PGE	1.1100	1.1108	+0.0008	1.1167	1.1145	-0.0022
330-5BDE	1.1311	1.1311	+0.0001	1.1333	1.1302	-0.0031
330-20BDE	1.1263	1.1234	-0.0029	1.1270	1.1240	-0.0030
330-50BDE	1.1128	1.1117	-0.0011	1.1182	1.1155	-0.0027

$$\rho_{\text{mix}} = (\rho_{330})(V_{330}) + (\rho_{\text{dil}})(V_{\text{dil}})$$

where ρ_{mix} is the density of the mixture, ρ_{330} and ρ_{dil} are the densities of the epoxy resin and the diluent, while V_{330} and V_{dil} are the volume fractions of the resin and diluent in the mixture. Excellent agreement was found between the measured and calculated values (Table Ib) for the uncatalyzed solutions. Since there was no change in volume on mixing, these solutions can be considered ideal.¹⁴ When the epoxy solutions were catalyzed with a stoichiometric amount of DTA (Table Ic), again the mixtures appeared to be ideal. With DPA curing agent, however, the measured densities were consistently higher than the calculated values indicating that these solutions are deviating from ideality.

The viscosities were also determined at 30°C for these solutions (Table II). Very little information is available concerning the prediction of the solution viscosity of two miscible liquids from their individual viscosities.¹⁵ When the log of viscosity was compared to the concentration of diluent (Fig. 1), the PGE solutions gave a linear relationship while the BDE solutions were found to be nonlinear. Addition of DTA (Fig. 2) reduced the viscosity further, but the linear response for PGE and the nonlinear response for BDE were still apparent. When DPA was the curing agent, the viscosities of the solutions were very similar except at lower diluent concentrations (Fig. 3).

The surface tensions of the epoxy solutions (Table III) were obtained at room

TABLE II
Viscosity at 30°C of Uncatalyzed and Catalyzed Epoxy Solutions

Formulation	Viscosity, mPa·s		
	None ^a	DTA ^a	DPA ^a
330	4690	480	1075
330-5PGE	2160	305	550
330-20PGE	550	125	170
330-50PGE	118	45	60
PGE	4.64	—	—
330-5BDE	2440	340	560
330-20BDE	695	145	280
330-50BDE	205	60	100
BDE	14.46	—	—
DTA	4.64	—	—
DPA	1.13	—	—

^a Curing agent.

temperature (22°–25°C) and corrected to 30°C using a correction factor of -0.1 dyne/cm per °C. In determining the validity of this temperature coefficient, it was found that if the epoxy resin sample was not stirred prior to each surface tension measurement or replaced with a new sample, the temperature coefficient was abnormally high. This is attributed to an impurity in the resin that is surface active and has a surface tension lower than the epoxy. At room temperature this impurity requires several days to affect the surface tension of the resin, but at elevated temperatures it occurs quite rapidly. By using fresh samples of the epoxy solutions, the temperature coefficient was found to agree with the one used for correcting the surface tensions from ambient to 30°C.

The surface tensions of the two series of diluted epoxy resin solutions either uncatalyzed (Fig. 4) or catalyzed with DTA (Fig. 5) were found to be very similar.

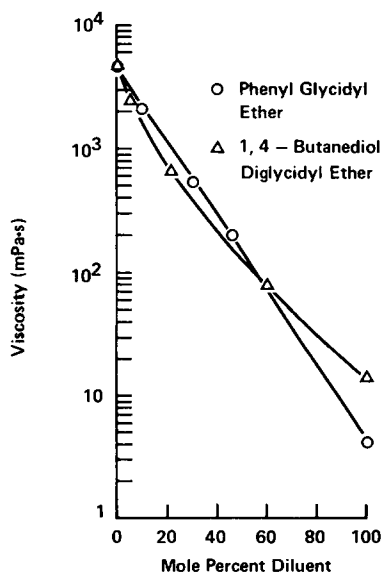


Fig. 1. Viscosity at 30°C for uncatalyzed epoxy solutions: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

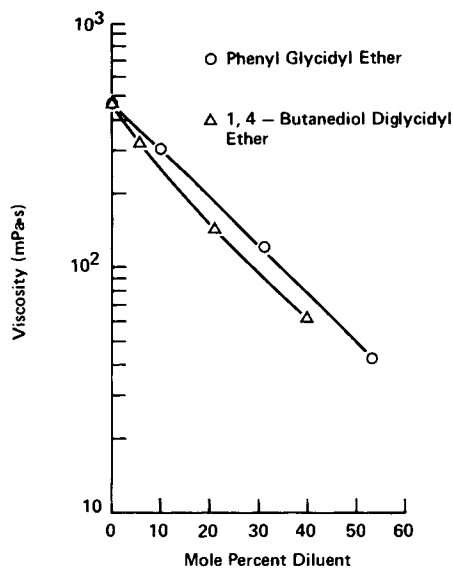


Fig. 2. Viscosity at 30°C for epoxy solutions catalyzed with diethylenetriamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

However, with the DPA curing agent (330-DPA6, Fig. 6) a dramatic increase was observed in the surface tension of this adhesive as a function of time after mixing. This rise in surface tension continued for over 3 hr before stabilizing. After this observation was confirmed in duplicate experiments, the role of atmospheric moisture in this change was investigated. A sample of 330-DPA6 was mixed and stored under dry nitrogen for 3 hr. When its surface tension was then determined, it duplicated exactly the values that had been previously obtained (Fig. 6). The surface tension versus time for the PGE diluted series catalyzed with DPA is shown in Figure 7, and for the BDE series, in Figure 8. The increase in surface tension with time after mixing was less at higher diluent concentrations. A comparison of the equilibrium surface tension versus volume percent diluent (Fig. 9) for the DPA-catalyzed epoxy solutions shows that at the higher diluent

TABLE III
Surface Tension at 30°C of Uncatalyzed and Catalyzed Epoxy Solutions

Formulation	Surface tension, dynes/cm		
	None ^a	DTA ^a	DPA ^{a,b}
330	47.2	46.5	33.3–46.5
330-5PGE	46.6	45.8	31.0–45.2
330-20PGE	45.9	45.1	33.8–44.7
330-50PGE	44.6	44.3	32.3–44.4
PGE	41.9	41.3	34.7–42.0
330-5BDE	46.8	45.8	34.0–45.4
330-20BDE	45.6	45.3	31.8–44.2
330-50BDE	44.1	44.4	34.5–43.5
BDE	41.9	41.1	38.1–41.5
DTA	42.0	—	—
DPA	27.0	—	—

^a Curing agent.

^b Initial and equilibrium values.

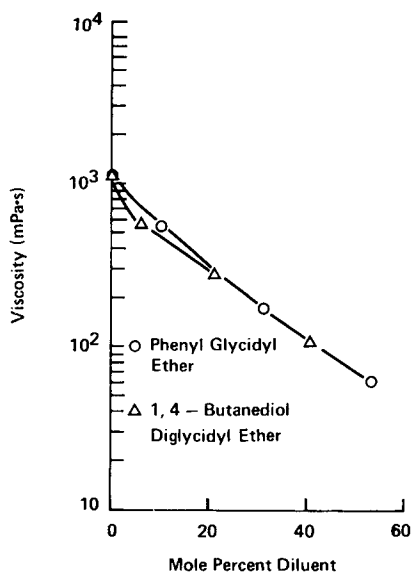


Fig. 3. Viscosity at 30°C for epoxy solutions catalyzed with diethylaminopropylamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

levels the BDE solutions have a lower surface tension than the PGE diluted systems.

As discussed previously, the physical properties of the uncatalyzed and catalyzed epoxy solutions indicate that the epoxy-diluent mixtures form ideal solutions. When catalyzed with DTA, the solutions still did not show any deviation from their expected properties. When DPA was used as the curing agent, the solutions underwent a contraction in volume indicating some nonideality. The dynamic nature of the surface tension versus time for this system showed that the DPA is surface active. This yielded the initial low values, and as the DPA became attached to the epoxy resin, the surface tension of these adhesives approached the expected values.

If the rate and degree of wetting of an adhesive on a substrate are major factors in its bond strength, then the increasing diluent level in the epoxy solutions should yield higher bond strength. This would be a result of the observed decrease in solution viscosity and surface tension with increased diluent level.

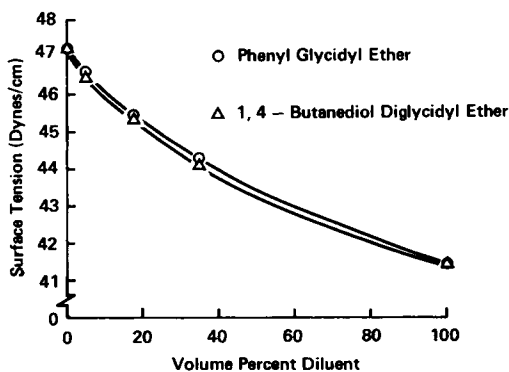


Fig. 4. Surface tension at 30°C for uncatalyzed epoxy solutions: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

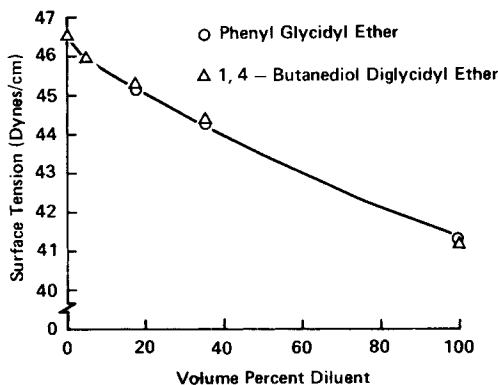


Fig. 5. Surface tension at 30°C for epoxy solutions catalyzed with diethylenetriamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

Bond Strengths

The steel-to-steel lap shear strengths of the diluted epoxy solutions cured with DTA for seven days at ambient temperatures or after a 4-hr, 100°C postcure are shown in Figures 10 and 11. The room temperature cures showed that increasing levels of diluent greatly increased the bond strength of the adhesive. However, when the adhesives were postcured at 100°C, the bond strength of the system containing no diluent doubled in strength over that observed with the room temperature-cured samples. The postcured samples did not show the wide range of strengths as did the room temperature-cured samples. Of interest is the initial drop in strength with a small addition of diluent followed by an increase in strength at higher diluent levels.

If the lap shear strength were dependent on the rate or degree of wetting of the adhesive, then the undiluted samples would not be expected to give a large increase in strength as a result of the elevated temperature postcure. Also, the observed strengths were the same whether or not the adhesive samples were allowed to cure at ambient prior to the post cure at 100°C.

The bond strengths of the epoxy solutions cured with DPA are shown in Figures 12 and 13. The results from the seven-day cure at room temperature yielded an increase in strength with increased diluent level like that observed previously

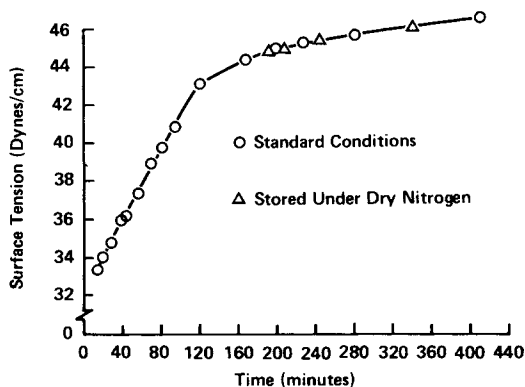


Fig. 6. Surface tension at 30°C as a function of time for undiluted epoxy resin catalyzed with diethylaminopropylamine: (O) standard conditions; (Δ) stored under dry nitrogen.

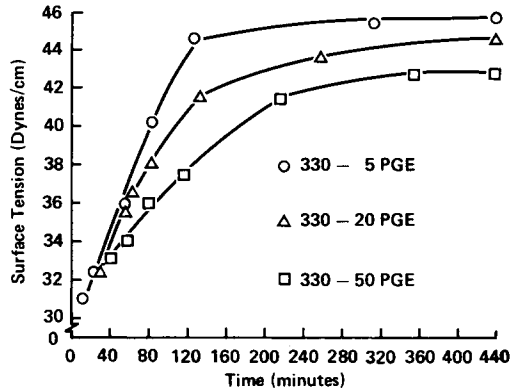


Fig. 7. Surface tension at 30°C as a function of time for epoxy resin diluted with phenyl glycidyl ether and catalyzed with diethylaminopropylamine: (○) 330-5 PGE; (△) 330-20 PGE; (□) 330-50 PGE.

with the DTA-cured systems. The 100°C postcure gave a very large increase in strength for the systems with low diluent levels and modest increases with the adhesives containing higher diluent concentrations. With the postcure, the 330-50 PGE system underwent almost a three fold increase in strength, while the 330-50 BDE system had a major reduction in strength. The increase in strength with the PGE diluent cannot be readily explained since the PGE is monofunctional and causes chain termination in the curing of the epoxy resin. The 100°C cure gives, with the tertiary amine portion of the DPA, crosslinks that are necessary to improve the strength of the adhesive. The loss in strength with postcuring of the adhesive containing the high level of BDE is not easily explained. However, the adhesive had the appearance of being only partially cured and when the 330-50 BDE solution was cured with a higher concentration of DPA (Fig. 13), the lap shear strength improved dramatically.

All the lap shear test samples for both the DTA and DPA curing agents appeared to have failed adhesively; that is, the failure was at the interface between the adhesive and steel surfaces. If the initial properties of the adhesive play a

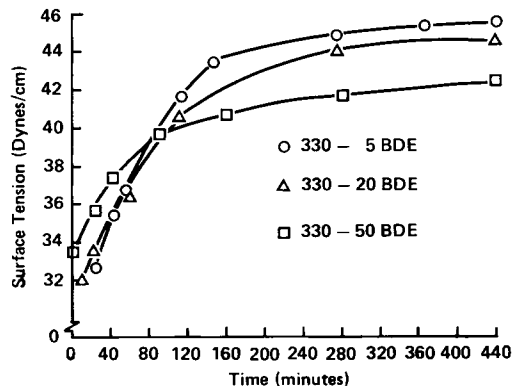


Fig. 8. Surface tension at 30°C as a function of time for epoxy resin diluted with 1,4-butandiol diglycidyl ether and catalyzed with diethylaminopropylamine: (○) 330-5 BDE; (△) 330-20 BDE; (□) 330-50 BDE.

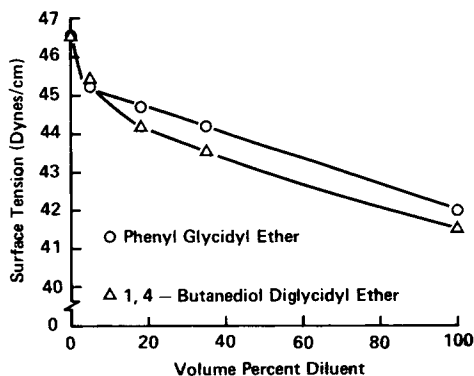


Fig. 9. Equilibrium surface tension at 30°C for epoxy solutions catalyzed with diethylaminopropylamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

major role in determining the strength of the bonded sample, then the postcure cycle should not result in major changes in the bond strengths. This would be especially true for the DTA cured adhesives where the seven-day cure at room temperature results in a high degree of polymerization and the postcure contributes only a small amount of additional polymerization.

It was also found that there was no difference whether the lap shear samples were cured for seven days at room temperature followed by 4-hr, 100°C postcure or whether they were cured immediately for 4 hr at 100°C. In both instances the lap shear strengths were also found to be the same. This would not be expected with the DPA-cured adhesives if the initial surface tension of the adhesive influenced its strength, since these systems were observed to undergo a large change in surface tension with respect to time.

SUMMARY

Since the initial properties, such as surface tension and viscosity, of the diluted epoxy adhesives did not show a correlation to their lap shear strengths, bulk properties of the cured adhesives could be a strong factor in their performance.

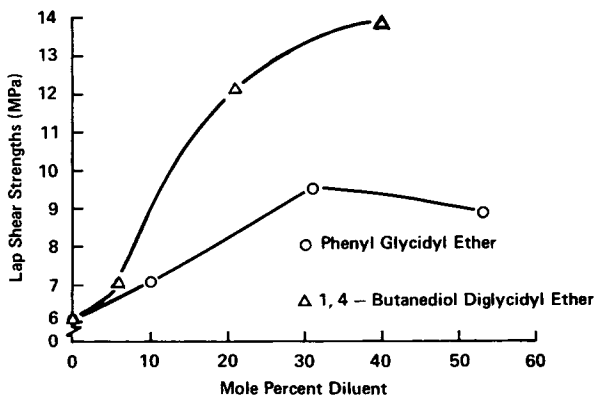


Fig. 10. Lap shear strength for epoxy solutions cured seven days at room temperature with diethylenetriamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

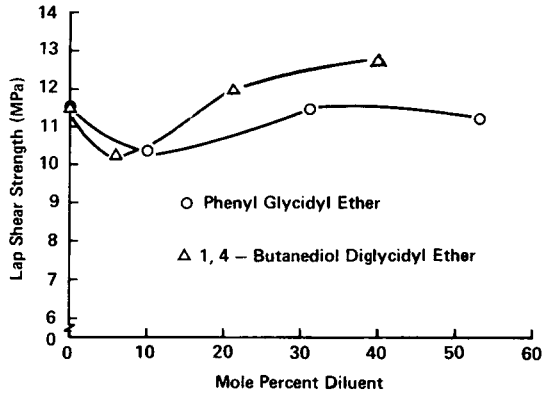


Fig. 11. Lap shear strength for epoxy solutions cured four hours at 100°C with diethylenetriamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

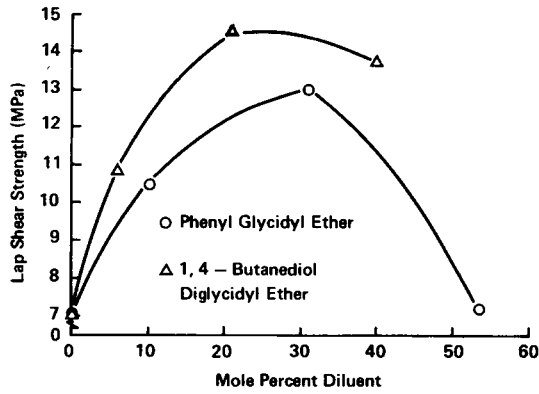


Fig. 12. Lap shear strength for epoxy solutions cured seven days at room temperature with diethylaminopropylamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

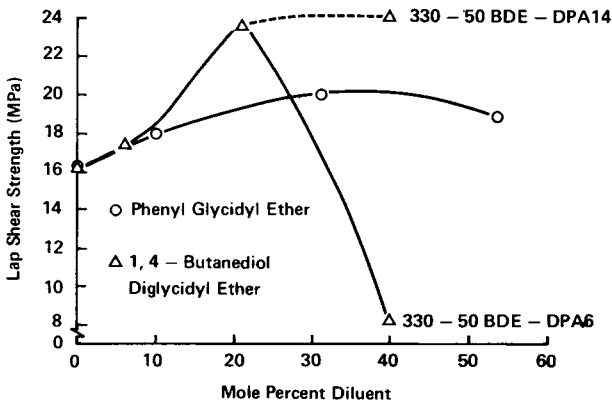


Fig. 13. Lap shear strength for epoxy solutions cured 4 hr at 100°C with diethylaminopropylamine: (O) phenyl glycidyl ether; (Δ) 1,4-butanediol diglycidyl ether.

Some of the bulk properties of interest include the shrinkage during cure, residual stresses, and flexural modulus. The relationship of these parameters to the adhesive strength will be the subject of future papers.

References

1. W. A. Zisman, *Adv. Chem. Ser.*, **No. 43**, 11 (1963).
2. R. J. Good, R. A. Grifalco, and G. Kraus, *J. Phys. Chem.*, **62**, 1418 (1958).
3. D. H. Kaelble, *The Physical Chemistry of Adhesion*, Wiley-Interscience, New York, 1971, Chap. 5.
4. F. M. Fowkes, *Ind. Eng. Chem.*, **56**, (12), 40 (1964).
5. F. M. Fowkes, *J. Phys. Chem.*, **66**, 382 (1962).
6. S. Wu, *J. Polym. Sci. C*, **34**, 19 (1971).
7. M. Levine, G. Ilkka, and P. Weiss, *Polym. Lett.*, **2**, 915 (1964).
8. H. Schonhorn and L. H. Sharpe, *Polym. Lett.*, **2**, 719 (1964).
9. H. Schonhorn and L. H. Sharpe, *J. Polym. Sci. A*, **3**, 3087 (1965).
10. Y. Kitazaki and T. Hata, *J. Adhes.*, **4**, 123 (1972).
11. H. Lee and K. Neville, *Handbook of Epoxy Resins* McGraw-Hill, New York, 1967, Chap. 13.
12. H. H. Zuidema and G. W. Waters, *Ind. Eng. Chem., Anal. Ed.*, **13**, 312 (1941).
13. H. N. Vaziranai, *J. Adhes.*, **1**, 22 (1969).
14. W. J. Moore, *Physical Chemistry*, 3rd ed., Prentice-Hall, Englewood, New Jersey, 1962, p. 125.
15. R. H. Perry and C. H. Chilton, *Chemical Engineers Handbook* 5th ed., McGraw-Hill, New York, 1973, pp. 3-247.

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