DEVELOPMENT OF IMPROVED STRUCTURAL EPOXY-RESIN ADHESIVES AND BONDING PROCESSES FOR METAL

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DEVELOPMENT OF IMPROVED STRUCTURAL EPOXY-RESIN ADHESIVES AND BONDING PROCESSES FOR METAL[1]

By

J. M. BLACK, Chemist
and
R. F. BLOMQUIST, Chemist

Forest Products Laboratory,[2] Forest Service
U. S. Department of Agriculture

SUMMARY

Investigations of new experimental adhesive formulations with improved operating and performance properties for structural bonding of metal to wood and metal to metal in aircraft fabrication have been under way at the Forest Products Laboratory for several years, in cooperation with the Navy Bureau of Aeronautics. Particular attention was given to development of adhesives that were less critical of variations in bonding techniques and that had better strength in joints over the range from -70° to +250° F. Earlier results have been reported to the cooperator in yearly progress reports.[3] During the past 3 years particular attention was given to utilization of epoxy resins in such adhesive formulations. The current status of this last phase of the work is discussed herein. The superior performance of three adhesives, designated as FPL-828, FPL-852a, and FPL-866, is illustrated. Maximum joint strength in aluminum bonds is obtained when the adhesives are cured at 200° F. and joints of intermediate strength are obtained when cured at room temperature. No one formulation was developed that possessed all of the properties desired in an aircraft structural adhesive, such as ability to cure equally well at both room and elevated temperatures, while retaining such desirable properties as satisfactory

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[1] This study made in cooperation with the Bureau of Aeronautics under Order No. NAer 01389.

[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[3] The first progress report on this project was submitted on Feb. 24, 1949; the second on Jan. 24, 1951; the third on Feb. 1, 1952; and the fourth on Sept. 5, 1952.

pot life, spreadability, strength at subzero, normal and elevated temperatures, resistance to creep, and acceptable bend strength or reduced brittleness. A number of epoxy-resin adhesives were formulated that possessed desirable combinations of several of these properties.

INTRODUCTION

During the period from 1945 to 1950 interest in developing better commercial adhesives for structural metal bonding for aircraft applications declined. For this reason the Forest Products Laboratory was requested by the Navy Bureau of Aeronautics in 1946 to investigate methods of formulating adhesives for metal-to-wood and metal-to-metal bonding that would be simpler to use and would perform more reliably under various conditions of service. This final report covers primarily the results of work done during the past year. Results of earlier work were described in previous yearly progress reports.[3] Since 1950 particular attention has been given to utilization of the epoxy resins in these adhesive formulations because of their advantageous low curing pressures and temperatures. This report also summarizes variables affecting epoxy-resin-base adhesive performance based on all of the work done on these adhesives under this project.

PREPARATION AND APPLICATION PROCEDURES

The preparation and recommended application procedures for the three most promising adhesive formulations to be discussed later are described in this section.

Preparation of FPL-828, FPL-852a, and FPL-866

Adhesives FPL-828, FPL-852a, and FPL-866 are epoxy-resin-base adhesives capable of curing at room temperature and at slightly elevated temperatures and are recommended for bonding aluminum pieces together. Adhesive FPL-828 has the following composition:

Epoxy resin, E-2	100 grams
Polysulfide elastomer, PS-1	10 grams
Milled glass fibers, 1/32 inch H.M.7	10 grams
Dimethylaminoethyl alcohol	4 grams
Triethylamine	4 grams

Adhesive FPL-852a has the following composition:

Epoxy resin, E-2........................	100 grams
Resorcinol..............................	20 grams
Polysulfide elastomer, PS-3.............	20 grams
Hexamethylenetetramine solution[4]........	25 grams

Adhesive FPL-866 has the following composition:

Epoxy resin, E-2........................	100 grams
Resorcinol..............................	1 gram
Domestic china clay, 325 mesh...........	50 grams
Dimethylaminoethyl alcohol..............	4 grams

The adhesives were prepared by heating the epoxy resin, resorcinol, and polysulfide elastomer (FPL-852a) or china clay (FPL-866), or the polysulfide elastomer and glass fibers (FPL-828) on a steam bath with constant stirring until all components were completely dissolved. The base adhesives may then be stored for as long as 3 months at room temperature. The adhesives were activated by the addition of the curing agents, dimethylaminoethyl alcohol and triethyl amine for FPL-828, hexamethylenetetramine solution for FPL-852a, and dimethylaminoethyl alcohol for FPL-866. The pot life of FPL-828 in quantities of 50 grams or so is about 2.5 hours, that of FPL-852a is about 1.5 hours, and that of FPL-866 about 4 hours at 75° to 80° F.

Recommended Application and Bonding Procedures for FPL-828, FPL-852a, and FPL-866

The following steps in bonding are recommended for most consistent results:

1. Clean the aluminum surfaces by immersion for 5 to 10 minutes in a solution of concentrated sulfuric acid (10 parts) and sodium dichromate (1 part) in 30 parts by weight of water at 140° to 160° F., followed with a rinse in cold running water and then in hot running water or steam.

2. Apply one brush coat to each surface to be bonded.

3. The parts to be bonded may be assembled immediately or at any time up to 60 minutes of open assembly at room temperature.

4. Only contact pressure is required during cure of the adhesive.

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[4] A saturated aqueous solution, 45 percent hexamethylenetetramine by weight.

5. These adhesives may be cured at 80° or 200° F. Bonds cured at 80° will reach maximum strength in about 1 week. A cure of about 1 hour is required at 200°. Bonds cured at 200° will be superior in strength properties to bonds cured at 80°.

6. The adhesive may be removed from brushes and containers with methyl ethyl ketone, acetone, or cellosolve.

TEST METHODS

In most of the investigations test specimens of 0.064-inch 24S-T3 clad aluminum alloy with a 0.5-inch lap joint, as described in Air Force Specification No. 14164,[2] were used to evaluate shear strength in tests made at room temperature, -70° F., and immediately at 180° and 250° F., and bend strength in tests at room temperature. Tests to determine the shear strength at room temperature and -70° and the bend strength at room temperature were conducted according to the methods described in Air Force Specification No. 14164. The tests made at 180°, 250°, and -70° F. were made immediately after the specimen reached the desired temperature, which required a period of 3 to 5 minutes in the test chamber.. The temperature of the test chamber in the tests at elevated temperature was controlled to within ±3° of the desired temperature.

RESULTS AND CONCLUSIONS

The work covered in the fourth progress report[3] indicated that dimethylaminoethyl alcohol (DMAEA) was a particularly promising curing agent for epoxy-resin adhesives that would cure at both room temperature and slightly elevated temperatures. An adhesive, FPL-828, was developed that was superior in spreading properties, shear strength at 180° F., longtime strength at 180° F. or resistance to creep, and performance characteristics after very short and relatively long open-assembly conditions. Maximum joint strength in aluminum bonds was obtained when the adhesive was cured at an elevated temperature, and joint strength of intermediate quality was obtained when the adhesive was cured at room temperature. Adhesive FPL-828, as well as the better commercially available epoxy-resin adhesives, however, possessed one important limitation that restricted their general wide use and application in aircraft construction. This limitation was the marked thermoplastic softening of the epoxy-resin adhesives at temperatures of 250° F. and above.

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[2] U. S. Air Force Specification No. 14164, Adhesive, Metal to Metal, Structural, Sept. 20, 1949.

Work during the past year was centered on this problem of overcoming the thermoplastic characteristics of the epoxy-resin adhesive. The following discussion of the results is a summary of the most important effects of variations in formulation and bonding procedures and is divided into three parts that describe the work conducted on three different types of adhesive formulations. The various strength values given in this report are the average of at least five test specimens.

PART I - ADHESIVE FORMULATIONS OF EPOXY RESIN, POLYSULFIDE, AND AMINE

Shear Strength at 250° F.

A typical adhesive of the epoxy-polysulfide-amine type is FPL-828, which was reported in the fourth progress report[3] as the most promising adhesive formulation developed in last year's work. This adhesive is composed of epoxy resin E-2 with 10 percent polysulfide elastomer (PS-1), 10 percent of milled glass fibers, 4 percent of dimethylaminoethyl alcohol (DMAEA), and 4 percent of triethylamine (TEA). Shear tests were made at room temperature and at 250° F. on metal joints bonded with this formulation and certain selected modifications cured for 45 minutes at 180° F. The results are shown in table 1 and gave insight into some of the factors influencing the joint strength of epoxy-resin adhesives at 250° F.

Table 1.--Results of shear tests on metal joints bonded with various epoxy-resin formulations

Formulation of adhesive[1]					Shear strength of metal joint	
PS-1	Glass fiber	DMAEA[2]	TEA[3]	China clay	Room temperature	250° F.
Percent	Percent	Percent	Percent	Percent	P.s.i.	P.s.i.
10	10	4	4	....	2,896	430
10	....	4	4	....	2,600	500
10	....	4	4	50	2,856	640
....	....	4	....	....	2,068	750
....	....	4	....	50	2,392	830
....	....	....	4.5	....	1,550	140

[1]Based on the weight of epoxy resin E-2.

[2]Dimethylaminoethyl alcohol.

[3]Triethylamine.

The original adhesive FPL-828 developed a bond strength of about 430 pounds per square inch at 250° F.; deleting glass fibers from the formulation increased the strength to 500 pounds per square inch; and substituting the 10 percent of glass fibers with 50 percent of china clay increased the bond strength to about 640 pounds per square inch. When the polysulfide elastomer, milled glass fibers, and TEA curing agent were deleted from adhesive FPL-828, an average strength of 750 pounds per square inch was obtained. A formulation employing epoxy resin, DMAEA, and china clay developed a shear strength of 830 pounds per square inch. When TEA was employed alone as curing agent and without further modification of the resin, only 140 pounds per square inch was obtained in shear at 250° F. The results of this work indicated that the strength of the epoxy-resin adhesive at 250° F. was related both to the type of extender or filler employed and to the type of amine employed as curing agent. Further work was undertaken to study the effect of various amine curing agents on formulations employing epoxy resin E-2. These results are described in Part II of the report.

Effect of Method of Cleaning the Metal

A study was made of the effect of different methods of preparing the clad aluminum surfaces for bonding in which adhesive FPL-828 was employed as the bonding agent. The following tabulation shows the effect of different cleaning processes on the shear strength of clad aluminum lap joints at room temperature, after 30 days' immersion in water, and after 7 days' immersion in hydrocarbon fluid. Adhesive FPL-828 was initially cured for 60 minutes at 200° F.

The best adhesion and highest joint strength were consistently obtained on aluminum surfaces that had been cleaned by the sulfuric acid-sodium dichromate process at 140° F. as previously described. Preparing the surfaces by treating with a short dip in either 1-normal hydrochloric acid or 1-normal sodium hydroxide at room temperature was also moderately effective. The aluminum surfaces that had been wiped with ethyl acetate, cleaned with a warm meta-silicate degrease, or heated in a Bunsen burner flame showed very poor adhesive properties. The test after 30-day immersion in water proved to be more severe than either the test after 7-day immersion in hydrocarbon fluid or the dry test made at room temperature immediately after the adhesive was cured.

Table 2.--Effect of method of cleaning metal on strength of clad aluminum lap joints bonded with adhesive FPL-828

Cleaning process	Joint strength					
	At room temperature		After 30-day soak in water		After 7-day soak in hydrocarbon fluid	
	P.s.i.	Percent[1]	P.s.i.	Percent[1]	P.s.i.	Percent[1]
Sulfuric acid-sodium dichromate	3,054	0	2,046	0	2,880	0
Abraded with aluminum oxide cloth	1,770	0	1,092	0	....	....
Ethyl acetate wipe	1,968	80	222	100	....	....
Meta-silicate degrease	1,186	100	512	100	....	....
Sulfuric acid (25 percent solution)	2,130	20	1,176	20	2,040	20
Sodium dichromate (3.3 percent solution)	2,300	20	832	20	2,060	20
Chromic acid (10 percent solution)	2,104	20	1,100	20	2,094	20
Sodium hydroxide (1 Normal)	2,470	0	1,524	10	2,450	0
Hydrochloric acid (1 Normal)	2,510	0	1,966	0	2,530	0
Surface heated with Bunsen burner	1,902	20	350	100	1,992	20

[1]Percent of failure in adhesion to the metal.

Factors Affecting Bend Strength

Only a limited amount of work had been done in the past on effect of variables in adhesive formulation on the bend strength of epoxy-resin adhesives. An investigation of some of the factors affecting the bend strength of aluminum-to-aluminum bonds made with adhesive FPL-828 and several modifications showed that the curing temperature and the type of amine curing agent employed had a marked effect. The results of testing lap joints in flatwise bending over a span of 1.5 inches are shown in table 3.

The results of the bend tests showed that adhesive FPL-828, when cured at room temperature, had low bend strength (108 pounds) but was much stronger when heat-cured for 45 minutes at 180° F. (174 pounds). A comparison of adhesives employing TEA and DMAEA individually as curing agents revealed that the adhesive with DMAEA was superior to the adhesive with TEA curing agent. An adhesive employing tetraethylene pentamine curing agent had very high bend strength (204 pounds) when cured at room temperature, but the bend strength was reduced to 126 pounds with this adhesive when heat-cured.

Table 3.--Results of bend tests on aluminum lap joints made with adhesive FPL-828 and several modifications

Adhesive formulation[1]					Cure		Bend strength
PS-1	Glass fiber	DMAEA[2]	TEA[3]	TEPA[4]	Time	Temperature	
Percent	Percent	Percent	Percent	Percent	Hr.	°F.	Lb.
10	10	4	4	....	96	80	108
10	10	4	4	....	3/4	180	174
10	10	....	5	....	3/4	180	143
10	10	5	....	....	3/4	180	186
10	10	....	....	10	3/4	180	126
10	10	....	....	10	96	80	204

[1]Percent based on weight of epoxy resin E-2.

[2]Dimethylaminoethyl alcohol.

[3]Triethylamine.

[4]Tetraethylene pentamine.

Bonding Titanium Metal

A comparison of results of shear tests on lap joints of 24S-T3 clad aluminum alloy and of type RC-70 titanium bonded with FPL-828 adhesive is shown in table 4. Both of the metals had been prepared for bonding by treatment with the sulfuric acid-sodium dichromate solution, but a marked difference existed in the degree of adhesion obtained with the adhesive on the two metals. These data are further evidence that the adhesion of epoxy resins to metals is readily affected by the type of metal and the method of surface preparation.

Table 4.--Shear strength of 24S-T3 clad aluminum alloy and type RC-70 titanium bonded with adhesive FPL-828

Metal	Cure		Shear strength at room temperature	
	Time	Temperature		
	Hr.	°F.	P.s.i.	Percent[1]
Clad aluminum	96	80	1,640	0
Clad aluminum	3/4	180	2,770	0
Titanium	144	80	608	100
Titanium	3/4	180	832	100

[1] Percent of failure in adhesion to the metal.

PART II - ADHESIVE FORMULATIONS OF EPOXY RESIN AND AMINES

Effect of Different Amines

The results of the previous work on adhesive formulations employing epoxy resin E-2, polysulfide elastomer PS-1, and amine curing agent (Part I) indicated that the amine curing agent had a significant effect on the strength of bonded joints at 250° F. In the work undertaken to study the effect of the different amine curing agents, 14 related amines employed in equal molar amounts were used individually as curing agents for epoxy resin E-2, without further modification with fillers or other components. This work was done to gain a better understanding of the effect of the molecular structure of the amine on the rate of cure of the adhesive and on the degree of crosslinking obtained, as would be measured by the bond strength of the adhesive at 180° and 250° F. The mol ratio of epoxy resin E-2 to amine was 6.2 to 1 for each formulation. The bonds of the various formulations were cured at room temperature and for 60 minutes at 200° F. and the results of lap shear tests at 80° F., 180° F., and 250° F., made immediately after glue lines reached these temperatures, are given in table 5.

It was shown by these tests that, as the ethanol groups of triethanolamine were replaced with methyl groups, as in the methyl (No. 4) and dimethylethanolamine (No. 5), the reactivity of the amine with the resin was sharply increased (as evidenced by decrease in pot life) and the strength of the joints at 250° F. was increased. When the ethanol groups were replaced with ethyl groups, as in diethylethanolamine (No. 10), the reactivity and thermal strength was increased over that of triethanolamine but not to the extent that was obtained with methyl substitution (No. 5). Replacement of the ethanol groups in triethanolamine with hydrogen (Nos. 1 and 2) resulted in the formation of unreactive adhesives.

Table 5.--The effect of equal molar amounts of various amine curing agents for epoxy resin E-2 on the strength properties of aluminum-to-aluminum bonds

Amine	Amount of amine[1]	Pot life at 75 - 80° F.	Cure: Time	Cure: Temperature	Average shear strength: At 80° F.	Average shear strength: At 180° F.	Average shear strength: At 250° F.
	Percent	Hr.	Hr.	°F.	P.s.i.	P.s.i.	P.s.i.
1. Monoethanolamine	2.74	......	.....	.....	(2)	(2)	(2)
2. Diethanolamine	4.72	......	.....	.....	(2)	(2)	(2)
3. Triethanolamine	6.7	......	.....	.....	(2)	(2)	(2)
4. Methyldiethanolamine	5.35	16	216	80	830	670	316
Do.	5.35	......	1	200	2,312	1,750	458
5. Dimethylethanolamine	4.0	5	.....	.....	1,190	656	234
Do.	4.0	......	1	200	2,070	2,628	1,034
6. Methyl morpholine	4.55	24+	216	80	758	314	120
Do.	4.55	......	1	200	546	470	176
7. N-hydroxyethyl morpholine	5.9	......	.....	.....	(2)	(2)	(2)
8. N-aminopropyl morpholine	6.48	......	.....	.....	(2)	(2)	(2)
9. Triethylamine	4.55	12+	216	80	816	410	166
Do.	4.55	......	1	200	1,550	400	142
10. Diethylethanolamine	5.26	30	216	80	462	690	210
Do.	5.26	......	1	200	1,894	616	238
11. Diethylaminopropylamine	5.85	6	216	80	240	330	246
Do.	5.85	......	1	200	2,464	2,278	490
12. Monoisopropanolamine	3.37	......	.....	.....	(2)	(2)	(2)
13. Dimethylisopropanolamine	6.0	12	216	80	1,140	498	184
Do.	6.0	......	1	200	2,504	2,130	608
14. Dimethyl benzylamine	6.0	5	216	80	1,024	466	62
Do.	6.0	......	1	200	2,744	2,400	544

[1] Based on the weight of epoxy resin E-2.

[2] Did not cure at 80° or 200° F.

When the two ethanol groups of methyldiethanolamine (No. 4) were linked together by oxygen, as in an ether ring compound known as methylmorpholine (No. 6), the reactivity at room temperature was reduced and the strength of the joints at 250° F. was decreased. If the methyl group in methylmorpholine was replaced with either an ethanol group (No. 7) or an N-propylamine group (No. 8), the change resulted in the formation of unreactive materials. Diethylaminopropylamine (No. 11), on the other hand, which differs from N-aminopropyl morpholine (No. 8) in that its two ethyl groups are not linked together by oxygen, was significantly more reactive and developed a bond with appreciable heat resistance, whereas N-aminopropyl morpholine did not even cure. The particular catalytic effect of methyl groups in the amine was further shown by the shorter pot life and greater strength at 250° F. of a formulation with dimethylisopropanolamine (No. 13) over that with monoisopropanolamine (No. 12). The relative effectiveness of another dimethyl tertiary amine is shown by the results obtained with dimethyl benzylamine (No. 14). This study of the effect of the chemical structure of the amine curing agents on the reactivity with epoxy resin and the ultimate resistance of the adhesives to heat at 250° F. has shown that methyl groups attached to the nitrogen appear to enhance the rate of cure and also increase the degree of cross linkage of the resin. This results in improved thermal properties of the adhesive at 250° F. and indicates that trimethylamine is one of the most promising curing agents for epoxy resins--probably superior to triethylamine (No. 9). Unfortunately, trimethylamine, being a gas, cannot be employed practically in adhesive bonding operations. These findings, however, do confirm an earlier observation, arrived at more empirically, that dimethylaminoethyl alcohol (DMAEA) is a very promising curing agent.

Effect of Varying Amounts of DMAEA

The rate of setting of epoxy resin E-2 and the strength properties of bonded aluminum joints were found to be dependent to great degree on the amount of dimethylaminoethyl alcohol (DMAEA) employed as curing agent. Table 6 presents the data on pot life and shear strength of lap joints at 80°, 180°, and 250° F. when the DMAEA content was varied from 3 to 25 percent of the weight of the resin, and bonds were initially cured for 60 minutes at 200° F.

The results of these tests show that the pot life of the adhesive is shortened progressively as more DMAEA is employed, and that the shear strength of bonded lap joints at 80° F. is increased with an increase in DMAEA, reaching a maximum at 15 percent. The strength of joints at 180° F., however, increases with increasing percentages of DMAEA only to 6 percent, thereafter decreasing as greater amounts of DMAEA are used. The shear strength of joints at 250° F. also increases with increasing amounts of DMAEA up to 6 percent but decreases very significantly with greater quantities.

Table 6.--Pot life of adhesive and shear strength of bonds in aluminum made with epoxy-resin formulations containing various amounts of DMAEA[1]

DMAEA content	Pot life at 75-80° F.	Average shear strength at: 80° F.	180° F.	250° F.
Percent	Hr.	P.s.i.	P.s.i.	P.s.i.
3	6	2,130	1,800	760
4	4	2,144	2,286	950
5	3	2,220	2,975	960
6	2	2,232	3,120	1,122
8	1-1/2	2,096	2,220	416
15	1	3,040	1,836	460
20	3/4	2,624	464	162
25	1/2	2,872	682	324

[1]Dimethylaminoethyl alcohol.

On the basis of these results, 4 percent of DMAEA appeared to be the most promising amount because of the pot life of 4 hours and generally good strength properties.

Effect of Cure Temperature

The shear strength of lap joints at 80° and 250° F. bonded with a formulation of epoxy resin E-2, with 4 percent of DMAEA was higher when bonds were cured at temperatures of 200° to 250° F. for 1 hour than when cured at room temperature. Postcuring this adhesive, particularly at 450° F. for 1 hour after a 250° F. cure, appeared to increase the strength of bonds at 80° F. but decreased it at 250° F., as shown in table 7.

Table 7.--Effect of various curing and post-cure temperatures on shear strength of aluminum lap joints bonded with epoxy resin E-2 containing 4 percent of DMAEA[1]

Cure conditions		Post-cure conditions		Average shear strength	
Time	Temperature	Time	Temperature	80° F.	250° F.
Hr.	°F.	Hr.	°F.	P.s.i.	P.s.i.
336	80	.....	....	1,742	350
1	200	.....	....	2,296	950
1	250	.....	....	2,176	1,075
1	250	1	320	2,230	890
1	250	1	450	2,710	580

[1]Dimethylaminoethyl alcohol.

Effect of Various Chemicals Employed as Catalysts

Table 8 presents the results of tests on an adhesive formulation of epoxy resin E-2 with 4 percent of dimethylaminoethyl alcohol (DMAEA) and combining small amounts of various chemicals that were employed as possible catalysts for the reaction of DMAEA with the resin at 200° F. Resorcinol, at a concentration of 1 percent, appeared to be the only one of the chemicals investigated that increased the strength of the bonds at 250° F. without seriously reducing the pot life of the adhesive. The bonds were initially cured for 60 minutes at 200° F.

Effect of Filler

The effect of modifying the adhesive composed of E-2 resin and 4 percent of DMAEA curing agent with milled glass fibers and china clay is shown in table 9 when bonds were cured for 60 minutes at 200° F. Both fillers increased the shear strength at 250° F. slightly over that obtained without filler. When 50 percent of china clay was employed in a formulation also containing 1 percent of resorcinol, the shear strength of bonded joints at 250° F. averaged 2,000 pounds per square inch. This adhesive, denoted as FPL-866 and composed of epoxy resin E-2 with 4 percent of DMAEA, 1 percent of resorcinol, and 50 percent of china clay, was considered the most promising adhesive formulation developed in this year's work.

Table 8.--Effectiveness of various chemicals as catalysts for DMAEA[1] reaction with epoxy resin E-2, as evidenced by shear strength of bonds in aluminum lap joints

Catalyst	Amount of catalyst	Pot life	Average shear strength	
			Room temperature	250° F.
	Percent	Hr.	P.s.i.	P.s.i.
None	....	4	2,144	950
Water	1	4	1,480	645
Resorcinol	1	4	2,110	1,245
Ethanolamine	1	3	1,510	530
Do.................	2.74	1-1/2	2,292	952
Triethanolamine	1	4	1,630	630
Do.................	6.7	3	2,568	710
Dimethyl hydroresorcinol	1	4	1,700	630
Dimethyl glyoxime	1	4	1,880	790
Sodium dichromate	1	4	1,600	680
Chromic acid	1	4	1,600	740
Boron trifluoride (phenol complex)	1	4	180	860
Benzoyl peroxide	1	4	1,770	680

[1]Dimethylaminoethyl alcohol.

Table 9.--Effect of glass fiber or china clay filler on formulations of epoxy resin E-2, as evidenced by shear and bend strength of adhesive bonds in aluminum lap joints

China clay	Glass fiber	Resorcinol	Bend strength	Shear strength	
				80° F.	250° F.
Percent	Percent	Percent	Lb.	P.s.i.	P.s.i.
....	....	....	177	2,070	1,035
....	10	....	152	2,340	1,170
50	....	....	155	1,980	1,260
50	....	1	....	2,320	2,000

PART III - ADHESIVE FORMULATIONS OF EPOXY RESIN, RESORCINOL, AND HEXAMETHYLENETETRAMINE

The strength of the epoxy-resin adhesives at 250° F. was improved by formulations of resin that contained resorcinol and hexamethylenetetramine (hexa) and without other amine curing agents. In this type of adhesive the resorcinol and hexa presumably react with heat in the presence of the epoxy resin to form a resorcinol-formaldehyde resin cross-linked with the epoxy resin to form a thermosetting and heat resistant type of bond. In this study, epoxy resin E-2 was modified with several different phenolic-type compounds, of which resorcinol was the most effective and promising. Varied amounts of resorcinol and hexa were studied, and the results of these tests are shown in table 10, which presents the data on shear tests on aluminum lap joints tested at 80° and 250° F. after an initial cure of 60 minutes at 200° F.

An adhesive formulation employing 20 percent of resorcinol based on the weight of the epoxy resin, with sufficient hexa added to give a mol ratio of 2.5 mols of formaldehyde per mol of resorcinol, developed the highest immediate strength at 250° F. (2,095 pounds per square inch) and was even higher in strength at 250° F. (2,940 pounds per square inch) after a post-cure of 20 minutes at 320° F. A further evaluation of the adhesive with 2.5 mols of formaldehyde per mol of resorcinol, designated as FPL-852, was made immediately at temperatures from -70° to 400° F. after a cure of 60 minutes at 200° F., with the following strength results:

Test temperature	Shear strength
°F.	P.s.i.
-70	1,388
80	1,940
180	2,440
250	2,095
300	2,154
350	694
400	366

These tests revealed that adhesive FPL-852 possessed improved resistance to thermal softening up to 300° F. The adhesive, however, possessed several undesirable limitations. When allowed to cure at 80° F., it was extremely brittle and had no measurable strength; and it had a pot life of only about 1 hour.

In other work to correct the limitations of adhesive FPL-852, a study was made of the effect of certain amine curing agents, such as triethylamine, dimethylaminoethyl alcohol, or diethylaminoethyl alcohol, which were known to cure the epoxy resin at room temperature. The work on amine curing agents revealed that the pot life of the adhesive could be extended slightly without sacrificing strength at 250° F. in a few cases, but the adhesive failed to develop any appreciable strength when cured at 80° F.

Table 10.--Effect of various amounts of resorcinol and hexamethylenetetramine in epoxy resin on shear strength of adhesive bonds in aluminum lap joints

Percentage of resorcinol[1]	Mol ratio of formaldehyde to resorcinol[2]	Shear strength		
		Room temperature	250° F.	250° F. after postcure[3]
		P.s.i.	P.s.i.	P.s.i.
5	1.0	160	....	....
5	1.5	120	....	....
5	2.0	600	140	130
5	3.0	1,620	380	810
10	1.0	(4)	(4)	(4)
10	1.5	760	450	1,320
10	2.0	710	390	1,320
10	2.5	1,140	800	2,430
15	1.0	(4)	(4)	(4)
15	1.5	1,000	600	1,400
15	2.0	1,600	940	2,170
15	2.5	2,050	980	2,080
20	1.0	1,400	100	1,110
20	1.5	1,000	420	2,480
20	2.0	1,990	1,067	2,800
20	2.5	1,860	2,095	2,940

[1]Percent by weight based on the weight of E-2 resin.

[2]Formaldehyde added in the form of hexamethylenetetramine in 45 percent solution in water.

[3]Postcure of 20 minutes at 320° F.

[4]Broke in sawing.

Effect of Modification with Polysulfide Elastomer

When various polysulfide elastomers were added to adhesive FPL-852, the shear strength of bonds cured at 80° F. was greatly improved, and the strength of joints at 250° F. was only slightly reduced when bonds were cured for 60 minutes at 200° F. Polysulfide elastomer greatly improved bend strength also. The pot life of the polysulfide-modified formulation was not materially different from that of FPL-852. The most promising of the polysulfides investigated was PS-3. An adhesive designated as FPL-852a, which contained 20 percent of PS-3 based on the weight of the epoxy resin, was most promising. The results of bend and shear tests at 80° and 250° F. on joints bonded with FPL-852a and FPL-852 are shown in table 11.

Table 11.--Results of bend and shear tests on aluminum lap joints bonded with epoxy-resin adhesives modified with polysulfide elastomers

Adhesive	Polysulfide (PS-3)	Cure		Shear strength		Bend strength
		Time	Temperature	80° F.	250° F.	
	Percent	Hr.	°F.	P.s.i.	P.s.i.	Lb.
FPL-852a	20	192	80	1,080	450	104
Do.....	20	1	200	2,060	1,785	138
FPL-852	0	192	80	(1)	(1)	....
Do.....	0	1	200	1,860	2,095	44

[1]Broke in handling.

Comparison of Strength Properties of FPL Adhesives

A summary of the strength properties of bonds of aluminum to aluminum made with adhesives FPL-828, FPL-852a, and FPL-866, when cured at 80° F. and at 200° F., is presented in table 12 along with data obtained under similar conditions on the commercially available epoxy-resin adhesive CA-12 now currently being widely evaluated for the aircraft industry. As shown by these results, adhesives FPL-828 and FPL-866, in particular, developed higher shear strength at -70° F. and 80° F. and greater bend strength than adhesive CA-12 when bonds are cured initially at room temperature. When the bonds were cured initially at 200° F. for 60 minutes, adhesive CA-12 was generally superior to adhesive FPL-828, FPL-852a, and FPL-866 in shear strength at -70° and 80° F. and in bend strength. In tests conducted at 250° F., however, adhesives FPL-852a and FPL-866 were noticeably superior to CA-12 when heat-cured. The results obtained with adhesive FPL-866 cured at 200° F. were particularly interesting in that this adhesive had uniformly high shear strength at temperatures from -70° to 250° F.

Table 12.--Shear and bend strength of aluminum lap joints bonded with various Forest Products Laboratory epoxy-resin formulations and commercial formulation CA-12

Adhesive	Cure		Shear strength				Bend strength
	Time	Temperature	-70° F.	80° F.	180° F.[1]	250° F.[1]	
	Hr.	°F.	P.s.i.	P.s.i.	P.s.i.	P.s.i.	Lb.
FPL-828	192	80	2,230	1,660	1,450	220	108
FPL-852a	192	80	625	1,080	350	450	104
FPL-866	192	80	1,300	1,680	1,180	400	132
CA-12	192	80	600	790	....	500	73
FPL-828	1	200	2,180	2,895	3,744	436	174
FPL-852a	1	200	1,635	2,060	2,260	1,785	138
FPL-866	1	200	3,010	2,320	2,850	2,000	155
CA-12	1	200	3,140	2,940	....	930	203

[1]Tests were made immediately after the specimens reached the desired temperature which was attained in 3 to 5 minutes in the test chamber.

Summary of Formulation Variables Affecting Epoxy-resin Adhesive Performance

The effect of different adhesive components and modifiers on the use characteristics and strength properties of epoxy-resin adhesives employing epoxy resin E-2 as the base resin, which have been investigated in the course of the work for the Bureau of Aeronautics, may be summarized generally as follows:

(1) Adhesive formulations employing primary and secondary amine curing agents, such as ethylene diamine, tetraethylenepentamine, and other polyethylene amines, have the following characteristics:

- (a) Exothermic reaction and short pot life.
- (b) High shear strength at room temperature when cured at room temperature.
- (c) High bend strength at room temperature.
- (d) Low strength properties at 180° F. and higher--depends on amount of amines.
- (e) No appreciable advantage in heat-curing.

(2) Adhesive formulations employing a tertiary amine curing agent such as dimethylaminoethyl alcohol have the following general characteristics:

(a) Slightly exothermic reaction and moderate pot life.
(b) Moderate strength properties when cured at room temperature.
(c) High shear strength at room temperature and at 180° F. and good bend strength when heat-cured.
(d) Excellent resistance to creep and long-time strength at 180° F. (see fourth progress report[2]).
(e) Moderate shear strength at 250° F.
(f) Good resistance to immersion in water and aromatic fluids.

(3) The use characteristics and strength properties of the adhesive vary widely, depending upon the amount and type of amine curing agent employed.

(4) The use of polysulfide elastomer as a modifier in the adhesive results in:

(a) Increased shear strength at room temperature.
(b) Increased peel resistance.
(c) Decreased shear strength at elevated temperature.
(d) Decreased long-time strength at elevated temperature.
(e) Decrease in pot life.
(f) Reduced brittleness.

(5) Modification of the adhesive with reactive diluents, such as allyl glycidyl ether, results in:

(a) Improved spreadability.
(b) Increased strength at room temperature.
(c) Reduced strength at elevated temperature.
(d) Reduced resistance to creep and long-time strength at elevated temperatures.
(e) Reduced brittleness.

(6) Modification of epoxy resin with resorcinol reduces pot life and increases brittleness and strength at elevated temperature.

(7) Modification of epoxy resin with resorcinol and hexamethylenetetramine results in:

(a) Short pot life.
(b) Increased brittleness.
(c) An adhesive requiring a cure at an elevated temperature.
(d) Increased strength at elevated temperature.

(8) Modifying the adhesive with milled glass fibers has the following effects:

(a) Reduces brittleness.
(b) Increases shear strength at 80° and 180° F.
(c) Reduces spreadability.
(d) Reduces shear strength at -70° F.

(9) Modifying the epoxy-resin adhesives with domestic china clay increases shear strength at -70°, 80°, 180°, and 250° F.

(10) Curing the epoxy-resin adhesives at an elevated temperature improves joint strength properties except when the polyethylene amines are employed as curing agents.

(11) Based on rather limited tests, epoxy-resin adhesives seem to have inferior adhesion to metals unless the metal is carefully prepared for bonding by a chemical process. The sodium dichromate-sulfuric acid process was consistently superior to other methods on clad aluminum alloy.

(12) At the present time there seems to be no single epoxy-resin adhesive formulation that has all the desirable use characteristics and strength properties required in aircraft constructions for both a room-temperature-setting and elevated-temperature-curing adhesive.