

## Effect of Polarity of Bisphenol A Epoxy Resins on Adhesion at Cryogenic and Elevated Temperatures

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### Synopsis

Substituted bisphenol A epoxy resins have been prepared with substituents on the aromatic ring varying in polarity. The substituent effect on adhesion at cryogenic and elevated temperatures has been determined and shown to be of minor importance as compared to the epoxy content. The adhesives were evaluated on aluminum and stainless steel for tensile shear strength over the temperature range of  $-320^{\circ}$  to  $+400^{\circ}$ F. and in one case at  $-453^{\circ}$ F.

### INTRODUCTION

During the course of investigating epoxy resins for their effectiveness as cryogenic adhesives which also show good elevated temperature properties, it was of interest to explore the use of substituted bisphenol epoxy resins for this purpose.

In the literature there appeared no systematic study of bisphenol epoxy resins as cryogenic adhesives. However, Erich and Bodnar<sup>1</sup> had reported a preliminary investigation of the effect of molecular structure on the mechanical properties of epoxy resins which left many questions unanswered. It was not clear from their work what the epoxy content of each material was. In addition the adhesives were tested only at  $73.5$  and  $160^{\circ}$ F.; nevertheless, Erich and Bodnar showed that a decrease in shear strength is obtained at  $160^{\circ}$ F. when the methyl groups in bisphenol A are replaced by increasingly longer aliphatic chains. These correlations would have been more meaningful had they all been related in some way to their epoxy content.

The object of this investigation was to compare the effect of polarity of substituted bisphenol epoxy resins with the epoxy content of these resins as factors in adhesion to aluminum over the temperature range from  $-320^{\circ}$ F. to  $+400^{\circ}$ F. The curing agent used was 4,4'-diaminodiphenylmethane.

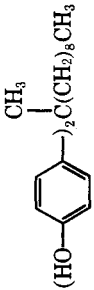
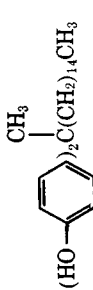
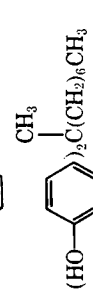
### EXPERIMENTAL

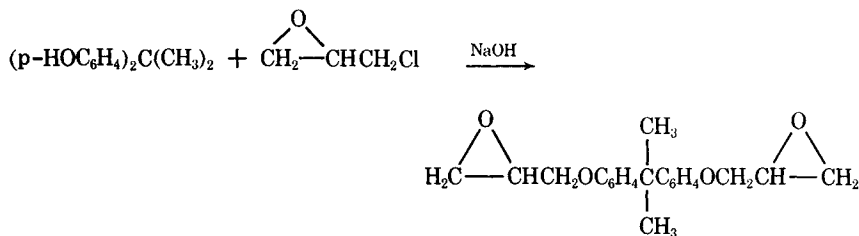
#### Synthesis

Epoxy resins were prepared by a procedure<sup>2</sup> known to produce compounds of low molecular weight and high epoxy content.

TABLE I  
Preparation of Epoxy Resins

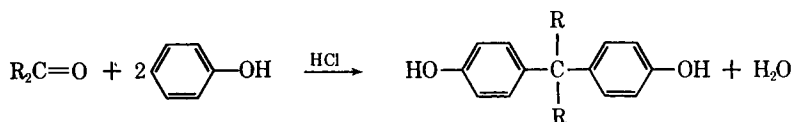
Sample no.	Starting material	Product	Yield, %	Epoxy content	
				Calcd.	Found
428-48	1,1,3-Tri(4-hydroxyphenyl)propane	Amber viscous liquid	86	0.613	0.439
428-86	1,1-Bis-(4-hydroxyphenyl)cyclohexane	Tan soft solid	85	0.510	0.355
409-142	1,1-Di(4-hydroxyphenyl)-4-methylcyclohexane	Yellow viscous liquid	76	0.508	0.452
391-98	Tetrachlorobisphenol A	Amber liquid	93	0.418	0.361
391-139	Tetrabromobisphenol A	Brown syrup	71	0.305	0.302
391-141	2,2-Methylenebis(4-ethyl-6- <i>tert</i> -butyl)-phenol	Brown soft solid	39	0.417	0.162
409-11	2,2-Bis(4-hydroxy-3-methylphenyl)butane	Amber viscous liquid	91	0.524	0.427
409-59 (409-13)	2,2-Bis(4-hydroxy-3,5-dimethylphenyl)-propane	Amber viscous liquid	100	0.505	0.422
409-53	2,2-Bis(4-hydroxy-3-methylphenyl)propane	Amber viscous liquid	100	0.543	0.485

409-70	Bisphenol A					
409-110	Bis(4-hydroxyphenyl) sulfone			Amber viscous liquid	89	0.588
409-115	Bis(4-hydroxyphenyl) ether			Brown solid	41	0.552
409-117	2,2-Bis(4-hydroxy-3,5-dibromophenyl)-hexafluoropropane			Tan solid	100	0.641
				Solid, m.p. 28-29°C.	65	0.261
409-118	2,2-Bis(4-hydroxyphenyl)- <i>sym</i> -tetrafluoro-dichloropropane			Amber syrup	83	0.417
428-5				Amber viscous liquid	64	0.372
428-7				Amber viscous liquid	74	0.441
428-29				Amber viscous liquid	87	0.472



The bisphenol compound (1.0 mole), epichlorohydrin (10.0 mole), and 5 ml. of water were mixed in a resin kettle fitted with a stirrer, condenser, and thermometer. Solid NaOH (2.05 mole) was added in six or seven small portions. After the first addition, the flask was heated and cooled alternately as required, while the NaOH additions were made, the pot temperature being maintained between 95 and 100°C. After the final addition, no further cooling was applied. When the exotherm had subsided, the epichlorohydrin was distilled off under vacuum (50 mm.) until the temperature in the flask reached 150°C. To the residue, cooled to 70°C., was added 50 ml. of benzene. The precipitated salt was filtered out and washed with 50 ml. of benzene. The benzene solutions were distilled until the temperature in the flask reached 125°C. and then the distillation was continued at 5 mm. until the temperature reached 170°C. The results are summarized in Table I.

Bisphenols were prepared by the reaction of the ketone with phenol according to the procedure described by Erich and Bodnar<sup>1</sup> from aliphatic ketones.

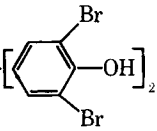
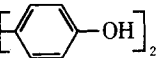


A typical preparation is the synthesis of 1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane starting with 1 mole of 4-methylcyclohexanone and 4 moles phenol in the presence of 40 g. calcium chloride, 4 g. hydrochloric acid, and 3 ml.  $\beta$ -mercaptopropionic acid. The reactants were stirred at 110°C. for 4½ hr. and then allowed to stand overnight. The reaction mixture changed color going from yellow to red. The excess phenol was carefully distilled and the residue dissolved in hot toluene. The hot toluene was filtered, decolorized, concentrated and cooled to give 74 g. (25%) of a solid, m.p. 156–164°C. A sample on recrystallization melted at 166–170°C.

ANAL. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_2$ : C, 80.8%; H, 7.85%. Found: C, 81.09%; H, 7.88%.

The analysis of some new bisphenol A compounds are listed in Table II.

TABLE II  
Analysis of Bisphenol Derivatives\*

Sample no.	Bisphenol	C, %		H, %	
		Calcd.	Found	Calcd.	Found
409-117	$(F_3C)_2C$ —  _2	27.64	28.13	0.93	0.99
409-118	$(F_2ClC)_2C$ —  _2	48.83	49.03	2.74	2.83

\* These compounds were provided by the courtesy of Mr. Strickling of the General Chemical Research Laboratory, Allied Chemical Corporation, Morris Township, New Jersey.

### Physical Testing

The physical testing data are presented in Table III. In most cases the adhesives were tested at 73, 250, 400, and  $-320^{\circ}F$ . by use of 0.064 in. thick Alclad aluminum 2014-T6, Federal Specification QQ-A-255. Some adhesives were tested on No. 321 stainless steel, 0.064 in. thick, Federal Specification QQ-S-766. The stainless steel and aluminum were etched according to the procedure described below. Panels used were  $1 \times 3 \times 0.064$  in.

### Preparation of Metal Surfaces for Bonding

#### *Scrubbing*

All visible dirt and markings were removed by rubbing the metal with a cloth dipped in acetone. The panels were handled with clean rubber gloves or forceps.

#### *Degreasing*

The scrubbed panels were suspended by small clips from a rod which was mounted about 2 in. above the surface of gently boiling trichloroethylene. The panels were kept in the vapor bath for 10 min. (minimum) and stored in a wide-mouthed container of distilled trichloroethylene.

#### *Etching*

The degreased panels were removed individually with forceps from trichloroethylene and laid on paper towels to air-dry. When the surfaces appeared dry, the panel was turned over and placed on a fresh towel.

**Aluminum.** The etching solution was made up as follows: potassium or sodium dichromate, 10 g.; distilled water, 300 ml.; concentrated sulfuric acid, 100 g. (54.5 ml.). The dichromate was added to the water and

stirred until most of the salt was dissolved. The acid was added very slowly with stirring. Stirring was continued until all the solid was dissolved. The solution was poured into a Pyrex dish approximately 6 in. in diameter and 3 in. high and warmed on a hot plate to 70°C.

The dry panels were placed in the bath by leaning them at a small angle against the wall of the dish so that at least  $\frac{3}{4}$  in. of the metal was immersed in the bath. The temperature, which usually dropped a few degrees when the metal was placed in the bath, was maintained at 66–68°C. The dish described accommodated 14–20 panels. After 10 min., the panels were removed with forceps and dropped into a beaker of water. The panels were rinsed at least five times with tap water, then rinsed individually with distilled water and laid on clean paper towels to air dry. After most of the water had been absorbed, the panels were turned over onto clean towels and used as soon as they appeared dry. They were used within 3 hr. The etching bath was used for no more than 60 panels.

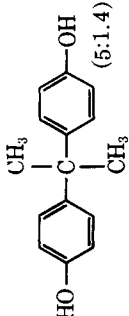
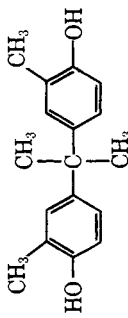
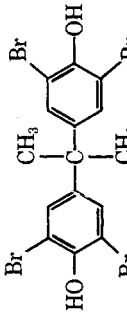
**Stainless Steel.** The etching solution was made up as follows: concentrated hydrochloric acid, 262.0 ml.; orthophosphoric acid, 27.5 ml.; hydrofluoric acid, 13.2 ml. The phosphoric acid was added to the hydrochloric acid with stirring, then the hydrofluoric acid was stirred in and the solution was transferred to a Pyrex dish, approximately 6 in. in diameter, and 3 in. high. The dish was heated on a hot plate to 82°C. Boiling occurred and subsided before this temperature was reached.

The dried panels were placed in the bath so that at least  $\frac{3}{4}$  in. was immersed in the solution (see procedure for aluminum). At the end of 2 min., the panels were removed and rinsed as described in the procedure for aluminum. If a carbon residue was visible on the etched portion of the stainless steel panels after rinsing, they were immersed for 10–15 sec. in a 10% nitric acid bath and rinsed thoroughly with distilled water.

The adhesive was prepared by adding the melted curing agent to the resin (solid resins were first liquefied) and stirring the mixture thoroughly. Generally, 5.0 g. resin was treated with the theoretical equivalent of curing agent, calculating one epoxide group equivalent to one active (amine) hydrogen. The adhesive was applied with a spatula to both etched surfaces to be bonded. One panel was placed on a jig designed to allow 0.50 in. overlap of 1 × 3 in. panels. The second panel was put in place and the 0.50 in. bonded area was clamped at each edge with a small spring clip.

The samples were cured at 100°C. for 2 hr., unless otherwise specified, and equilibrated before testing for 7 days at room temperature (73°F.) in a constant temperature-humidity room. The tensile shear strength was determined by using a Tinius Olsen Electromatic universal testing machine. The cryostat was obtained from Hofman Laboratories, Inc., Newark, New Jersey. It is a stainless steel Dewar flask having the dimensions 20 $\frac{3}{4}$  in. height, 7 $\frac{1}{4}$  in. outside diameter, 18 in. inside depth, and 6 in. inside diameter. It is constructed with a copper heat radiation shield between the inner and outer walls. The Dewar is evacuated to about  $2 \times 10^{-6}$  mm. Hg by connecting it to the high vacuum system of a Kinney

TABLE III  
Epoxy Resins Cured with an Equivalent of 4,4'-Diaminodiphenylmethane (MDA)\*

Com- pound no.	Sample no. of epoxy resin	Structure of starting bisphenol	Tensile shear strength, psi							
			Epoxy content found		Aluminum		Stainless steel			
			-453° F.	-230° F.	73°F. F.	250°F. F.	73°F. F.	250°F. F.		
1	Epon 826	 (5:1.4)	0.542	2795	3630	2170	1754	4300	2850	2052
2	Epon 828 or DER 822 <sup>b</sup>	Same as above	0.518	—	4200	2610	1804	4070	2690	1931
3	Epon 830	Same as above	0.500	—	4270	2310	1685	3160	2420	1258
4	409-53		0.485	—	3570	1478	351	3000	1757	1549
5	391-139		0.302	—	680	1391	557	864	1005	~0

(continued)

TABLE III (continued)

Com- pound no.	Sample no. of epoxy resin	Structure of starting bisphenol	Epoxy content found	Tensile shear strength, psi						
				Aluminum			Stainless steel			
				-453° F.	-230° F.	73°F.	250°F.	73°F.	250°F.	
6	391-141		0.162	—	0	0	0	0	0	
7	409-11		0.427	—	3510	2890	850	2200	1800	1660
8	409-13		0.422	—	2680	2240	943	462	645	227



9	409-117		0.235	—	1143	1330	1799	1325	1577	1605
10	409-118		0.336	—	1950	1867	959	3120	2580	352
11	409-115		0.532	—	3910	1736	564	—	—	—
12	409-142		0.452	—	4800	3490	2079	3870	2350	2095

<sup>a</sup> The epoxy resins were cured with the calculated equivalent of 4,4'-diaminodiphenylmethane (methylenedianiline) and the results are the average of three determinations.

<sup>b</sup> Tensile shear strength on aluminum at 400°F. is 556 psi and on stainless steel 547 psi.

evaporator, Model KSE-2. All internal surfaces facing the vacuum are gold plated. The liquid nitrogen was added to the cryostat which was used in conjunction with the Timuis Olsen Electomatic universal testing machine.

## RESULTS AND DISCUSSION

The bisphenols listed in Table I were converted to diglycidyl ethers by means of epichlorohydrin and sodium hydroxide as described in the experimental section. The resulting products are shown in Table I along with their epoxy contents, calculated and analytically found. In some cases the experimentally obtained epoxy contents are close to those calculated. The discrepancy in values is probably due to the nature of the synthesis such that some polycondensation takes place via the glycidyl group to give higher molecular weight resins.

The physical testing results are listed in Table III, where tensile shear strengths on aluminum are reported from  $-320$  to  $+250^{\circ}\text{F}$ . in most cases, with some results also listed at  $-453^{\circ}\text{F}$ .

Examination of these results indicates that the tensile shear strength at  $-320^{\circ}\text{F}$ . increases with epoxy content of the starting resins, regardless of the nature of the polar groups as in the halogenated resins numbered 5, 9, 10, and tetramethyl bisphenol A resin, number 8. The results are plotted in Figures 1A and 1D as tensile shear strength, psi, at  $-320^{\circ}\text{F}$ . versus epoxy content for aluminum and stainless steel test specimens. The results at 73 and  $250^{\circ}\text{F}$ . for aluminum are shown in Figure 1B and 1C. For stainless steel the results at  $-320$ , 73, and  $250^{\circ}\text{F}$ . are shown in Figures 1D, 1E, and 1F. From Figure 1 it is seen that polarity of the molecule is not as important as epoxy content. It was expected that compound 9 would deviate greatly.

In Figure 2 the plot of theoretical epoxy content against the theoretical tensile shear strengths obtained by extrapolation indicates that even compound 9 does not deviate. The correlations for all the epoxy compounds do not give straight lines for stainless steel; the values are more scattered.

The presence of alkyl groups appears also not to have a significant effect on increasing the tensile shear strength values other than giving values expected from their epoxy contents. Removing the alkyl bridge from the bisphenols as in compound number 7 (4,4'-dihydroxydiphenyl ether) gives no marked change.

The preparation of bisphenol epoxy resins with long chain aliphatic groups (428-7 in Table III) gave a drastic reduction in the adhesive strength at  $73^{\circ}\text{F}$ . It was hoped that the long hydrocarbon chain would flexibilize the adhesive and increase its adhesive strength at  $-320^{\circ}\text{F}$ . It is possible that a more polar chain (polyether type) would be more effective in giving adhesion to aluminum. The adhesive strength of DER 332 was decreased by the use of 20% 428-5 in it. However, replacing the propane bridge in

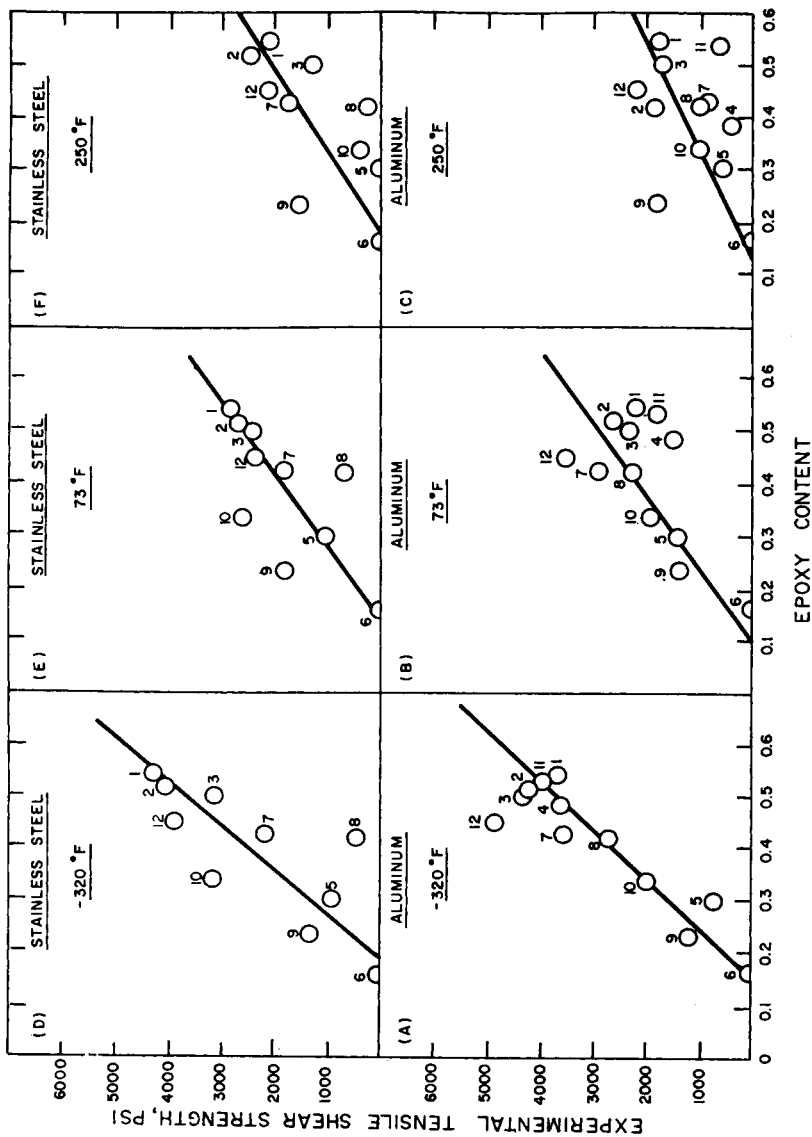


Fig. 1. Tensile shear strength vs. epoxy content for substituted bisphenol A epoxy resins evaluated on aluminum and stainless steel. (See Table III for the definition of the numbered compounds.)

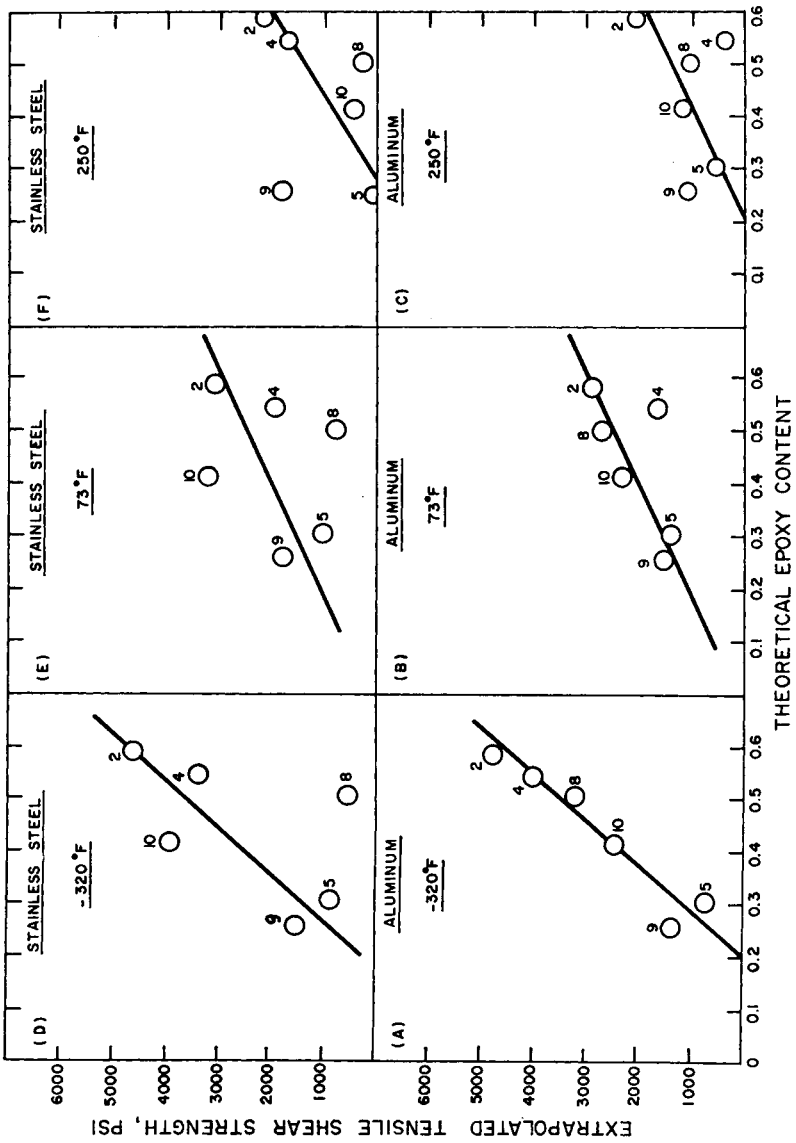
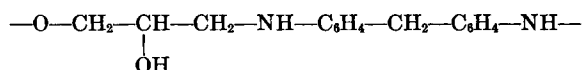


Fig. 2. Extrapolated theoretical tensile shear strengths vs. the theoretical epoxy contents for substituted bisphenol epoxy resins evaluated on aluminum and stainless steel at  $-320^{\circ}\text{F}$ ,  $73^{\circ}\text{F}$ , and  $250^{\circ}\text{F}$ . (See Table III for the definition of the numbered compounds.)

the biphenols by a cyclohexyl group (compound number 12) appeared to increase the tensile shear strength at all temperatures.

It does not appear that the tensile shear strength of the diglycidyl ethers of the substituted bisphenols shows a Hammett substituent effect, since no correlation of polarity appears to exist other than that of the epoxy content as described above. Since these epoxy compounds are cured with 4,4'-diaminodiphenylmethane they all have the common polymer backbone group



and other related forms of it crosslinked via the OH and NH groups. This structure may be more important in its effect on adhesion to aluminum and stainless steel than the effect of substituents on the aromatic ring of the bisphenol.

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### References

1. Erich, W., and M. J. Bodnar, *J. Appl. Polymer Sci.*, **3**, 296 (1960).
2. Sorenson, W. R., and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 309.

### Résumé

On a préparé des résines époxy bisphénoliques A substituées possédant des groupements à polarité variable sur le noyau aromatique. On a déterminé l'effet des substituants sur l'adhésion pour des températures de congélation et pour des températures élevées. L'effet de cette substitution est de moindre importance comparé à la quantité d'époxy. On compare les adhésifs sur de l'aluminium et de l'acier inoxydable par mesure de la force d'arrachement dans un domaine de température s'étendant de  $-320^\circ$  à  $+400^\circ\text{F}$  et aussi à  $-453^\circ\text{F}$ .

### Zusammenfassung

Substituierte Bisphenol-A-Epoxyharze wurden mit Substituenten verschiedener Polarität am aromatischen Ring dargestellt. Der Substituenteneinfluss auf die Adhäsion bei sehr tiefen und erhöhten Temperaturen wurde bestimmt und erwies sich im Vergleich zum Epoxygehalt als von geringerer Bedeutung. Die Adhäsive wurden auf Aluminium und rostfreiem Stahl auf die Zug- und Schubfestigkeit im Temperaturbereich von  $-320^\circ$  bis  $+400^\circ\text{F}$  und in einem Fall bei  $-453^\circ\text{F}$  untersucht.

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