

## Evaluation of Polyglycidyl Esters as Cryogenic Adhesives

STANLEY R. SANDLER, *Central Research Laboratory,  
The Borden Chemical Company, Philadelphia, Pennsylvania 19124*

### Synopsis

Polyglycidyl esters of aromatic polycarboxylic acids were evaluated as adhesives for aluminum over the temperature range  $-453$  to  $+400^{\circ}\text{F}$ . The esters were cured either with amines or anhydrides. Cyclopentanetetracarboxylic acid dianhydride was found to be a superior curing agent and gave adhesives with tensile shear strengths in excess of 1000 psi at  $400^{\circ}\text{F}$ .

### INTRODUCTION

As a result of the availability<sup>1</sup> of pure glycidyl esters of monobasic and polybasic aromatic acids from our synthesis program, the compounds were evaluated as adhesives by reacting them with amines and anhydrides in order to polymerize them to high molecular weight materials. It was thought that glycidyl esters would offer greater advantages than glycidyl ethers since the ester group, being more polar, would enhance adhesion to aluminum. The physical testing procedure is given in detail and is representative of the method used to test the compounds described in this investigation.

### EXPERIMENTAL

#### General Procedure for the Physical Testing of Adhesives

The physical testing data are presented in Tables I-IV. In most cases the adhesives were tested at 400, 73,  $-60$ , and  $-320^{\circ}\text{F}$ . on Alclad aluminum 2014-T6, 0.064 in. thick, Federal Specification QQ-A-255. Some adhesives were tested on #321 stainless steel, 0.064 in. thick, Federal Specification QQ-S-766. The aluminum was etched with sulfuric acid-dichromate. The samples were cured at  $100^{\circ}\text{C}$ . for 2 hr., unless otherwise specified, and equilibrated before testing for 7 days at room temperature ( $73^{\circ}\text{F}$ .) 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 consisted of a stainless steel Dewar flask having the dimension  $20\frac{3}{4}$  in. height,  $7\frac{1}{4}$  in. outside diameter, 18 in. in-

TABLE I  
Adhesive Properties of Epoxy Esters Cured with 4,4'-Diaminodiphenylmethane (MDA)

Sample no.	Composition (proportions by weight shown in parentheses)	Tensile shear strength on aluminum, psi <sup>a</sup>					T-peel, <sup>b</sup> lb./in.
		-453°F.	-320°F.	73°F.	250°F.	400°F.	
432-144-5	Diglycidyl terephthalate + MDA (2.1/0.5)	2270	3350	2740	2220	428	<1
432-72-3	Diglycidyl 2,5-dichloroterephthalate + MDA (2.1/0.3)	—	2930	2700	—	1120	—
432-150-5	Diglycidyl hexahydroterephthalate + MDA (1.4/0.5)	—	3390	—	—	282	—
462-27-1 <sup>c</sup>	Diglycidyl isophthalate + MDA	—	4200	3780	2660	385	<2
432-21-1	Diglycidyl phthalate + MDA (2.5/0.9)	—	5037	4057	1166	—	<2
432-113-1	Triglycidyl trimellitate + MDA (3.0/0.6)	2920	2700	2700	2410	1700	—
462-10-3	Triglycidyl trimellitate + MDA (3.6/1.0)	—	—	1370	—	—	—
462-150-9	Tetraglycidyl pyromellitate + MDA (2.4/1.0)	—	1810	2220	2960	1098 <sup>d</sup>	—
432-129-3	Diglycidyl diphenate + MDA (3.0/0.6)	—	1030	1540	92	—	—

<sup>a</sup> Average of three determinations. The samples were cured at 100°C. for 2 hr. and equilibrated 7 days prior to testing.

<sup>b</sup> T-peel strength on aluminum was less than 2 psi at 73°F. NASA obtained 4120 and 3740 psi at 73 and 250°F., respectively.

<sup>c</sup> Diglycidyl isophthalate prepared from epoxidation of diallyl isophthalate used in place of the material above prepared from glycidol and isophthaloyl chloride gave tensile shear strength on aluminum of 3720 psi at -320°F. and 180 psi at 400°F.

<sup>d</sup> Values as high as 1190 have been obtained.

TABLE II  
Adhesive Properties of Epoxy Esters Cured with 1,2,3,4-Cyclopentanetetracarboxylic Acid Dianhydride (CPDA)<sup>a</sup>

Sample no.	Composition (proportions by weight shown in parentheses) <sup>b</sup>	Tensile shear strength on aluminum, psi <sup>c</sup>				T-peel, lb./in.
		-320°F.	73°F.	250°F.	400°F.	
462-29-5	Diglycidyl phthalate + CPDA + BDA (1.4/2.1/0.06 ml.)	1280	2120	2530	1030	<2
462-27-4	Diglycidyl isophthalate + CPDA + BDA (2.8/2.1/0.06 ml.)	1650	1560 <sup>d</sup>	1730 <sup>d</sup>	1210	<2
432-142-7	Diglycidyl terephthalate + CPDA + BDA (1.7/1.0/0.03 ml.)	1746	3150	3390	1535	<2
462-50-6	Diglycidyl hexahydroterephthalate + CPDA + BDA (0.7/1.1/0.04 ml.)	2150	—	—	579	<2
462-48-3	Diglycidyl 2,5-dichloroterephthalate + CPDA + BDA (1.2/1.0/0.03 ml.)	1350	—	—	1500	<2
462-30-1	Triglycidyl trimellitate + CPDA + BDA (1.3/2.1/0.06 ml.)	901	1920	1970	1040	<2
462-45-2	Tetraglycidyl pyromellitate + CPDA + BDA (1.2/1.0/0.03 ml.)	888	—	—	862	<2
462-31-1	Triglycidyl trimellitate + CPDA + BDA (1.3/2.1/0.06 ml.)	1270	1830	1810	1100	<2

<sup>a</sup> The samples were cured at 100°C. for 2 hr. and equilibrated 7 days prior to testing.

<sup>b</sup> BDA = benzylidimethylamine.

<sup>c</sup> An average of three determinations.

<sup>d</sup> NASA obtained 2450 and 3200 psi at 73 and 250°F., respectively.

side depth, and 6 in. inside diameter, and was constructed with a copper heat radiation shield between the inner and outer walls. The Dewar was evacuated to about  $2 \times 10^{-6}$  mm. Hg by connecting it to the high vacuum system of a Kinney evaporator, Model KSE-2. All internal surfaces facing the vacuum were gold-plated. The liquid nitrogen was added to the cryostat used in conjunction with the Tinius Olsen Electromatic universal testing machine.

TABLE III  
Comparison of Anhydrides as Curing Agents for Diglycidyl  
Terephthalate (450-26-2a, 428-109-3)

Sample No.	Composition (proportions by weight shown in parentheses)	Tensile shear strength on aluminum, psi <sup>a</sup>			
		-320°F.	73°F.	250°F.	400°F.
432-142-5	450-26-2a (diglycidyl terephthalate) + pyromellitic dianhydride + BDA (1.7/1.1/0.03 ml.)	2000	2620	2410	1286
432-142-7	450-26-2a (diglycidyl terephthalate) + CPDA + BDA (1.7/1.0/0.03 ml.)	1746	3150	3390	1535
432-141-3	428-109-3 (diglycidyl terephthalate) + phthalic anhydride + BDA (2/1/0.04 ml.)	2060	2194	2450	127
432-142-3	450-26-2a (diglycidyl terephthalate) + trimellitic anhydride + BDA (1.7/1.3/0.03 ml.)	1440	2420	1823	139

<sup>a</sup> Average of three determinations. The samples were cured at 100°C. for 2 hr. and equilibrated 7 days prior to testing.

### T-Peel Testing of Adhesives

The T-peel results appear in Table I; data were obtained on samples on 0.032-in. thick aluminum without wire spacers cured for 2 hr. in a heated press at approximately 25 psi.

### Synthesis

The synthesis of the glycidyl esters described in this investigation has been reported elsewhere.<sup>1</sup>

### Discussion

It has been shown in a related work on diglycidyl ethers of bisphenol A that the tensile shear strength varies with epoxy content.<sup>2</sup> Consequently glycidyl esters of high purity are required in order to get the maximum adhesive potential of each material.

Glycidyl esters have been prepared for this investigation (Table I) by reacting the acid chloride and triethylamine by separate additions at 0-5°C. with glycidol (2,3-epoxypropanol).<sup>1</sup>

The physical testing results shown in Table I indicate that as the (epoxy)-glycidyl groups/molecule increase, so does the tensile shear strength of the adhesives at 400°F. The opposite trend appears to be indicated for the tensile shear strengths at -320°F. The latter may be true, since the di-

TABLE IV  
Evaluation of Room Temperature Curing Epoxy Esters

Sample no.	Composition (proportions by weight shown in parentheses)	Pot life, min.	Tensile shear strength, psi		
			73°F.	250°F.	400°F.
462-40-3	461-95 (Tetraglycidyl pyromellitate) + triethylene-tetramine (1.2/0.13 ml.)	—	1100	—	—
462-37-9	461-89 (Diglycidyl phthalate) + triethylenetetramine (TETA) (1.7/0.13 ml.)	>60	1410	240	—
462-40-1	461-91 (Triglycidyl trimellitate) + triethylenetetramine (1.8/0.13 ml.)	>60	1000	—	—
462-40-2	461-93 (Triglycidyl trimesoate) + triethylenetetramine (1.3/0.13 ml.)	30	2230	156	—
462-37-2	461-89 (Diglycidyl phthalate) + diethylenetriamine (DETA) (1.4/0.15 ml.)	>60	1740	239	—
462-37-3	461-91 (Triglycidyl trimellitate) + diethylenetriamine (1.3/0.15 ml.)	>60	1560	403	—
462-37-5	461-95 (Tetraglycidyl pyromellitate) + diethylenetriamine (1.2/0.15 ml.)	10	2110	657	—
462-24-3	461-72-3 (Diglycidyl terephthalate) + DETA (2.0/0.17 ml.)		499	—	—
462-24-4	467-55 (Triglycidyl trimesoate) + DETA (2.4/0.17 ml.)		1920	—	—
462-24-5	467-57 (Diglycidyl phthalate) + DETA (2.2/0.17 ml.)		407	—	—
462-24-8	461-72-3 (Diglycidyl terephthalate) + TETA (2.0/0.28 ml.)		223	—	—
462-25-1	467-55 (Triglycidyl trimesoate) + TETA (2.4/0.14 ml.)		1700	157	—
462-25-2	467-57 (Triglycidyl trimesoate) + TETA (2.2/0.10 ml.)		587	—	—

glycidyl esters are probably more flexible when cured with MDA at -320°F. as a result of the lower degree of crosslinking.

Diglycidyl phthalate gave better low temperature properties than its other two isomers but it had poor high temperature strength. These results indicate that the steric conformation of the system plays an important role in adhesion. The more symmetrical isomer, diglycidyl terephthalate, shows enhanced strength.

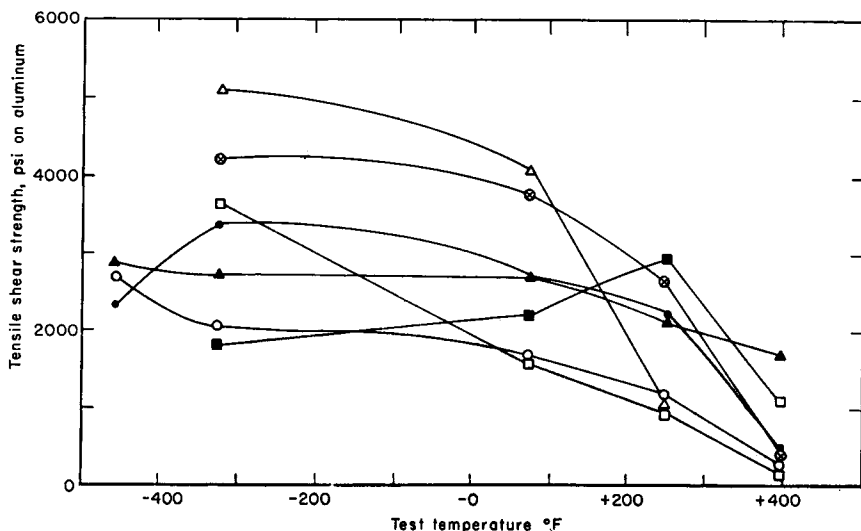


Fig. 1. Comparison of some epoxy esters and commercial epoxy resins cured with MDA: ( $\Delta$ ) diglycidyl phthalate; ( $\otimes$ ) diglycidyl isophthalate; ( $\square$ ) Epiphen 825 (Borden Chemical Co.); ( $\bullet$ ) diglycidyl terephthalate; ( $\blacktriangle$ ) triglycidyl trimellitate; ( $\circ$ ) DER 332 (Dow Chemical Co.); ( $\blacksquare$ ) tetraglycidyl pyromellitate.

Substitution of two chlorine groups into the aromatic portion of a diglycidyl terephthalate increased the tensile shear strength at 400°F. This may be due to the increase in polarity resulting in a polymer which is more firmly bound to the aluminum surface. The increase in strength of the tri- and tetraglycidyl esters may also be due to a polarity effect in addition to the enhanced crosslinking of such a system.

Diglycidyl diphenate was synthesized with the hope of giving an adhesive with good strength at 400°F. However, the poor results shown may also be due to the decrease in polarity of such a diaryl system in comparison to the monoaryl glycidyl esters used in this investigation.

The use of a saturated diglycidyl ester as diglycidyl hexahydroterephthalate gave slightly reduced results at 400°F.

The results of two adhesives tested by NASA as shown in Tables I and II gave satisfactory agreement with our results.

Use of 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride as (CPDA) the curing agent (Table II) yielded stronger adhesives at 400°F. This is probably due to the greater rigidity and crosslinking of this dianhydride. The surprising fact is that the 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride is slightly better than pyromellitic dianhydride (PMDA) as a curing agent to give high temperature adhesives (Table III). 1,2,3,4-Cyclopentanetetracarboxylic acid dianhydride is aliphatic, whereas pyromellitic dianhydride is aromatic, and one would ordinarily expect that an aromatic system would be more stable at higher temperatures. A comparison of several anhydrides as curing agents is shown in Table III.

Benzyltrimethylamine (BDA) has been found to accelerate the reaction of anhydrides with glycidyl groups and thus is used as a catalyst.

Substituting other aliphatic amines for 4,4'-diaminodiphenylmethane and curing at room temperatures resulted in poor adhesives. This probably is a result of the lower degree of aromaticity and crosslinking.

A comparison of glycidyl ester adhesives with other commercial epoxy adhesives is shown in Figure 1. The results shown here indicate that bisphenol or phenolic diglycidyl ethers give lower strengths at  $-320$  and  $+400^{\circ}\text{F}$ .

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### References

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### Résumé

Les esters polyglycidiqes des acides aromatiques polycarboxyliques ont été évalués comme adhésifs sur aluminium sur une domaine de température de  $-453^{\circ}$  à  $+400^{\circ}\text{F}$ . Les esters ont été recuits en présence d'amines ou d'anhydrides. Le dianhydride de l'acide cyclopentane tétracarboxylique est un agent supérieur pour le traitement qui fournissait des adhésifs avec des forces de tension au cisaillement supérieures à 1000 psi à  $400^{\circ}\text{F}$ .

### Zusammenfassung

Die Anwendung von Polyglycidylestern aromatischer Polycarbonsäuren als Klebstoffe für Aluminium im Temperaturbereich von  $-453$  bis  $+400^{\circ}\text{F}$  wurde untersucht. Die Ester wurden mit Aminen oder Anhydriden gehärtet. Cyclopentantetracarbonsäuredianhydrid erwies sich als günstigstes Härtungsmittel und lieferte Klebstoffe mit einer Zug-Scherfestigkeit von mehr als 1000 psi bei  $400^{\circ}\text{F}$ .

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