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Thermochemical Tests on Resins - Char Resistance
of Selected Phenolic Cured Epoxides

Fred L. Keck

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Thermochemical Tests on Resins - Char Resistance
of Selected Phenolic Cured Epoxides

Fred L. Keck
Lockheed Missiles & Space Company, Inc.
P. O. Box 504
Sunnyvale, California 94086

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National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

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FORWARD

This report summarizes work conducted by the Advanced Manufacturing Technology organization, Missile Systems Division (MSD), of Lockheed Missiles & Space Company, Inc., Sunnyvale, California, 94086, under NAS 2-10207 Contract. Previous work had been done by the Manufacturing Research organization which was partially absorbed into Advanced Manufacturing Technology. The administration of the work is under the direction of NAS/Ames Research Center with D. A. Kourtides the Technical Monitor. Technical assistance on novalac phenolic cured epoxides was provided by Dr. H. A. Newey and C. J. Busso of Newey & Busso Associates.

SUMMARY

Curing epoxy resins with novalac phenolic resins is a feasible approach for increasing intact char of the resin system. Char yields above 40% at 700°C were achieved with epoxy novalac (DEN 438)/novalac phenolic (BRWE 5833) resin systems with or without catalyst such as ethyl tri-phenyl phosphonium iodide. These char yields are comparable to commercially used epoxy resin systems like MY-720/DDS/BF₃. Stable preregs are easily made from a solvent solution of the epoxy/phenolic system and this provides a feasible process for fabrication of same into commercial laminates.

INTRODUCTION

A basic problem associated with graphite composites is the release of free carbon fibers when burned. These carbon fibers can provide conductive paths which can lead to serious electrical problems. To minimize this possibility, the resin matrix used in the composite should have the property of producing a large quantity of intact char when burned that clings to the graphite fibers. Other properties desired of the resin matrix include good handling properties, good mechanical properties when cured, good moisture resistance and a glass transition temperature high enough for the intended application. A class of resin systems that offer promise of meeting these requirements is phenolic cured epoxides. Accordingly the objective of NAS 2-10207 is to study the char resistance of this type of resin system using readily available commercial resins. If feasible, this approach would be cost effective.

EPOXIDE-PHENOLIC EVALUATION

It is known that highly crosslinked phenolic resins give higher char yields than epoxy resins cured with amines or anhydrides. It is also known that phenolic resins such as novalacs, i. e. polyphenols made by condensing phenol and formaldehyde under acidic conditions, will cure epoxide resins. Practically all vaulting poles and many of the best skis are made with a liquid bisphenol A epoxy resin, novalac phenolic and latent catalyst. Although this resin matrix has limited aircraft applications because of its low heat distortion temperature (90°C), it is included in the char resistance evaluation.

The initial screening evaluation for obtaining maximum char yield on epoxy/phenolic resin systems included the following epoxy resins cured with Celanese Epicure 8451.

<u>Epoxy</u>	<u>Supplier</u>
MY-720	Ciba-Geigy
Epon 828	Shell
SU-8	Celanese
XD-7855	Dow
Epon 1031	Shell
DEN 438	Dow

In all cases stoichiometric amounts of the epoxy and phenolic resins produced a black char prior to satisfactory fusing regardless of how slow the application of heat. Further investigation concluded that Celanese 8451 phenolic is too reactive to form stable resin systems, probably because it has a "built-in" catalyst. Replacing the Celanese 8451 with Carbide BRWE 5833 novalac phenolic resulted in satisfactory systems; however,

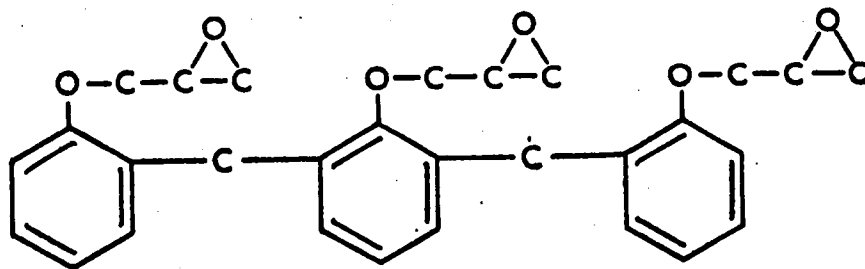
sample preparation through fusing was not suitable for practical applications. Consequently the solvent system technique was used for sample preparation. This consists of dissolving the epoxy resin and novalac phenolic (Carbide BRWE 5833) in methyl ethyl ketone. After solution, add catalyst if applicable and stir to complete solution.

The following cure with slight differences in time was used for the various systems.

1. Air dry overnight to remove majority of solvent.
2. Vacuum dry at room temperature increasing vacuum gradually to 500 microns exercising care to prevent boil over of the solvent system.
3. After removal of solvent return to atmospheric pressure, heat for 2 hours at 120°C followed by 6 hours at 160°C, then cool.

A compilation of epoxy/phenolic resin systems investigated plus "reference" epoxy resin systems and their respective char resistance (TGA) values at 700°C and 750°C is shown in Table 1. A near stoichiometric amount of novalac phenolic was used to cure the epoxy. The various types of epoxy resins as well as polyphenol evaluated along with their respective chemical formulations include:

a) Epoxy novalac - DEN 438



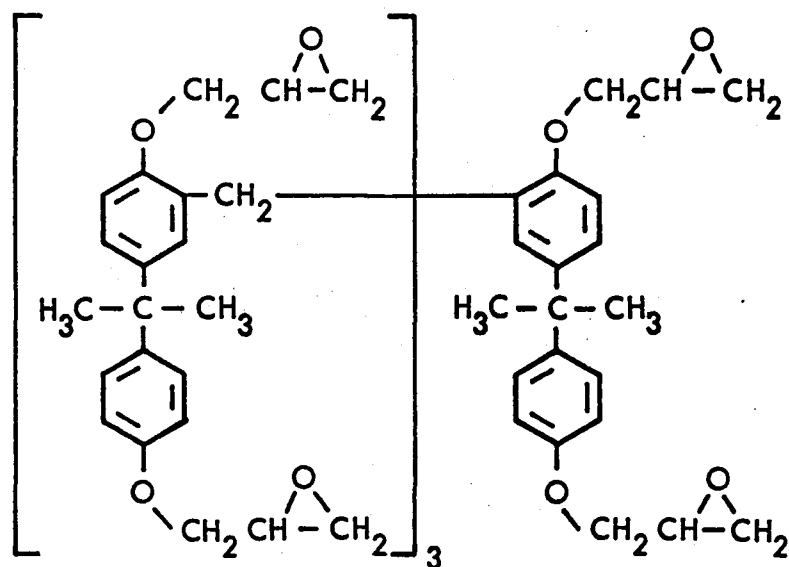
RESIN SYSTEMS

		REFERENCE				EPOXY/PHENOLIC							
<u>Resin System</u>		<u>A(1)</u>	<u>B(1)</u>	<u>C(1)</u>	<u>D(2)</u>	<u>E(2)</u>	<u>F(2)</u>	<u>G(2)</u>	<u>H(2)</u>	<u>I(3)</u>	<u>J(3)</u>	<u>K(3)</u>	<u>L(3)</u>
<u>Epoxy</u>	<u>Supplier</u>			Narmco 5208									
MY-720	Ciba-Geigy	100		90			100	100					
Epon 828	Shell		100						100				
SU-8	Celanese			10	100	100							
Epon 1031	Shell										100	100	
DEN 438	Dow									100			100
<u>Phenolic</u>													
BRWE 5833	Carbide				50	50	79.4	79.4	50	60	50		
TPE	Schnectady											45	45
<u>Catalyst</u>													
ETPPI, 0.1%						0.15		0.18		0.16	0.37	0.36	0.36
BF ₃ .400		1.5											
BDMA									0.6				
<u>Coreactant</u>													
DDS		32		30									
MDA			27										
<u>TGA Values, %</u>													
700°C		43.2	29.1	38.4	37.3	37.1	32.1	32.1	18.0	42.8	39.8	40.2	38.9
750°C		39.8	26.3	35.2	34.0	33.2	31.1	31.1	17.5	39.3	37.3	37.5	35.1

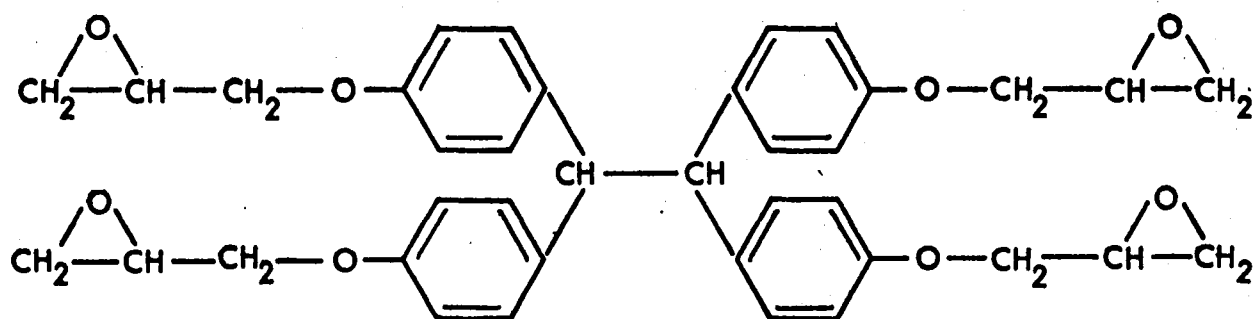
1. Cured 16 hrs at 93°C (200°F), 2 hrs at 121°C (250°F), 2 hrs at 149°C (300°F), 2 hrs at 177°C (350°F), 2 hrs at 205°C (400°F).
2. Cured 1 hr at 120°C (248°F), 4 hrs at 160°C (320°F)
3. Cured 2 hrs at 120°C (248°F), 6 hrs at 160°C (320°F)

TABLE 1

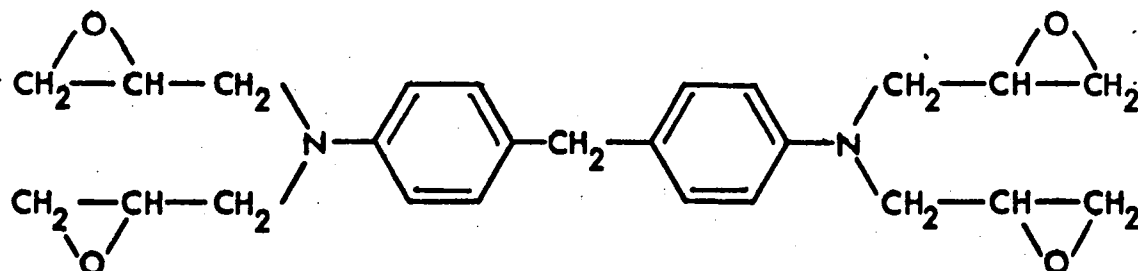
b) Epoxy bisphenol novalac - Celanese SU-8



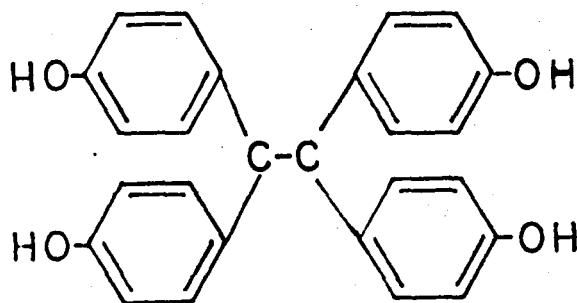
c) Glycidyl ether of polyphenol - Shell Epon 1031



d) Glycidyl amine - Ciba-Geigy MY-720



e) Tetraphenylol ethane - TPE (precursor of Epon 1031)



From the data in Table 1 the char resistance of most resin systems is lower than the best reference system, MY-720/DDS/BF₃. The only epoxy phenolic resin system having comparable char resistance is DEN 438/BRWE 5833. The use of triphenylol ethane in place of BRWE 5833 with Epon 1031 or DEN 438 did not increase char resistance. Higher char resistance had been expected because of higher aromatic ring content and cross link density.

Since DEN 438/BRWE 5833 had the highest char resistance of any epoxy/phenolic system evaluated, it was selected to study the effect of catalyst concentration. The data shown in Table 2 indicates that the amount of ethyl triphenyl phosphonium iodide catalyst has no significant effect on char resistance.

TABLE 2

SYSTEM	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Material</u>				
DEN 438	100			
BRWE 5833	60			
ETPPI, %	0	0.1	0.25	0.50

TABLE 2 (Cont'd)

TGA Values, %	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
700°C	43.7	42.8	46.1	41.8
750°C	39.4	39.3	42.7	38.9

Since the system containing 0.25% ETPPI had slightly better char resistance, it was chosen as the epoxy/phenolic candidate resin system for fabricating a graphite laminate under NAS 2-10130 contract. The physical properties of a 9-ply laminate cured at 350°F and 100 psi in an autoclave (detailed procedure in appendix of NAS 2-10130 contract) follow:

Thickness	118 mils	
Fiber volume	62.4%)	Based upon
		Resin sp. g. = 1.223
Void volume	0.2%)	Graphite sp. g. = 1.782
Short Beam Shear	8430 psi	
Photomicrograph (42X)	Figure 1	No indication of voids
Tg	105°C	

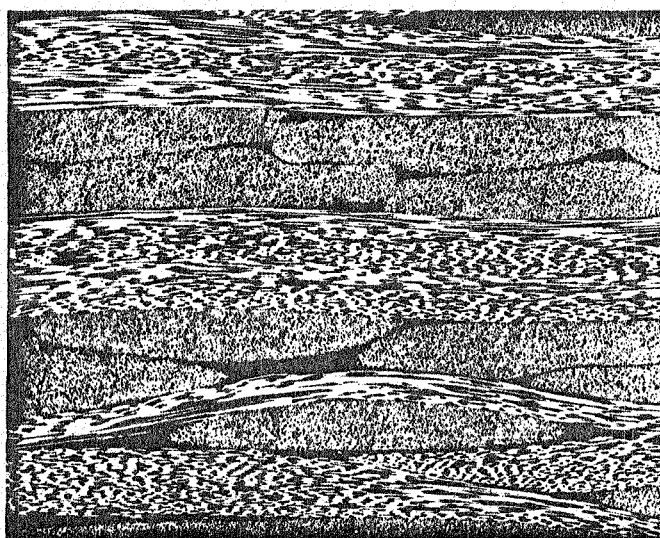


FIGURE 1

It should be noted that the char resistance was determined at 700°C and 750°C using a DuPont thermal analyzer. The test condition determined under NAS 2-10130 contract to produce maximum TGA values used 99.999% pure nitrogen at a flow rate of 50 ml per minute. A sample size of 8-9 mg obtained by filing the cast resin was used each time for comparison purposes.

CONCLUSIONS

As a result of the epoxy/phenolic investigation conducted under the NAS 2-10207 contract, the following conclusions are made.

- 1) The DEN 438/BRWE 5833 systems with or without ETPPI catalyst have char yields comparable to commercially used resin systems like MY-720/DDS/BF₃.
- 2) The DEN 438/BRWE 5833 resin system is cost effective.
 - . uses readily available commercial materials
 - . stable preregs from a solvent system provide a feasible process for fabricating laminates for commercial applications.
- 3) Curing epoxy resins with phenolic resins is a feasible approach for increasing intact char.
- 4) The optimum cure cycle including post cure was not established under this contract as time and funds were not available.

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