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SYNTHESIS OF IMPROVED PHENOLIC RESINS

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4 September 1979

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16 Abstract

Twenty seven addition cured phenolic resin compositions were prepared and tested for their ability to give char residues comparable to state-of-the-art phenolic resins. Cyanate, epoxy, allyl, acrylate, methacrylate and ethynyl derivatized phenolic oligomers were investigated. The novolac-cyanate and propargyl-novolac resins provided anaerobic char yields at 800°C of 58 percent. A 59 percent char yield was obtained from modified epoxy novolacs. A phosphonitrilic derivative was found to be effective as an additive for increasing char yields.

The novolac-cyanate, epoxy-novolac and methacrylate-epoxy-novolac systems were investigated as composite matrices with Thornel 300 graphite fiber. All three resins showed good potential as composite matrices. The free radical cured methacrylate-epoxy-novolac graphite composite provided short beam shear strengths at room temperature of 93.3 MPa (13.5 ksi). The novolac-cyanate graphite composite produced a short beam shear strength of 74 MPa (10.7 ksi) and flexural strength of 1302 MPa (189 ksi) at 177°C. Air heat aging of the novolac-cyanate and epoxy novolac based composites for 12 weeks at 204°C showed good property retention.

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SUMMARY

SYNTHESIS OF IMPROVED PHENOLIC RESINS

Twenty seven addition cured phenolic resin compositions were prepared and tested for their ability to give char residues comparable to state-of-the-art phenolic resins. Cyanate, epoxy, allyl, acrylate, methacrylate and ethynyl derivatized phenolic oligomers were investigated for processability, cure properties and heat distortion temperatures for applicability to provide state-of-the-art graphite composite mechanical properties at ambient and elevated temperatures.

The novolac cyanate resin essentially met all project goals by providing a 58 percent anaerobic char yield at 800°C. Composites made with Thornel 300 graphite exhibited a flexural strength at 177°C (350°F) of 1302 MPa (189 ksi) and short beam shear strength of 74 MPa (10.7 ksi). This system's cure temperature must be reduced before it can be considered as a replacement for currently used systems.

An anaerobic char yield of 59 percent at 800°C was obtained from epoxy novolacs by use of an additive and high temperature oxidative treatment of the resin system. While Thornel 300 graphite composite strengths were somewhat less than those of state-of-the-art composites, the heat resistance of this system at 204°C (400°F) is quite good. This system has potential for providing resin systems with anaerobic char yields in excess of 50 percent and state-of-the-art composite strengths.

The propargyl ether novolacs were the only other resin system which provided anaerobic char yields at 800°C in excess of 50 percent. Some promise was demonstrated for achieving good heat distortion temperatures

with this system. However, prepolymers were obtained in low yields.

Char yields of nearly 50 percent were demonstrated for the remainder of the derivatives investigated after inclusion of a phosphonitrillic derivative to the base resin. The allyl novolacs, epoxy novolac acrylates and methacrylates did not exhibit adequate heat distortion temperatures. The resole acrylates prepared from formaldehyde, acrolein and furfural also gave low heat distortion temperatures. They also exhibited shrink cracking during cure.

The epoxy-novolac-methacrylate system was investigated as a matrix resin for Thornel 300 graphite composites. This free radical cured system provided the very good short beam shear strengths at room temperature of 93.3 MPa (13, 540 psi). This system is available commercially.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

Commercially available low-cost, intermediate temperature matrix resins used in fiber-reinforced composite applications possess poor resistance to extreme temperature environments. On exposure to fire environments significant loss of the matrix resin results. This can lead to unsupported and exposed fibers. When such unsupported fibers are graphite and they are not consumed in the fire, a potentially serious danger of contaminating the immediate environment with these fibers exists.

One possible approach to minimize this potential danger is to employ matrix resins which produce a high char yield on exposure to severe oxidative environments. Phenolic resins as a class possess excellent char-forming characteristics. The oxidative weight loss characteristics of a typical phenolic resin and a typical high strength, medium modulus graphite fiber are shown in Figure 1. The fiber is more thermo-oxidatively stable than the phenolic resin which in turn is more stable than currently used epoxy resins.

Thus, maximum thermo-oxidative resin char yield is a useful goal for resin development programs directed toward minimizing potential fiber loss from composites in a fire environment. Resin systems developed on this program should have oxidative char yield characteristics at least equivalent to state-of-the-art phenolics such as SC1008.

Since all known resin systems prior to reaching typical fire temperatures decompose to give volatile products and may provide char, matrix resin

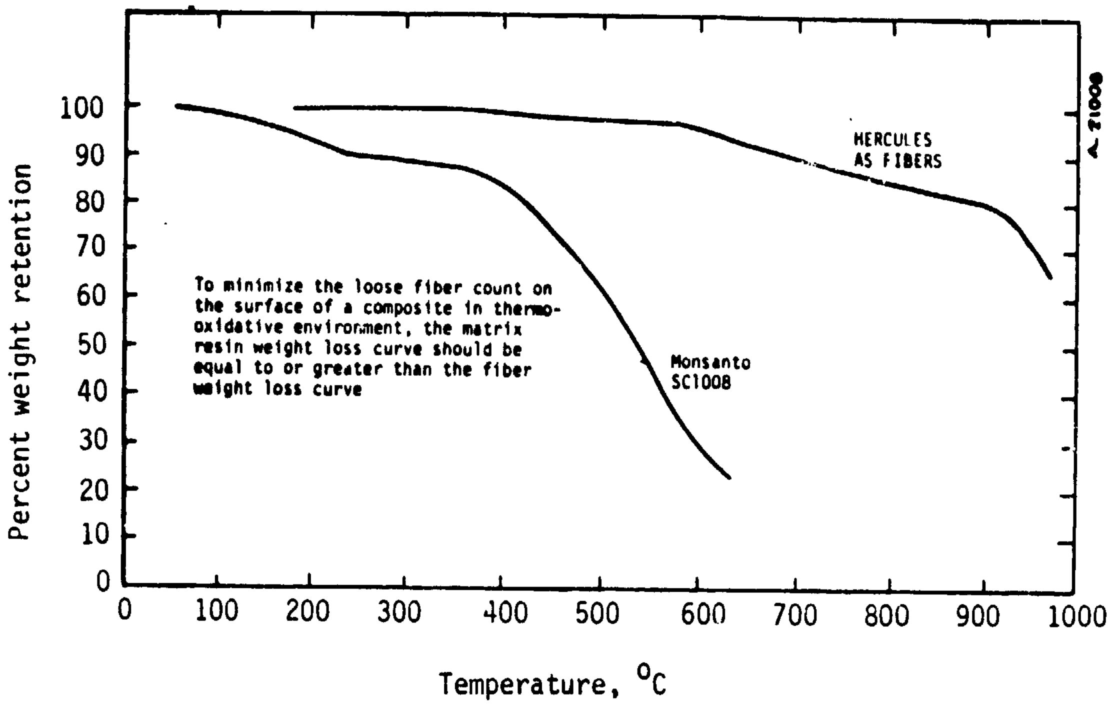


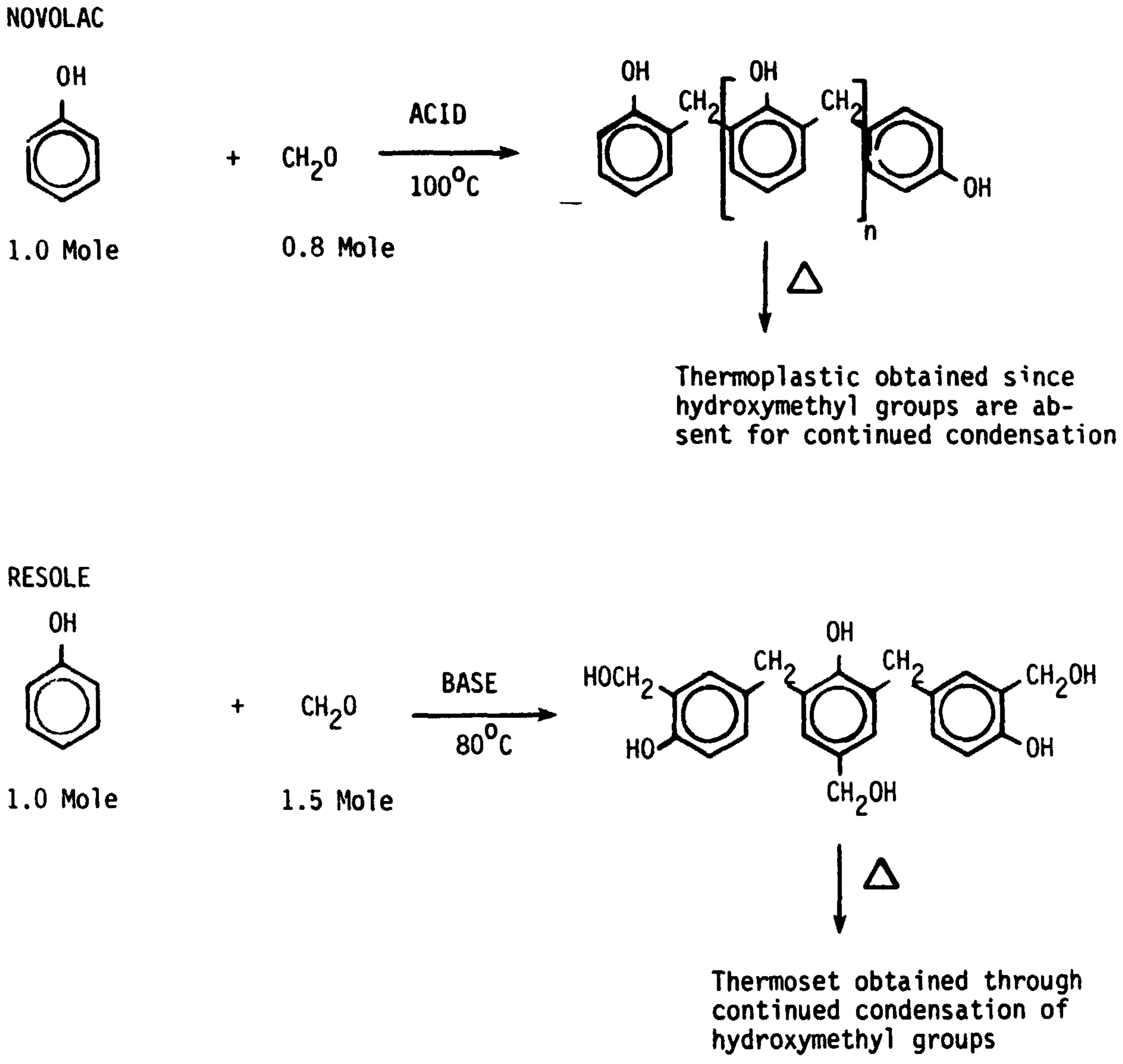
Figure 1. Oxidative weight loss characteristics of a phenolic resin and a graphite fiber.

char strength should be considered for fire scenarios where char occurs. For instance, fibers could easily be released from low-strength-charred matrix graphite composites by water issued from a high pressure fire hose.

Unfortunately, phenolic resins are poorly suited for use as matrix resins in high performance composites because the final cure is performed under high pressure and produces volatile byproducts which lead to formation of voids in the composites. It is well known that the presence of voids has a deleterious effect on composite mechanical properties. This problem could be eliminated if the intermediate phenolic oligomers could be chemically modified to cure by an addition mechanism without volatile evolution.

1.2 APPROACH

Phenolic prepolymers are obtained from the condensation of phenolic compounds with aldehydes by either base or acid catalysis. Both ortho and para condensation occur with the phenolic compound. Model prepolymers are shown in Figure 2. Novolacs due to their greater thermal stability are preferred to resoles for addition derivatization.



Thermoplastic obtained since hydroxymethyl groups are absent for continued condensation

Thermoset obtained through continued condensation of hydroxymethyl groups

Figure 2. Model phenolic prepolymers.

Suitable modification to either resoles or novolacs to achieve addition cure can involve a number of approaches. Groups can be reacted with the phenolic functionality to give esters or similar species. Groups can be added to the aromatic nucleus to give pendant groups with unsaturation and these species condensed with formaldehyde to give a phenolic oligomer. Groups can be made part of the reacting formaldehyde such as acrolein to give a suitable functionality for addition cure.

It was perceived at the beginning of the program that if the addition cure groups were aliphatic, a compensatory increase in the aromatic content of the derived resin would be required to maintain the high char yield associated with phenolic resins. Accordingly, significant useage of bisphenols such as 9,9-bis(4-hydroxyphenyl)fluorene and β-naphthol were planned. As will be discussed in Section 3, high aromatic content prepolymers per se do not necessarily provide high char yield. The chemistry of the char process is also important in obtaining high char yields.

Several additives could be considered for use with resin systems to increase their char yield in a fire environment. Additive investigations however were limited to a single PN polymer which was known to increase the char yield of phenolic resins.

SECTION 2

OBJECTIVE

The objective of this program was to investigate chemical modification of phenolic prepolymers to provide oligomers that can be cured without evolution of volatile byproducts. Additional target requirements for the prepolymers and polymers were:

- State-of-the-art processability (epoxy-like)
- No more than 204°C (400°F) and 1.4 MPa (200 psi) cure
- Low cost
- 177°C (350°F) to 204°C (400°F) performance capability (mechanical and thermal aging)
- Oxidative char yield characteristics equivalent to or better than state-of-the-art phenolic resins
- State-of-the-art graphite composite mechanical properties

SECTION 3

RESULTS AND DISCUSSION

Several addition type derivatives were investigated for suitability to provide addition cured novolacs. The derivatives investigated were cyanate, epoxy, allyl, acrylate, methacrylate and ethynyl.

Phenol-formaldehyde based novolacs and resoles are excellent candidates for addition derivatization due to the large variability in condensation conditions to produce either low melting or high melting prepolymers. These linear prepolymers however are soft at the program's minimum target mechanical performance temperature of 177°C (350°F). Standard phenolic cure of low melting linear prepolymers (hexamethylenetetramine) can result in very high crosslink densities and consequently resins with very high melting points. With many of the addition cured derivatives discussed below, resins with high softening temperatures were not obtained using linear phenol-formaldehyde precursors.

Due to the ease of obtaining processable phenolic prepolymers, prepolymer processability was not considered a problem and initial screening efforts were directed toward char yield and distortion temperature under load (DTUL)* characterization of the cured addition prepolymers. Selection of prepolymers for composite evaluation was based principally on high DTUL attainment since it was shown that anaerobic char yields at 800°C could be significantly increased through use of at least one additive.

---

*See Appendix A

The discussion given below describes the numerous addition cured derivatives investigated, their synthesis procedures, cure methods and characterization by char yield and DTUL measurements. Since resin cost is an important factor in successful resin systems, involved synthesis procedures and raw material costs weighed heavily into decisions to evaluate specific derivatives.

Initial composite characterization of three candidate resins follows the description of the addition cured systems investigated. This is followed by demonstration of the prepregability, processability and fabrication of 20.3 cm x 20.3 cm (8" x 8") graphite composites from two of the candidate resins.

3.1 BASELINE NOVOLAC SELECTION

For subsequent derivatization efforts a baseline novolac was required. Even though phenol and formaldehyde are low cost monomers for novolac production, based on the char yield and processability of the polycarbonate of 9,9-bis(4-hydroxyphenyl)fluorene (Reference 1) it was expected that novolacs containing this structure would produce higher char yields than only phenol-formaldehyde based novolacs. A idealized novolac structure is provided in Section 1.2.

The novolac prepolymers produced with the 9,9-bis(4-hydroxyphenyl) fluorene showed excellent processability potential. However, during one novolac preparation using formaldehyde with phenol and the 9,9-bis(4-hydroxyphenyl)fluorene, the product gelled and was no longer soluble in novolac solvents. Based on this and only minimal char yield benefits obtained from use of the 9,9-bis(4-hydroxyphenyl)fluorene, no further efforts were carried out with this monomer after the initial results described below were obtained.

A number of acids are useful for catalyzing the novolac reaction. The more important ones are listed in Table 1.

TABLE 1. CONDENSATION CATALYSTS

TYPE OF ACID	NOTES
Formic	The acidity of commercial formalin sometimes suffices at elevated temperatures
Halogenated organic	Natural resin acid or ester also present
Hydrochloric	In some cases, gives better results than sulfuric or phosphoric acids
Oxalic	Light-colored resins. Catalyst may be driven out under vacuum at end of the reaction
Phosphoric	Light-colored resins
Sulfamic	Resins of short cure and good water resistance
Sulfuric	Popular for price, lack of volatility, and ease of handling
Toluenesulfonic	Its solubility in oils helps utilization of the raw materials for the resin
Trichloroacetic	Catalyst may be decomposed into gases by heat at the end of the reaction. Light-colored resins

To obtain "clean" novolacs, an acid which could be easily removed from the novolac prepolymer was most desirable. Typically halogen and sulfuric acids are not washed from novolac prepolymers but left in to accelerate final cure or neutralized and the salt produced left in the product. Acids such as oxalic or trichloroacetic or ion exchange resins are more suited for obtaining acid and/or salt free novolacs.

Unreacted phenol is present in as-manufactured novolacs ($\sim$10 percent) and could be removed or left in depending on how the novolac was to be subsequently derivatized for addition cure.

A matrix of phenol, 9,9-bis(4-hydroxyphenyl)fluorene and formaldehyde stoichiometries was set up. It is given in Table 2 below. Based on phenol, the 80 percent of theory formaldehyde reactions should provide idealized prepolymer structures which consist of five phenolic units with four methylene bridges. Based on phenol, the 67 percent of theory formaldehyde reactions

TABLE 2. MATRIX OF PHENOLS FOR BASELINE NOVOLAC INVESTIGATIONS

- With 80% theoretical formaldehyde

	PARTS				
Phenol	100	75	50	25	0
9,9-Bis(4-hydroxyphenyl)fluorene	0	25	50	75	100
Reaction No.	A	B	C-1 C-2	D	E

- With 67% theoretical formaldehyde

	PARTS				
Phenol	100	75	50	25	0
9,9-Bis(4-hydroxyphenyl)fluorene	0	25	50	75	100
Reaction No.	F	G	H	I	J

should provide prepolymers whose idealized structures consist of three phenolic units with two methylene bridges. Since the reactivity of the 9,9-bis(4-hydroxyphenyl)fluorene with formaldehyde was unknown a mole of this compound was treated as equivalent to a mole of phenol for matrix purposes. In fact, it is theoretically tetrafunctional in its reactivity toward formaldehyde compared to phenol which is trifunctional.

The 9,9-bis(4-hydroxyphenyl)fluorene was prepared by the procedure described by Morgan (Reference 2).

The procedure given in Sorenson and Campbell (Reference 3) was used to prepare the novolacs with slight modification. In our case 8.00g of phenol (0.0851 mole), 5.25g of 37 percent aqueous formaldehyde (0.0681 mole) and 0.40g of oxalic acid dihydrate were placed in a polymerization tube which was subsequently immersed into a 100°C oil bath and allowed to react for 16 hours. During the first hour of the reaction the tube was shaken vigorously every 5 minutes.

The planned matrix of ten novolacs using 80 and 67 percent of formaldehyde to phenolic substrate was completed. Note that each composition was given a reaction number, i.e., A, B, C etc. These letters are used to subsequently reference the reactions. The procedure used to obtain the novolac compositions containing a large quantity of 9,9-bis(4-hydroxyphenyl) fluorene (C-2, D, E, I and J) was the same as those described above, except isopropyl alcohol was used to facilitate the melting of the 9,9-bis(4-hydroxyphenyl)fluorene and the oil bath temperature drifted to 130°C (16-hour reactions as conducted for A, B, C-1, F, G and H). In reactions D, E, I and J a trace of insolubles was noted. These insolubles are thought to be a little undissolved oxalic acid.

All of the novolacs were still molten at 100°C at the end of the 16 hour reaction time. The 80 percent formaldehyde reaction products all had higher viscosities at the reaction temperature than their corresponding 67 percent formaldehyde reaction products.

Cure of the prepolymers for TGA characterization was as follows: Two grams of each reaction mixture was dissolved in 10 ml of hot isopropyl alcohol and 10 percent by weight of hexamethylenetetramine (hexa) was dissolved in the isopropyl alcohol. The isopropyl alcohol was removed, the samples placed in an air circulating oven for two hours at 120°C and an additional two hours at 204°C (400°F). All of the reactions gelled in about 30 minutes at 125°C and all darkened in color during the 204°C (400°F) treatment except the 100 percent 9,9-bis(4-hydroxyphenyl)fluorene compositions which remained light yellow in color. The cured polymers were ground and their grindability roughly paralleled the phenol contents; the higher the phenol content, the harder the cured polymer was to grind. The powdered polymers were sieved (-30 mesh) and approximately ten milligram samples were subjected to TGA measurement at 15°C per minute heat rise in air and nitrogen.

Anaerobic char yield determinations on four reaction products were carried out in nitrogen. The Y_c^* at 800°C for the cured novolacs is given below and the weight residue curves are given in Figure 3.

---

*Y_c = Char yield.

Resin System	Percent Weight Residue
Reaction A	61
Reaction C-1	63
Reaction C-2	64
Reaction D	64

The anaerobic char yields are essentially the same for the four compositions tested.

Figure 4 shows the weight retention curves in air of reaction products A, B, and C-1. Figure 5 shows the weight retention curves in air of products C-2, D and E. The 50 percent weight loss temperature in air for each of the reactions is given below.

Resin System	50 Percent Weight Loss Temperature
Reaction A	557°C
Reaction B	579°C
Reaction C-1	563°C
Reaction C-2	544°C
Reaction D	516°C
Reaction E	493°C

The products from the melt reactions B and C-1 both show only slightly superior oxidative resistance to the classical novolac based on phenol (reaction A). This probably is due to the presence of the fluorenylidine bisphenol in the B and C-1 novolac prepolymers. The superiority of the C-2 reaction product (isopropyl alcohol fluxed, Figure 5) to the D and E reaction products may be due to molecular weight development with the hexa cured polymers.

Scale up (30 gram preparation) of the 50/50 phenol 9,9-bis(4-hydroxyphenyl)fluorene produced a crosslinked product. This prepolymer unlike the previously prepared prepolymers was solid at the reaction temperature (140°C)

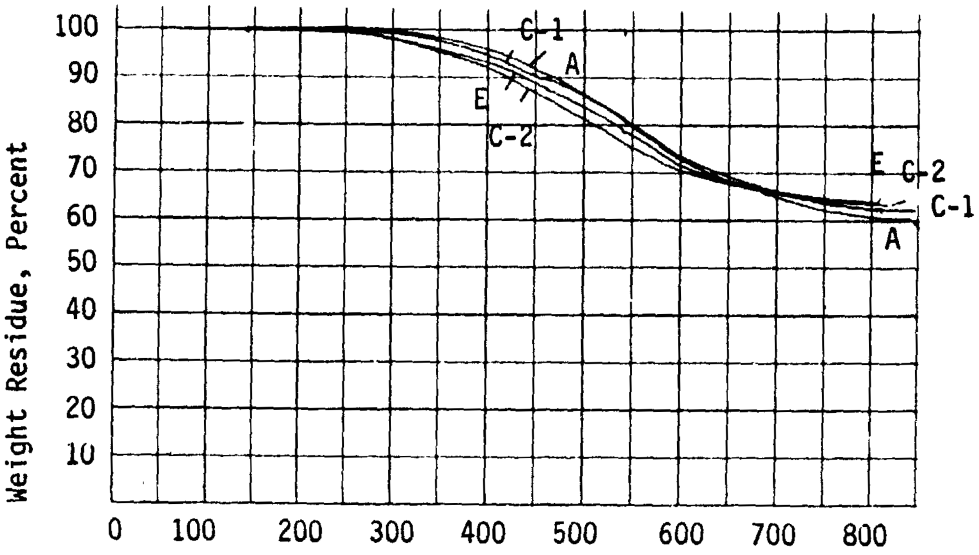


Figure 3. Weight loss curves of four novolac copolymers in nitrogen (15°C/min, 0.5ℓ/min, -30 mesh).

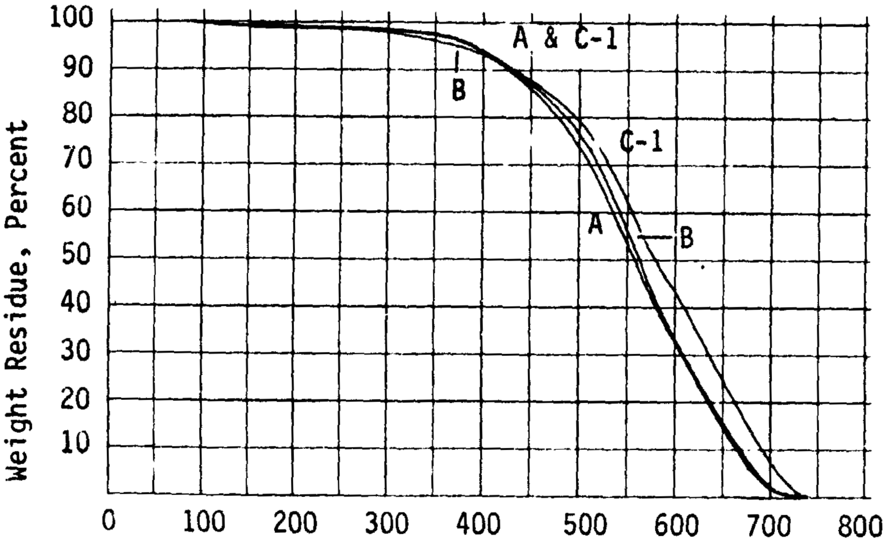


Figure 4. Weight loss curves with temperature of reaction products A, B and C-1 in static air (15°C/min, -30 mesh).

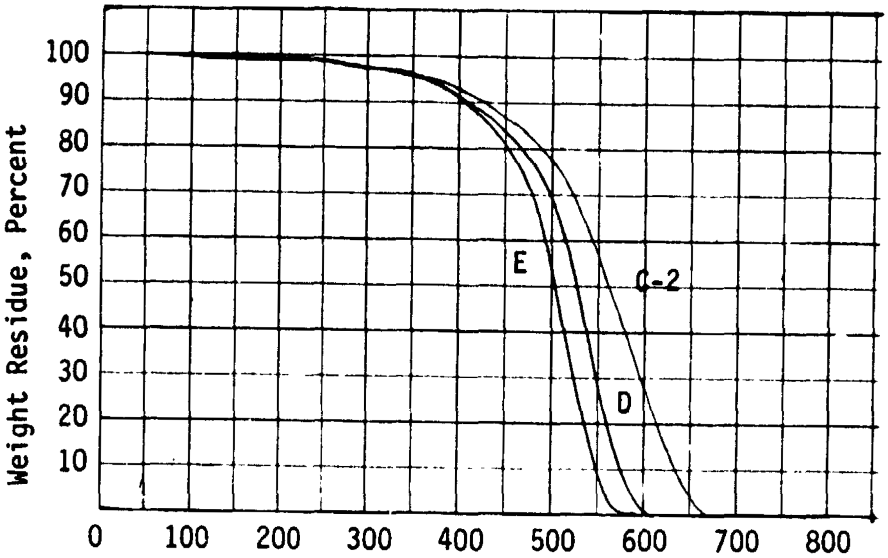


Figure 5. Weight loss curves with temperature of reaction products C-2, D and E in static air (15^{o}C/min, -30 mesh)

and only swelled in isopropyl alcohol and acetone. A companion 30 gram phenol novolac resulted in a product which was molten at the reaction temperature and soluble in both isopropyl alcohol and acetone.

Due to the formation of the unexpected gel and only marginal improvements to char yield, the Sorenson and Campbell described novolac from phenol and formaldehyde was selected as the program's baseline novolac.

3.2 CYANATE DERIVATIVES

Cyanate resins without additives provide high char yields as do phenolic resins. Commercially, they are prepared from cyanogen chloride and hydroxy aromatic substrates. Bisphenol A dicyanate is available in solution (methyl ethyl ketone) from Mobay Chemical Corporation as Triazine A Resin. They are conveniently prepared in the laboratory with cyanogen bromide.

The cyanate derivatives of the baseline novolac, 2,7-naphthalene diol and 9,9-bis(4-hydroxyphenyl)fluorene were easily prepared by known procedures. The synthesis of these polyfunctional cyanates is given in the experimental section of this report and their structures are indicated below with their cure method. The triazine ring compound, triphenoxytriazine is obtained from the cyclopolymerization of phenyl cyanate.

After derivatization of the baseline novolac with cyanogen bromide, the novolac-cyanate prepolymer produced was a liquid at room temperature with a viscosity similar to Epon 828 (10,000 cps). The baseline novolac had a melting point of about 80^{O}C. This product is significantly different from that reported in the literature (Reference 4). The literature product describes a novolac resin which when treated with cyanogen chloride provided a product which was acetone soluble, did not have a distinct melting point, softened to a gelatin like material at 175^{O}C, and resolidified again. The difference in the two products may be differences in starting molecular weights of the two novolac prepolymers or possibly a difference in completeness of derivatization with cyanate groups wherein cyanogen bromide was used in our case and cyanogen chloride in their case.

The novolac-cyanate prepolymer had a gel time of 4 minutes at 204^{O}C (400^{O}F) and approximately 2 hours at 100^{O}C (212^{O}F). The material after treatment for three hours at 204^{O}C (400^{O}F) was hard at that temperature suggesting its HDT* would be close to that temperature or slightly above that temperature. Concurrent with the cure of the novolac-cyanate prepolymer, small quantities of 2,7-dicyanatonaphthalene and 9,9-bis(4-cyanatophenyl) fluorene were cured into resins. The gel time of these latter two compounds at 204^{O}C (400^{O}F) were 10 minutes and 25 minutes respectively.

The series of spectra given in Figure 6 show the conversion of the novolac prepolymer to the novolac-cyanate prepolymer and the cure of the novolac-cyanate prepolymer at 204^{O}C (400^{O}F). The first spectrum shows a strong absorption at approximately 3 microns which is attributed to the hydroxyl functionality of the novolac prepolymer. This absorption is essentially

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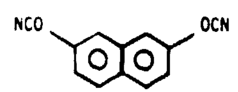
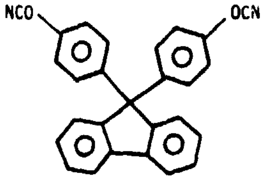
*HDT = Heat Distortion Temperature

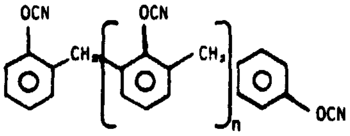
Cyanate Derivatives



2,7-Dicyanatonaphthalene

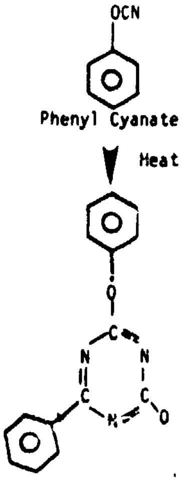


9,9-Bis(4-cyanatophenyl)fluorene



Novolac-cyanate

Cure Method

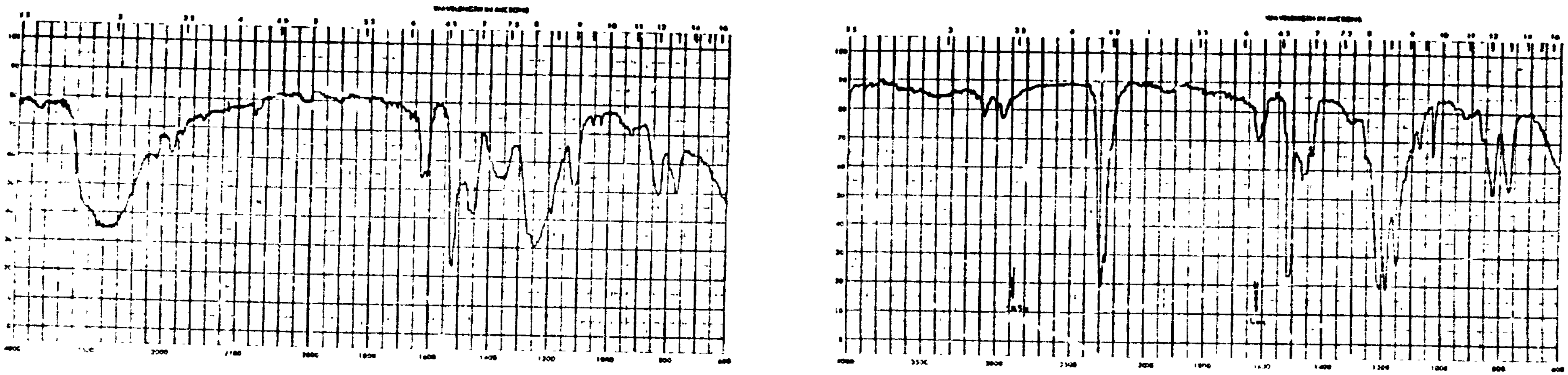


Triphenoxytriaz

absent in the second spectrum of the novolac-cyanate prepolymer and a strong absorption is seen at approximately 4.4 microns which is the cyanate absorption. After 1 hour at 204°C (400°F) the cyanate absorption intensity decreases and a strong absorption is found at approximately 6.4 microns (C=N) as well as an increase in the absorption at ∿12 microns which is attributed to the out of plane C-N stretching of the s-triazine ring (Reference 5). After 3 hours at 204°C little change between the 1 hour and 3 hour spectra is noted suggesting that cure will proceed essentially no further at this temperature probably due to vitrification.

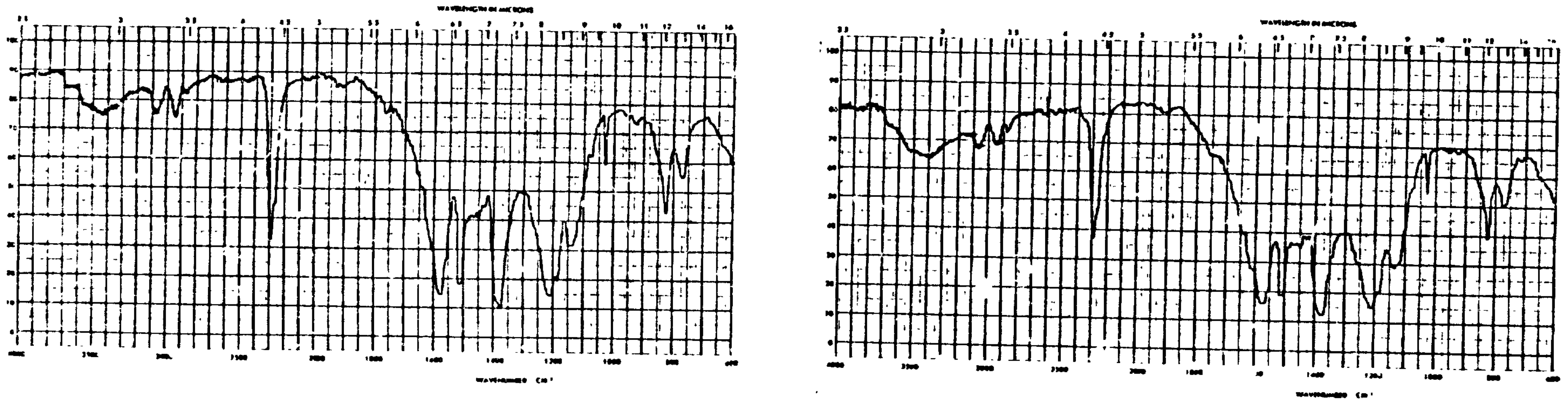
Heating the resin for 1½ hours at 316°C (600°F) caused the sample to turn from light orange to dark brown and resulted in essentially complete loss of the cyanate absorption and at the same time a decrease in the triazine ring vibration at ∿12 microns and in the appearance of carbonyl absorption at approximately 5.9 microns which is attributed to the presence of the isocyanurate structure (Reference 5).

Figure 7 shows DSC scans of the uncured novolac-cyanate prepolymer and this prepolymer cured for 3 hours at 204°C. The scan of the prepolymer shows two peaks, one at 242°C and the other at 415°C. After cure at 204°C two peaks were still evident, however it is clear that much of the first peak has been removed due to cure and the balance of this peak is shifted to higher temperatures.



Phenol-formaldehyde novolac

Novolac-cyanate prepolymer



Novolac-cyanate resin after
1 hour cure at 204°C (400°F)

Novolac-cyanate resin after
3 hour cure at 204°C (400°F)

Figure 6. IR spectra of phenol/formaldehyde novolac, novolac-cyanate prepolymer and novolac-cyanate resin.

Since cure exotherm is yet evident in the 204°C cured samples, it is clear that this system vitrifies prior to complete reaction of the cyanate groups. This was suggested by the spectral series described above. DSC scans of the 2,7-dicyantonaphthalene and 9,9-bis(4-cyantophenyl)fluorene showed very similar behavior.

The anaerobic char yields at 800°C of the three resin systems is given below:

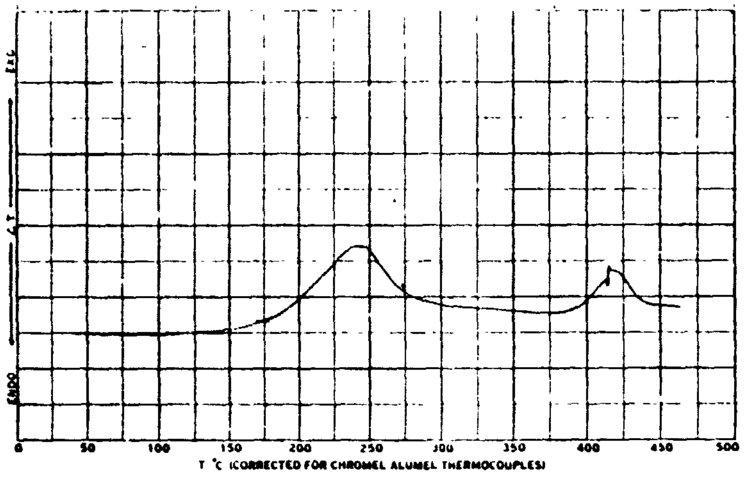
Resin System	Percent Weight Residue
9,9-Bis(4-cyanatophenyl) fluorene	64
2,7-Dicyanatonaphthalene	64
Novolac-cyanate	54

These values compare favorably with the anaerobic char yields at 800°C for the various hexa cured novolacs previously described above. The weight loss curves of the three cyanate resins are given in Figure 8.

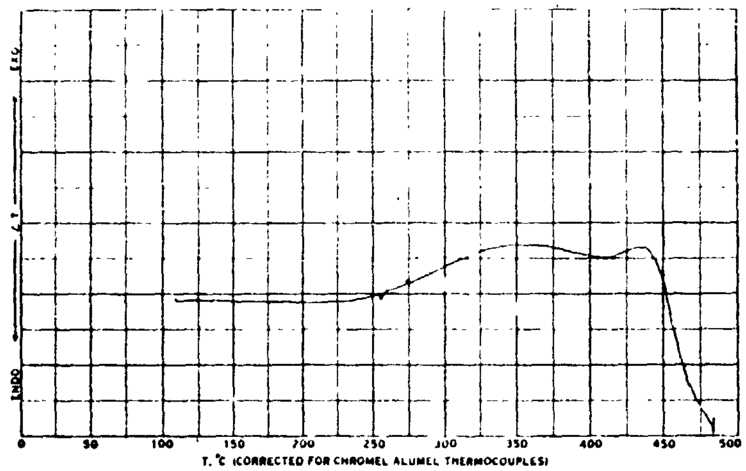
Oxidative weight loss curves are shown for the three resins in Figure 9. The 50 percent weight retention temperatures in air for each of the products is given below:

Resin System	50 Percent Weight Loss Temperature
Novolac-cyanate	530°C
2,7-Dicyanatonaphthalene	558°C
9,9-Bis(4-cyanatophenyl)fluorene	590°C

Both the 2,7-dicyanatonaphthalene and the 9,9-bis(4-cyanatophenyl) fluorene resins show slightly superior oxidative resistance to the novolac-cyanate resin.



Novolac-cyanate Prepolymer (5°C/min.)



Novolac-cyanate Prepolymer after
3 Hours at 204°C (15°C/min.)

Figure 7. DSC Curves of Novolac-cyanate Resin

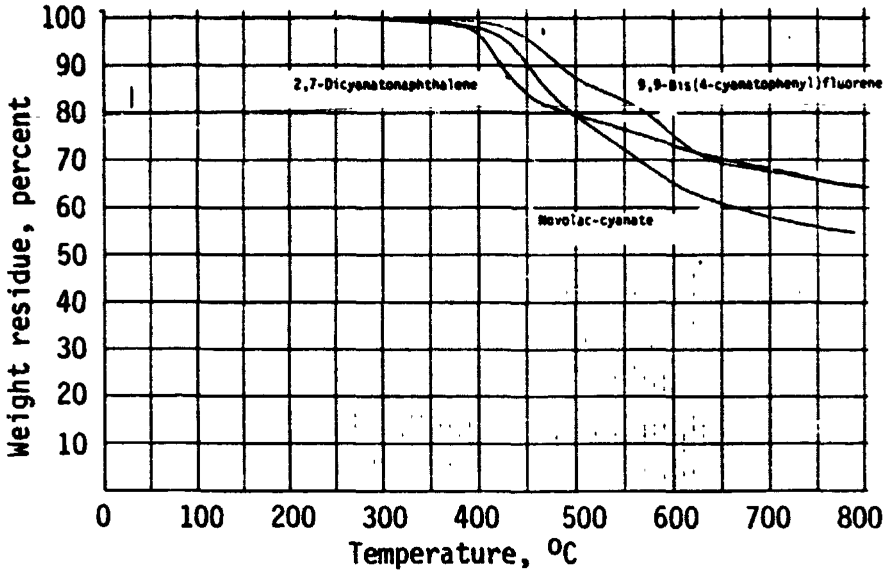


Figure 8. Weight loss curves with temperature of three cyanate resins in nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

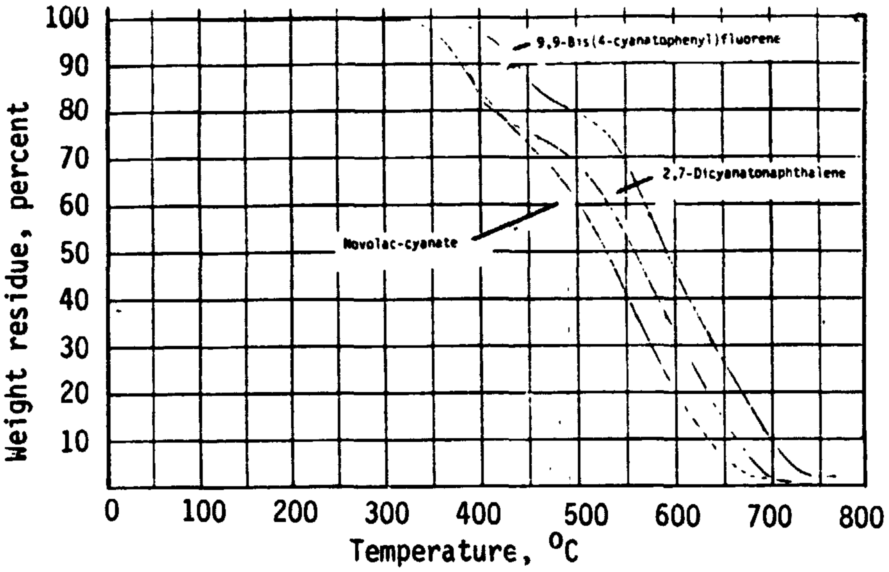


Figure 9. Weight loss curves with temperature of three cyanate resins in static air (15°C/min, -60 mesh).

It was concluded that the cyanato functionality provides char yields expected from phenolic resins (oxidative and non-oxidative conditions). The 9,9-bis(4-cyanatophenyl)fluorene appeared to have slight advantages in oxidative resistance.

DTUL measurements on the three resin systems are presented in Figure 10. The intersection of the expansion and softening curves was the temperature recorded. The three resin systems gave the following DTUL's after 3 hours cure at 204°C:

Resin System	DTUL
Novolac-cyanate	442°C
9,9-Bis(4-cyanatophenyl)fluorene	250°C
2,7-Dicyanatonaphthalene	220°C

The 422°C result obtained for the novolac-cyanate is unusual in that a DTUL only slightly above the cure temperature was expected. The 422°C value obtained is ∿200°C higher than expected. The results obtained for the latter two cyanate resins of 250 and 220°C are consistent with the expected result. The DSC curves presented in Figure 7 for the novolac-cyanate show that reaction must occur during the DTUL measurement, however the sample is capable of supporting the ∿450 psi compressive load throughout the measurement.

It was concluded that all three cyanate resin systems are capable of wide latitude for blending with Tg lowering diluents such as p-nonylphenyl cyanate and are capable of providing composite mechanical performance equivalent to 3501 and 5208 resin systems.

3.3 GLYCIDYL ETHER DERIVATIVES

Glycidyl ether derivatives of novolacs are commercially available and are more commonly known as epoxy novolacs (i.e. DEN 438 from Dow Chemical Company). It was originally thought that if the aromatic content of epoxy resins could be increased through use of resins such as 9,9-bis(glycidyloxyphenyl) fluorene, one would obtain higher char yield epoxy resin systems. As

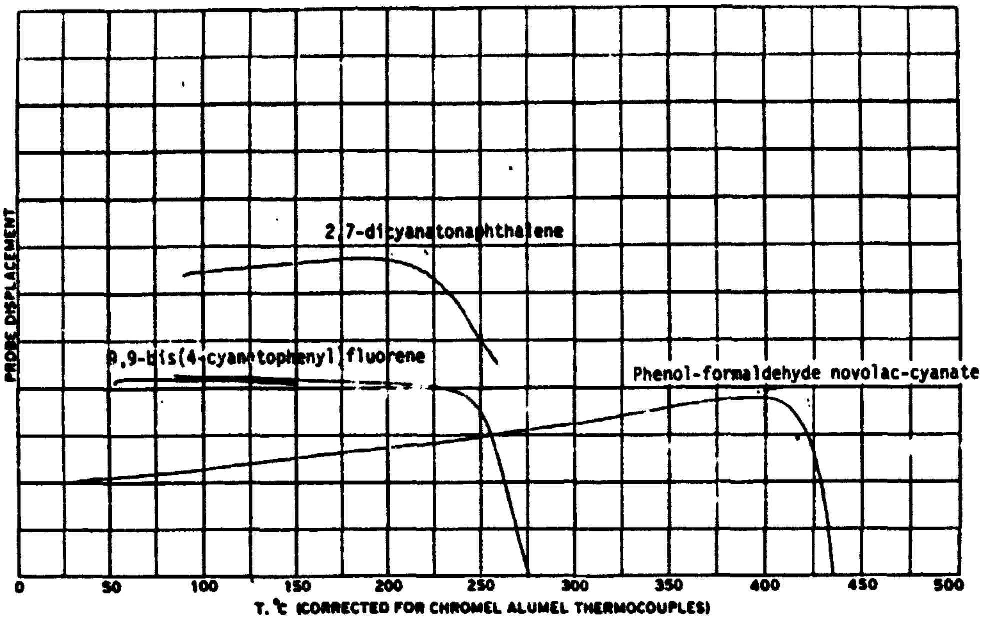


Figure 10. DTUL of cyanate resins cured at 204°C (15°C/min).

discussed below this proved to not be the case. However, one additive proved useful for increasing the char yields of epoxy resins. Further pretreatment of two epoxy resins in air at high temperatures was also found to increase their char yield. A 59 percent anaerobic char yield was obtained from DEN 438 through use of an additive in combination with oxidative pretreatment. The detailed investigation of glycidyl ether derivatives is discussed below.

Anaerobic char yields for several epoxy resins are shown in Figure 11. Anaerobic char yields at 800°C are seen to vary from 13 to 33 percent.

Table 3 gives the calculated total carbon atom contents, the aromatic carbon atom contents and the Y_c^{800*} values of the resins shown in Figure 11. Even though the carbon atom content of all of the systems is in excess of 64 percent, the aromatic carbon atom content of the systems is much less ranging from 27.2 to 45.2 percent.

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*Y_c^{800} = Char yield at 800°C.

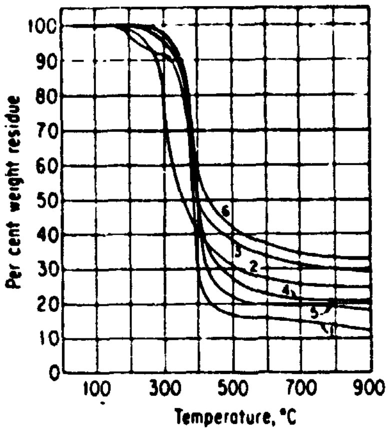
TABLE 3. CALCULATED CARBON ATOM CONTENTS OF EPOXY RESINS SHOWN IN FIGURE 11.

Number	Resin System	Carbon, Percent	Aromatic Carbon, Percent	Y_c^{800}, Percent
1	DGEBA + PA(A/E = 1/1)	69.8	45.2	13
2	DGEBA + CA(A/E = 1/1)	43.3	13.3	25
3	Tetraglycidyl ether of tetraphenylethane + 1 phr BF_3MEA	73.5	46.5	30
4	DGEBA + PMDA (A/E = .5/1)	69.8	41.1	21
5	DGEBA + MA(A/E = 1/1)	64.9	27.2(35.8)*	18
6	Tetraglycidyl ether of tetraphenylethane + MA(A/E = 1/1)	64.0	28.5(37.8)*	33

*Includes two doubly bonded carbon atoms of maleic anhydride (MA).

DGEBA systems show char yields varying from 13 to 25 percent. The two resins based on the tetraglycidyl ether of tetraphenylethane show char yields of 30 and 33 percent. For the very useful glycidyl ether derivatives of novolacs or other compounds to provide our program target of 50 percent char yield, improvements in the aromatic content of such systems appeared to be a key.

Table 4 gives the calculated total carbon atom contents and the aromatic carbon atom contents of several hypothetical polymers. The glycidyl derivatized phenol-formaldehyde has only a 44.4 percent aromatic carbon content and would not be predicted to give a 50 percent char yield as well as most of the other structures shown. Of the addition cureable resin systems shown, only the 9,9-bis(4-glycidyloxyphenyl)fluorene has an aromatic carbon content (64.9 percent) equivalent to the phenol-formaldehyde polymer (64.3 percent). It was surmised that most available epoxy resins will not provide a 50 percent char yield at 800°C.



Weight residue of cured epoxy resin heated at a rate of 150°C per hour. (1) DGEBA + PA (A/E = 1/1); (2) DGEBA + CA (A/E = 1/1); (3) tetraglycidyl ether of tetraphenyl-ethane + 1 phr BF_3MEA; (4) DGEBA + PMDA (A/E = 0.5/1); (5) DGEBA + MA (A/E = 1/1); (6) tetraglycidyl ether of tetraphenylethane + MA (A/E = 1/1).

Figure 11. Typical char yields of epoxy resins (from Reference 6).

The above analysis suggested that very high aromatic carbon atom contents might be designed into useful epoxy resin systems and also lead to char yields equivalent to phenolics. As discussed below, this was found not to be the case.

A number of epoxy novolac resin/curing agent combinations were investigated. In addition the epoxy of the 9,9-bis(4-hydroxyphenyl)fluorene was prepared and cured with a novolac resin. The investigation focused on phenolic cured and amine cured epoxy formulations even though Lewis acid and anhydride cured formulations would have led to different char yield results. (These later two cure possibilities for the epoxy novolacs exhibit some moisture sensitivity and would be difficult to formulate into a moisture insensitive stable B-stage resin system.)

TABLE 4. CALCULATED CARBON ATOM CONTENTS OF SEVERAL POLYMER STRUCTURES

Polymer System	Carbon, Percent	Aromatic Carbon. Percent
Phenol-formaldehyde phenolic	80.4	64.3
Allyl derivatized phenol-formaldehyde novolac	82.2	49.3
Glycidyl derivatized phenol-formaldehyde novolac*	74.1	44.4
9,9-bis(4-hydroxyphenyl)fluorene-formaldehyde phenolic	85.7	82.3
9,9-bis(4-glycidyloxyphenyl)fluorene*	80.5	64.9**
Bisphenol A-formaldehyde phenolic	81.0	57.1
Glycidyl derivatized bisphenol A-formaldehyde novolac*	75.8	39.6

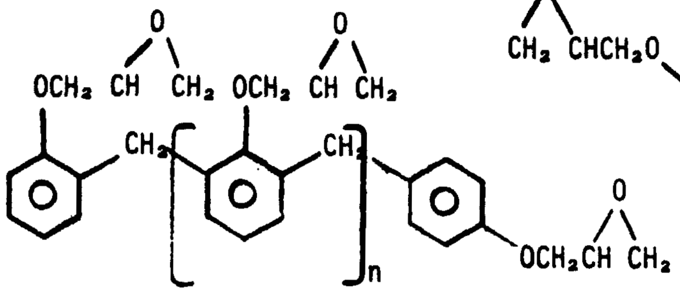
Note: The phenolic resins shown release volatiles upon cure.
*Homopolymerized with catalyst such as BF_3
**Includes geminal carbon atom

Table 5 gives the resin formulations investigated for char yield demonstration. In addition to the polyhydroxyaromatic cured compositions and the amine cured compositions, a small percentage of AA 406 resin was added to two of the formulations to investigate char yield benefits of this additive for these resins. The baseline novolac was used. The structures of DEN 438 and 9,9-bis(glycidyloxyphenyl)fluorene are given below.

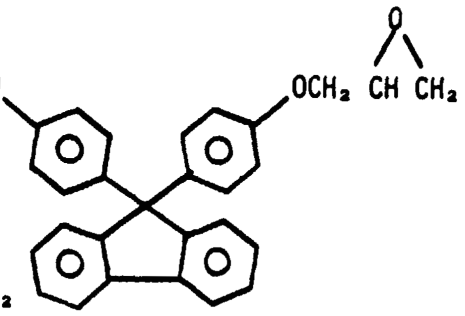
Attainment of small cast samples was expedited by use of a small quantity of solvent. After the solvent was removed gently on a hot plate, the samples were placed in a 120°C oven for gel for one hour at 120°C. The samples were then cured for one hour at 150°C and finally for three hours at 204°C. All of the systems with the exception of Number 6 (DEN 438/2,7-dihydroxynaphthalene) were hard to spatula probe at the 204°C final cure temperature. The resin systems after cure, upon cooling to room temperature, all exhibited difficulty to grind such as seen with state-of-the-art epoxy resin systems, except for System Number 3 (DEN 438/novolac/AA 406) which exhibited only moderate toughness.

TABLE 5. EPOXY RESINS INVESTIGATED FOR CHAR YIELD

Resin System (Parts by Weight, Resin-Hardener)	Epoxy Equivalents/Amine or Hydroxy Equivalents	Comments
1. DEN 438/9,9-bis(4-hydroxyphenyl) fluorene (50/50)	1/1	1 phr BDMA, casting from MEK, ~15 minute gel time at 120°C.
2. DEN 438/novolac (mp 80°C) (62/38)	1/1	1 phr BDMA, casting from MEK, ~30 minute gel time at 120°C.
3. DEN 438/novolac (mp 80°C)/AA 406 (62/24/14)	1/1	1 phr BDMA, casting from MEK, ~30 minute gel time at 120°C.
4. 9,9-bis(4-glycidyloxyphenyl)fluorene/ novolac (mp 80°C) (69/31)	1/1	1 phr BDMA, casting from MEK, ~25 minute gel time at 120°C.
5. 9,9-bis(4-glycidyloxyphenyl)fluorene/ novolac (mp 80°C)/AA 406 (69/15.5/15.5)	1/1	1 phr BDMA, casting from MEK, ~15 minute gel time at 120°C.
6. DEN 438/2,7-dihydroxynaphthalene (68/32)	1/1	1 phr BDMA, casting from MEK, ~15 minute gel time at 120°C.
7. DEN 438/4,4'-diaminobenzophenone	1/0.7	Casting from THF, ~1 hour gel time at 120°C.
8. 9,9-bis(4-glycidyloxyphenyl)fluorene/ 4,4-diaminobenzophenone (86/14)	1/0.7	Casting from THF, ~1 hour gel Time at 120°C.



DEN 438 (Epoxy novolac)



9,9-Bis(4-glycidyloxyphenyl)fluorene

Gel times of the BDMA catalyzed hydroxy reaction with the epoxy resins are short, however, this is adjustable with catalyst concentration. The gel times of the two amine cured compositions (Systems Numbers 7 and 8) were approximately one hour at 120°C. The amine compositions did not provide complete solubility of the 4,4'-diaminobenzophenone curing agent even after final cure at 204°C. Small quantities of this curing agent which crystallized from the tetrahydrofuran (THF) resin mixture upon THF removal did not redissolve upon cure.

The anaerobic char yields of the eight systems were measured and are given in Table 6.

Even though both the carbon atom and aromatic carbon atom contents were much higher in these epoxy resin systems as shown in Table 6 than those shown in Table 3, significant increases in the char yields were not obtained except for Systems 3 and 5 which contained the AA 406 resin. It was concluded that higher aromatic content in epoxy resins per se does not improve their char yield. If chemistry of char formation is changed however as seen with AA 406 systems, aromatic content of the starting epoxy resin may be important as

TABLE 6. ANAEROBIC CHAR YIELD OF EPOXY NOVOLACS

System Number	Percent Carbon Atom Content		Y_c^{800}, Percent
	Total	Aromatic	
1	80.1	65.9	27
2	76.1	53.7	33
3*	72.8	53.8	47
4	79.6	65.5	25
5*	75.9	63.9	39
6	74.3	54.5	20
7	73.9	51.9	34
8	79.5	65.4	22

*Contains 15 percent AA 406 by weight.

evidenced by the nearly 50 percent char yield obtained with System 3.

The char yield curves of the four polyhydroxyaromatic cured epoxy resins are given in Figure 12 (Systems 1, 2, 4 and 6 from Table 5). T^*_d onset for these four systems is seen to vary between about 403°C and 408°C. After T_d onset a precipitous weight loss occurs in all of the systems, however, the Number 2 system (DEN 438/novolac/BDMA) is found to give a less precipitous weight loss curve as well as a higher final char yield. These results appear to indicate that large aromatic fragments are easily lost from these resins. When the novolac skeletal backbone is present however, such as with the novolac curing agent in combination with the DEN 438, the system is better able to provide char. The 33 percent char yield (System 2) is the best of the four resin compositions even though its aromatic carbon content is the lowest of the four at 53.7 percent based on hypothetical structure (see Table 6).

$*T_d$ - Decomposition temperature.

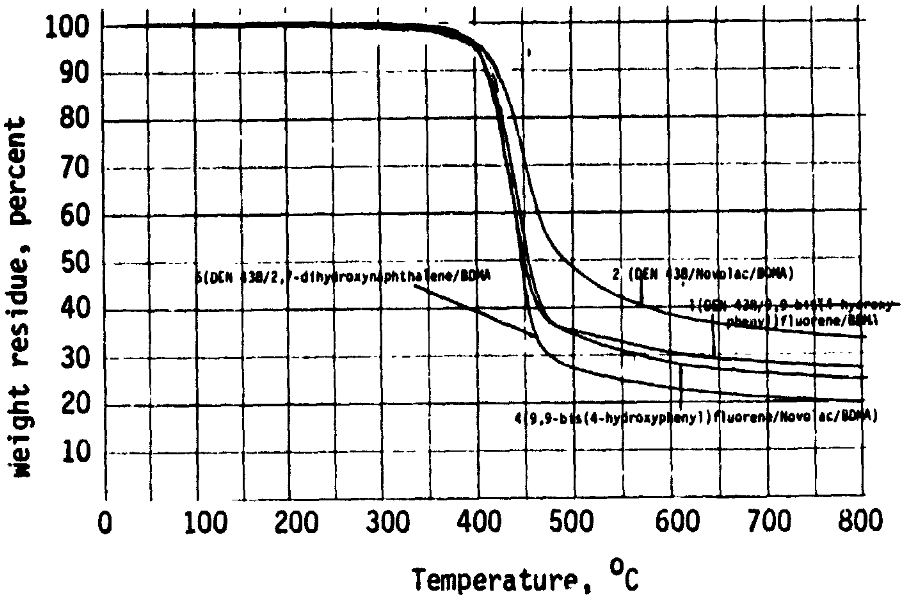


Figure 12. Weight loss curves of four epoxy resins in nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

When a small portion of the novolac curing agent is replaced with the AA 406 resin system,maintaining hydroxy cure, the char yield of the system is greatly increased. These char yield curves are given in Figure 13. Fourteen percent increases in char yield percentage points at 800°C are exhibited by the two epoxy resin systems which had about 15 percent of the AA 406 resin in their final formulations. As shown in Table 5, these formulation pairs have essentially the same quantity of epoxy resin and only a portion of a novolac curing agent was replaced by the AA 406 resin. These resin pairs are System Numbers 2 and 3 for DEN/438 resin and 4 and 5 for the 9,9-bis(4-glycidyloxyphenyl)fluorene resin.

T_d onset temperatures for the AA 406 modified epoxy resin formulations are significantly lower than for the unmodified resins. T_d onset temperatures as seen in Figure 13 for the two AA 406 modified resins are 366 and 373°C. This approximately 40°C decrease in T_d onset temperatures from the unmodified

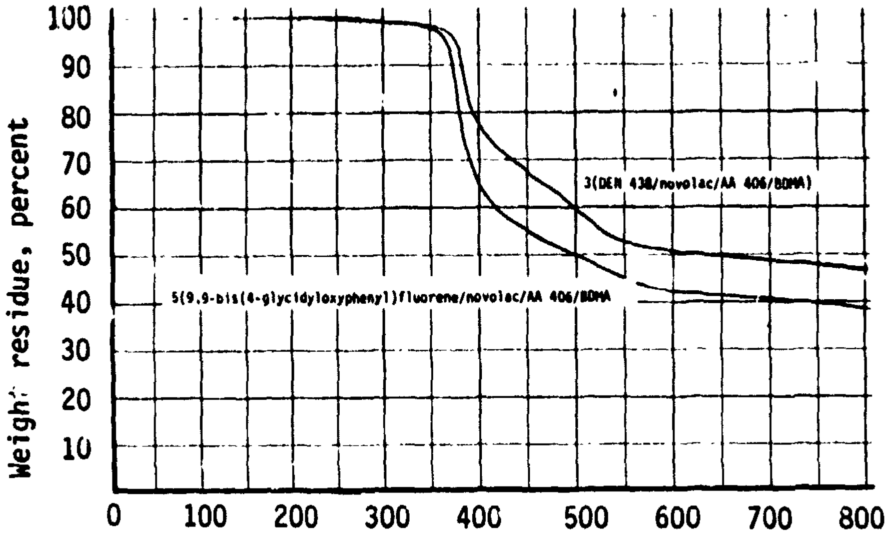


Figure 13. Weight loss curves of two epoxy resins blended with AA 406 in nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

resins (shown in Figure 12) is attributable to decomposition of the AA 406 resin system. As seen with the allyl novolacs which are discussed later, this decomposition becomes involved in the char chemistry and leads to improved anaerobic char yields.

The two TGA curves for the amine cured epoxy resins (Systems 7 and 8) are given in Figure 14. T_d onset temperatures are intermediate between the AA 406 blended phenolic cured resins and the bisphenol cured resins. They are 382° and 391°C. The rapid resin weight loss slope is slightly reduced for the DEN 438 resin compared to the 9,9-bis(4-glycidyloxyphenyl)fluorene resin. This is attributed to the rapid loss of large aromatic fragments from resin System 8 and the higher concentration of novolac skeletal contribution to the System 7 composition wherein 83 percent of DEN 438 was used. The contribution (negative or positive) of the diaminobenzophenone moiety to char yield is not clearly decipherable from Figure 14.

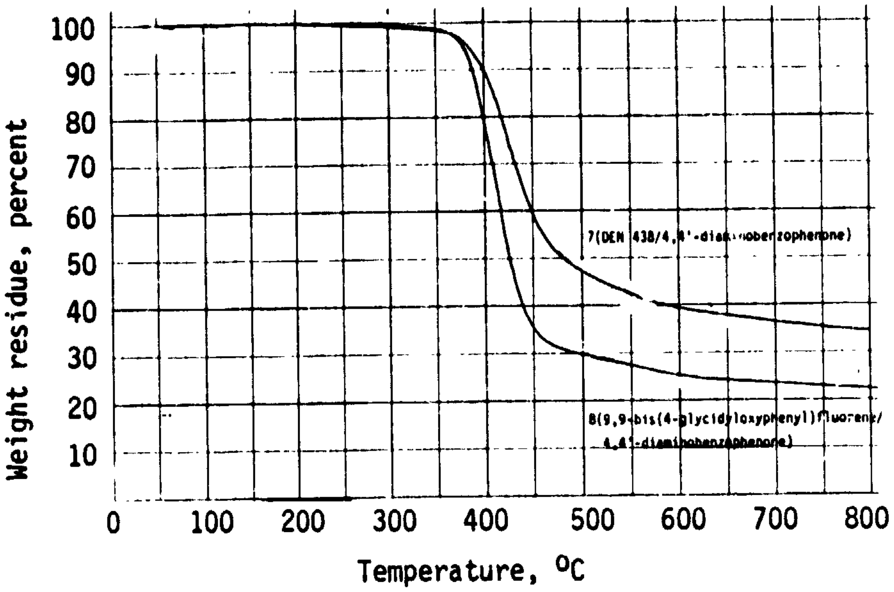


Figure 14. Weight loss curves of two amine cured epoxy resins in nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

TGA studies in both static and flowing air were carried out on several powdered (-60 mesh) epoxy resin compositions. The test results presented below are both interesting and provocative. They should be studied in greater depth.

The brief study discussed in the next few paragraphs was prompted by the results obtained and given below where static air char yields at 800°C were observed to be higher than those obtained in nitrogen for two epoxy compositions. In one case a 20 percentage point increase was observed.

Epoxy Resin Composition	Y_c^{800}/N_2, Percent	Y_c^{800}/Air, Percent
DEN 438/diaminobenzophenone	34	54
DEN 438/novolac/AA 406	47	48
DEN 438/novolac	33	19

Implicit in these results is the formation of a more thermally stable char in air testing than is obtained in nitrogen testing resulting from resin oxidation or the influence of oxygen on char chemistry to provide the more thermally stable char. The 54 percent char yield at 800°C for an epoxy resin was far in excess of typically reported values for epoxy resins (see Table 3).

The first study conducted was investigation of the relationship between resin sample size and measured weight loss curves in static air. ne compositions studied were the epoxy novolac (DEN 438) cured with the novolac and DEN 438 cured with the novolac and the AA 406 resin. These results are presented in Figures 15 and 16 respectively. Sample size is clearly related to the weight loss curves obtained. The higher the sample weight, the slower the sample loses weight in static air with increasing temperature. In the case of the DEN 438/novolac resin system, the 17.4 mg sample upon removal from the platinum boat was a free flowing powder. With the DEN 438/novolac/AA 406 resin system (18.8 mg sample) very slight fusion occurred. Very slight spatula pressure returned the sample to its powdered form. All of the curves in Figure 16 when compared to their closest weight counterparts in Figure 15 show lower weight losses, indicating benefit for the AA 406 additive in these tests.

Flowing air weight loss curves on the DEN 438/novolac/AA 406 resin system were determined. Air flow through the TGA cell was one standard cubic foot per hour (1 SCFH*). Sample size did not affect the shape or the weight residue at a specified temperature significantly as shown in Figure 17. The 3.16 mg sample is seen to lose weight slightly slower than the 17.00 mg sample. A repeat of this experiment with 5 and 18 mg samples gave essentially the same results.

The aerobic char yield curves present a striking feature. At 400° and 500°C, the curves all show higher weight retentions than their anaerobic counterparts as shown in Figure 17. Even in completely molten polymer samples the polymer would be expected to lose weight at approximately its rate of anaerobic weight loss since anaerobic weight loss is indicative of basic polymer stability. This behavior is unlike anaerobic char yield curves

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*1 SCFH $\approx$ 0.5ℓ/min

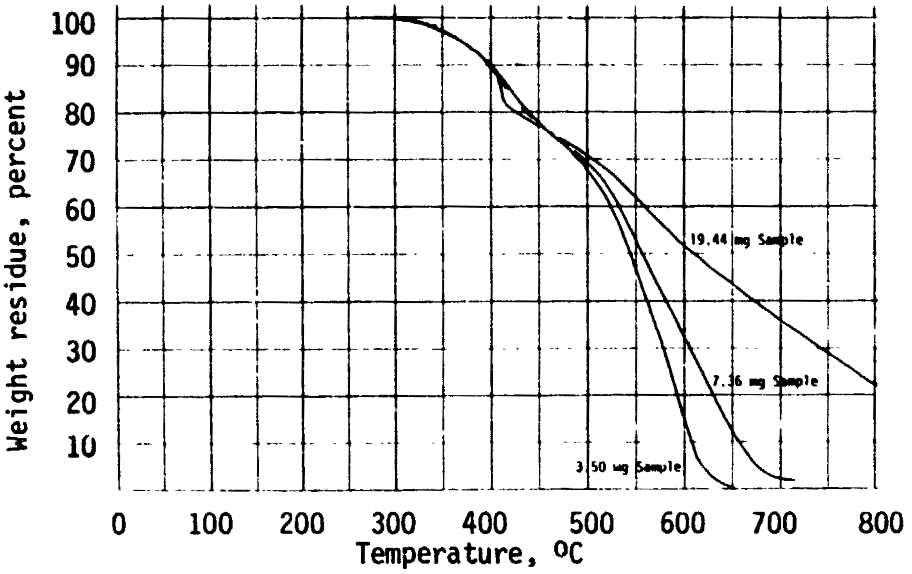


Figure 15. Weight loss curves of epoxy novolac/novolac resin in static air (15°C/min, -60 mesh).

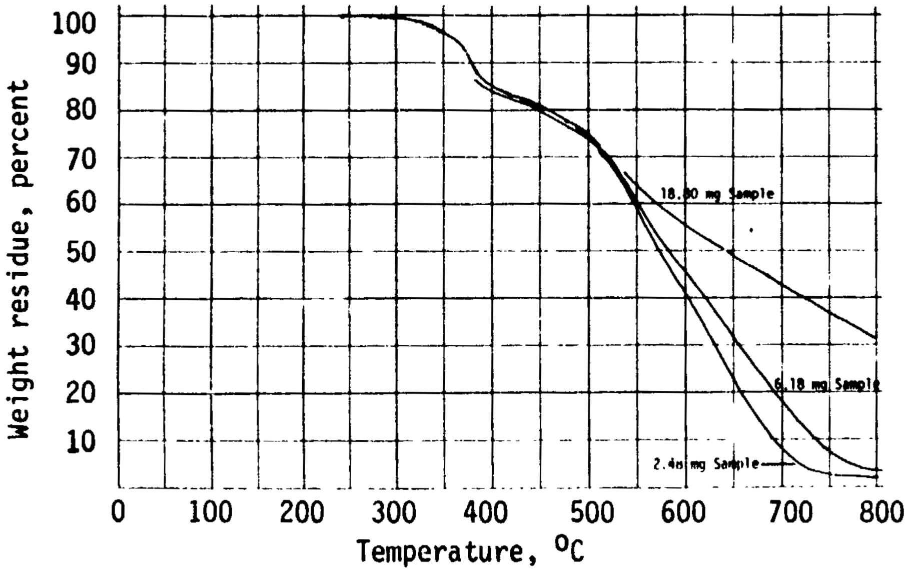


Figure 16. Weight loss curves of epoxy novolac/novolac/AA 406 resin in static air (15°C/min, -60 mesh).

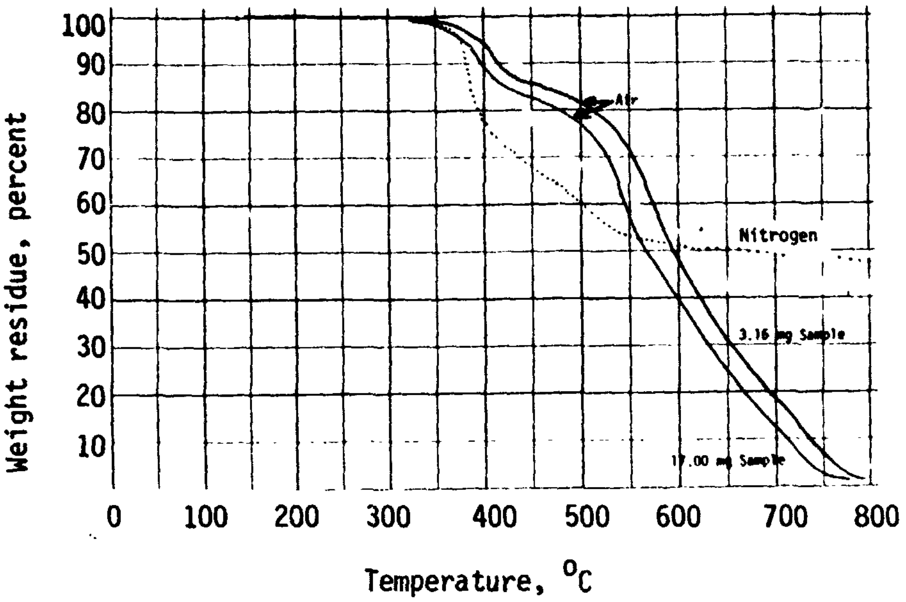


Figure 17. Weight loss curves of epoxy novolac/novolac/AA 406 resin in flowing air and nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

generated to date and as previously mentioned the bulk of oxidative char yield curves reported in the literature.

Next, both the DEN 438/novolac/AA 406 and the DEN 438/diaminobenzophenone resin systems were subjected to a combination nitrogen-air TGA analysis to demonstrate the apparent benefits of oxygen in increasing char yields obtained at 800°C. Accordingly, flowing air at one SCFH was used to maintain an oxidative environment in the TGA cell up to approximately 400°C and the pen was lifted from the chart paper while nitrogen was introduced at one SCFH. Upon pen stabilization, the pen was lowered to the chart paper to record the remainder of the TGA under nitrogen. Figures 18 and 19 show the results of these experiments on the two resin systems. A 59 percent char yield at 800°C was obtained for the DEN 438/novolac/AA 406 resin system

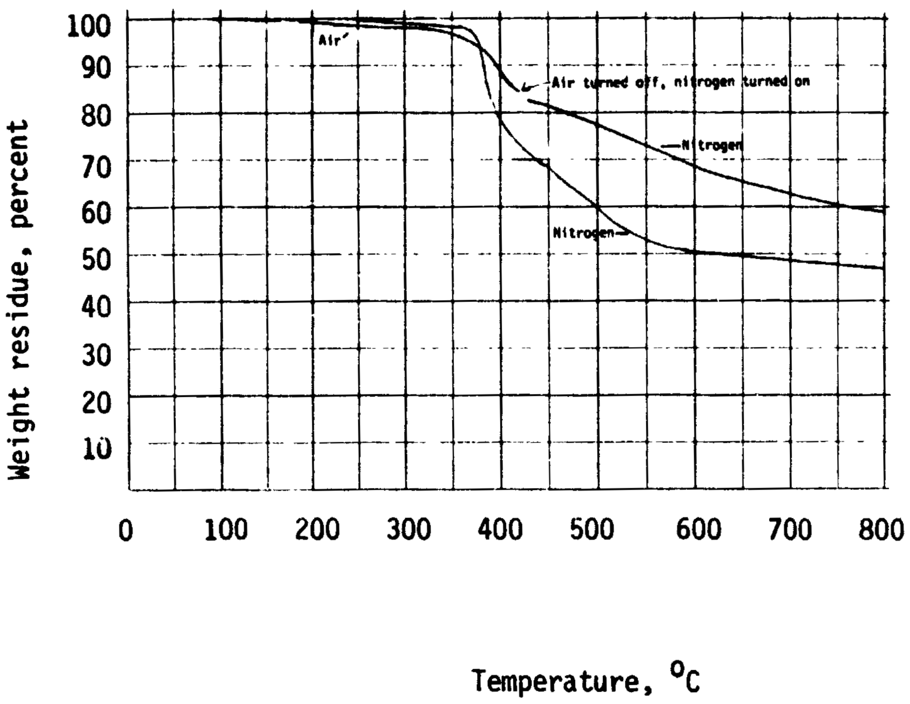


Figure 18. Weight loss curves of DEN 438/novolac/AA 406 Resin in air/nitrogen and nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

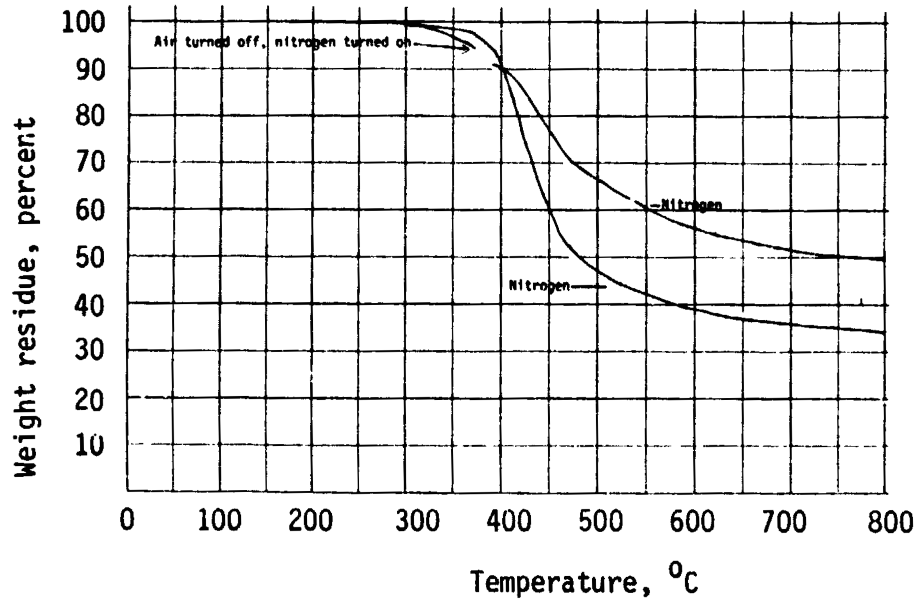


Figure 19. Weight loss curves of DEN 438/4,4'-diaminobenzophenone in air-nitrogen and nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

and a 49 percent char yield for the DEN 438/diaminobenzophenone resin system. (The former system was still powder at the end of this test whereas the later system was isolated as a single lump of char which required only mild spatula pressure to repowder.)

The anaerobic curves for the two systems are given in each figure for comparison. Char yield benefit for the oxidative pretreatment is seen to be 12 percentage points in Figure 18 and in Figure 19, 15 percentage points. It is presumed that all of the 800°C chars contain some amount of oxygen and a higher oxygen content is expected for the air-nitrogen chars than in the chars obtained in nitrogen alone. Oxidative weight gain per se however, would require the addition of 31 percent of this element to the DEN 438/4,4'-diaminobenzophenone resin system. $[(49-37) \div 49 = 0.31]$

Figure 20 shows the results of the air-nitrogen combined TGA atmosphere on a non-novolac epoxy resin. MY720 (94 parts)/diglycidyl aniline (6 parts)/ 4,4'-diaminobenzophenone (39 parts) after 204°C cure was ground to pass a 60 mesh screen and subjected to TGA testing. The anaerobic char yield was 27 percent and the combined air-nitrogen char yield was 41 percent. It appears as if the novolac structure per se is not required to obtain benefit from the oxidative pretreatment.

DTUL measurements were carried out on the epoxy resins given in Table 5. These results are given in Table 7. Improvements in the values shown are required to match state-of-the-art 176°C (350°F) performing epoxy systems with the possible exception of the 4,4'-diaminobenzophenone cured DEN 438 system.

In summary, it is clear why epoxy resins are known as a class to not be high char yield producers. The basic instability of the ether linkage apparently allows for large molecular fragments such as phenols and possibly even the starting bisphenol raw material to be lost from normal epoxy resins. Epoxy novolacs however were coaxed into producing a 59 percent char yield at 800°C (anaerobic). Although this char yield is not as good as the best bisphenol-cyanate (anaerobic char yield of 64 percent at 800°C), the oxidative weight loss curve of the best epoxy novolac resin showed a 50 percent weight

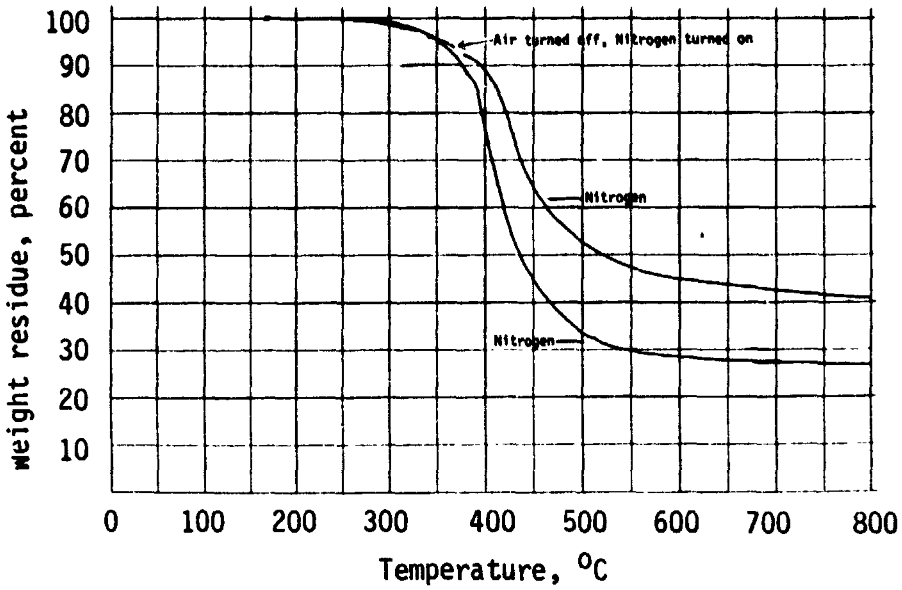


Figure 20. Weight loss curves of MY720/diglycidylaniline/4,4'-diaminobenzophenone in air-nitrogen and nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

TABLE 7. DTULs OF EPOXY RESIN SYSTEMS

Resin System (Parts by Weight)	DTUL, °C
1. DEN 438/9,9-bis(4-hydroxyphenyl) fluorene (50/50)	122
2. DEN 438/novolac (mp 80°C) (62/38)	150
3. DEN 438/novolac (mp 80°C)/AA 406 (62/24/14)	143
4. 9,9-bis(4-glycidyloxyphenyl)fluorene/ novolac (mp 80°C) (69/31)	163
5. 9,9-bis(4-glycidyloxyphenyl)fluorene/ novolac (mp 80°C)/AA 406 (69/15.5/15.5)	Insufficient Sample
6. DEN 438/2,7-dihydroxynaphthalene (68/32)	114
7. DEN 438/4,4'-diaminobenzophenone (83/17)	234
8. 9,9-bis(4-glycidyloxyphenyl)fluorene/ 4,4'-diaminobenzophenone (86/14)	155

TABLE 7. DTULS OF EPOXY RESIN SYSTEMS

retention in flowing air at 580°C. This temperature is only slightly lower than the best bisphenol-cyanate (590°C).

3.4 ACRYLATE ESTERS OF GLYCIDYL ETHER DERIVATIVES

A commercially available novolac prepolymer suitably derivatized for addition cure was evaluated. The product, Dow's Derakane 470-36 is an epoxy novolac (DEN 438) reacted with methacrylic acid and diluted with 36 percent by weight styrene. The unsaturated polyester industry refers to this novolac containing product as well as the Bisphenol A based products from both Dow and Shell as "vinyl esters." The Shell product, Epocryl 12 (Bisphenol A based) was found to have no anaerobic char yield at 800°C in nitrogen. This product was evaluated on the synthesis of Improved Polyester Resins Program (NAS3-21374).

For comparative purposes the vinyl ester resin of DEN 438 with acrylic acid was also prepared. Its preparation is given in the experimental section of this report and its structure indicated in Table 8.

Three resin samples were prepared for TGA and DTUL characterization. They are shown in Table 8. The high weight loss data obtained during cure of the resins is indicative of styrene lost by conducting the polymerizations under high vacuum in their early stages. Complete styrene removal was probably not achieved prior to gel. The Derakane resin lost 31 percent of its weight through polymerization (36 percent by weight styrene added by the manufacturer). The acrylate based vinyl esters showed weight losses in excess of the quantity of styrene added probably due to resin loss from the cure cup by spattering during styrene removal. Infrared spectra showed essentially complete polymerization of the acrylate unsaturation through final cure as indicated in Figure 21.

Anaerobic TGA determinations provided char yields at 800°C as shown in Table 8. The char yield values shown are consistent with the novolac contents of the vinyl ester resin systems. Addition of the AA 406 resin to the acrylate derivatized epoxy novolac increased the char yield of that system 18 percentage points to give a Y_c^{800} value of 47 percent.

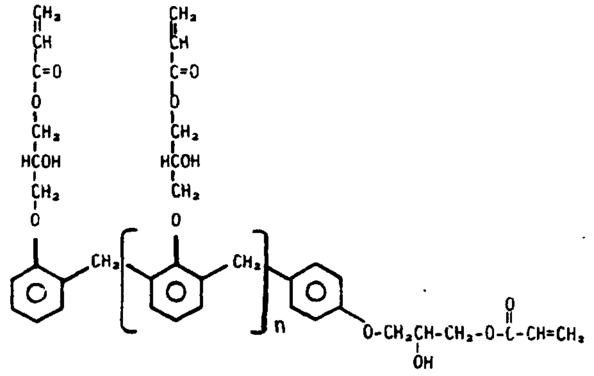
TABLE 8. VINYL ESTER RESIN SAMPLES FOR TGA AND DTUL CHARACTERIZATION

	Final Cure Condition	Total Weight Loss Through Final Cure, Percent	Loss from 80°C Through Final Cure, Percent	Percent Novolac Structure	$Y_c^{800}(N_2)$
Derakane 470-36	2 hrs @ 204°C	31.0	0.0	40.2	19%
Epoxy novolac-acrylate	4 hrs @ 190°C	41.6	5.3	45.5	27, 29%
Epoxy novolac-acrylate/AA 406 80 parts/20 parts	4 hrs @ 190°C	21.8	3.6	----	47%

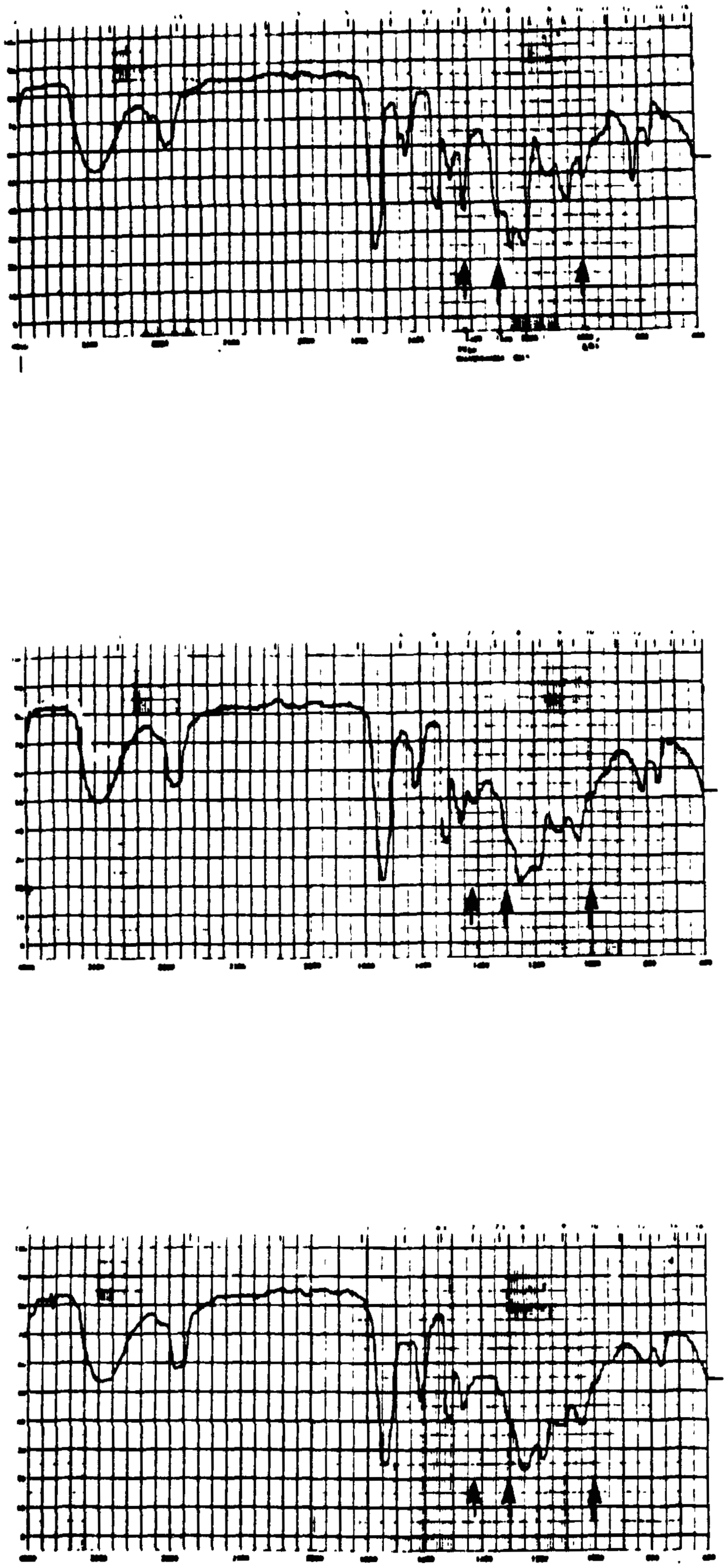
Notes: 1) All three samples catalyzed with 1.5 phr (benzoyl peroxide) plus 1.5 phr cumene hydroperoxide.

2) Polymerizations conducted with slowly increasing temperatures through 200°C. Polymerizations conducted under vacuum to 80°C then at atmospheric pressure under nitrogen. (Vacuum used to remove as much styrene as possible prior to gel.)

3) Gel occurred in the Derakane resin at 80°C, in the acrylate resin at 120°C and in the AA 406 modified acrylate resin at about 140°C.



Idealized structure of vinyl ester resin of DEN 438 with acrylic acid.



At $60^{o}C$ and after most of styrene removal.

After gel when temperature reached $160^{o}C$.

After 4 hours at $190^{o}C$.

Note: ↑ = $-CH=CH_2$

Figure 21. Infrared spectra of the acrylate ester of DEN 438 through cure.

These results clearly demonstrate the benefit of the novolac structure to provide char and further the use of the additive, AA 406 to provide nearly the program's target char yield of 50 percent with a polyester type resin.

DTUL measurements of the cured Derakane 470-36 and epoxy novolac-acrylate resins provided initial softening, expansion and finally penetration at about 350°C. This behavior is depicted in Figure 22. Curve Number 1 seen in Figure 22 shows the behavior of the epoxy novolac-acrylate resins. The Derakane 470-36 sample was removed from the TMA apparatus after exposure to 255°C, inspected for indentation under the microscope (Curve 2) and rerun until penetration occurred at 367°C (Curve 3). Examination under the microscope showed no permanent indentation had occurred. This type of behavior is discussed in a subsequent section of this report. DTUL measurement of the epoxy novolac-acrylate/AA 406 system gave a DTUL of only 97°C.

The prognosis for use of the Derakane 470-36 or vinyl ester type resins for the present application is good if additives such as the AA 406 could be developed to provide higher char yields. The potential processing of these resins into high quality graphite compositions appeared good. Although gel onset is quite rapid which could make pressure application schedules during composite fabrication tedious, the large number of catalysts and promoters available should provide adequate latitude for retardation of gel onset and/or gel rate as required.

3.5 ALLYL ETHER DERIVATIVES

Allylic cure represents another possible method to achieve addition cured phenolics. Due to the instability of the allyl group and degradative chain transfer which occurs during polymerization only a few allyl systems are important commercially, i.e., diallyl phthalate, triallyl cyanurate, and diethylene glycol bis(allyl carbonate). One method to introduce allyl groups into phenolic resins is through derivatization of the phenolic hydroxyl group with an allyl halide to obtain an allyl ether. The allyl ether can then subsequently rearrange (Claisen rearrangement) or polymerize. These reactions are sketched below.

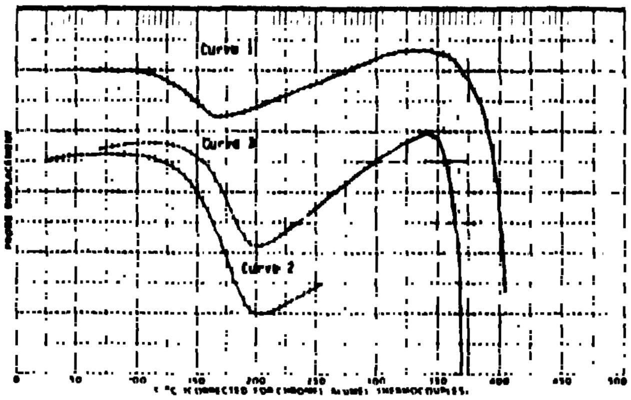
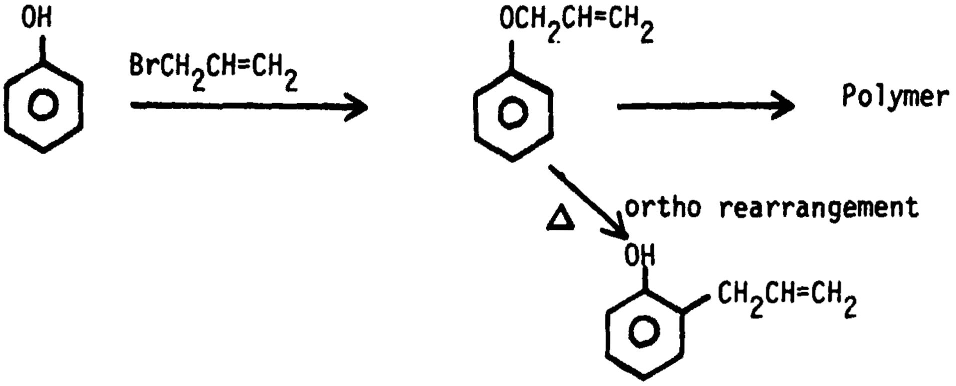
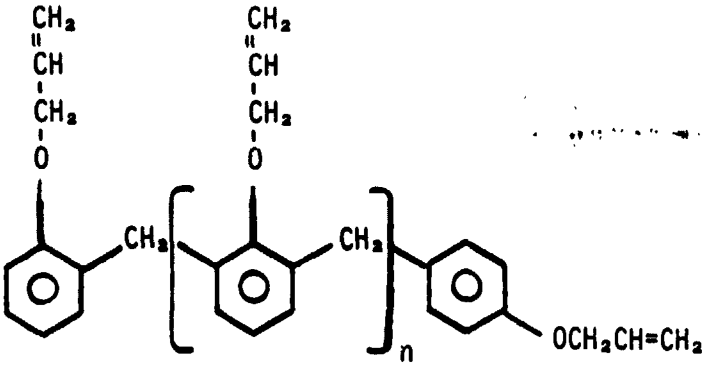


Figure 22. DTUL curves of cured Derakane 470-36 and the acrylate ester of DEN 438.



The allyl ether derivatives of the baseline novolac (mp 80°C), 9,9-bis(4-hydroxyphenyl)fluorene and 9,9-bis(3,5-dimethyl-4-hydroxyphenyl) fluorene were easily prepared by the procedure described by Hurd and Yarnall (Reference 7). The preparative procedures for these compounds are given in the experimental section of this report. The allyl novolac was obtained in approximately a 63 percent yield and was a liquid with a viscosity similar to that Epon 828 (10,000 cps). Its structure is indicated below. The 9,9-bis(4-allyloxyphenyl)fluorene was obtained in an 86 percent yield and was a low melting glass (∿35°C). The 9,9-bis(3,5-dimethyl-4-allyloxyphenyl) fluorene was prepared in an 84 percent yield and had a melting point of 182°C.



Allyl novolac structure

The three allyl derivatives were combined with the peroxides shown in Table 9 at 5 phr*.

The catalyzed samples were cured for two hours at 160°C and for one hour at 200°C. Since allyl is known to air cure these experiments were conducted under nitrogen. All three resin systems were soft to spatula probe at the end of the two hour cure at 160°C. At the end of the one hour cure at 200°C, the catalyzed allyl novolac and 9,9-bis(4-allyloxyphenyl)fluorene samples were hard under spatula probe at 200°C. The 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene sample (catalyzed) was still soft to spatula probe at 200°C at the end of the one hour at 200°C treatment. Vulcup R seemed to be slightly more effective relevant to obtaining harder samples at the end of the 160°C treatment however, the differences were not significant.

The allyl novolac system after treatment at 200°C and cooling to room temperature had properties similar to an epoxy resin in that it was difficult to grind and pulverize whereas the products from the 200°C treated 9,9-bis(4-allyloxyphenyl)fluorene and the 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene were brittle and easily ground suggesting no polymer or only very low molecular weight polymer formation.

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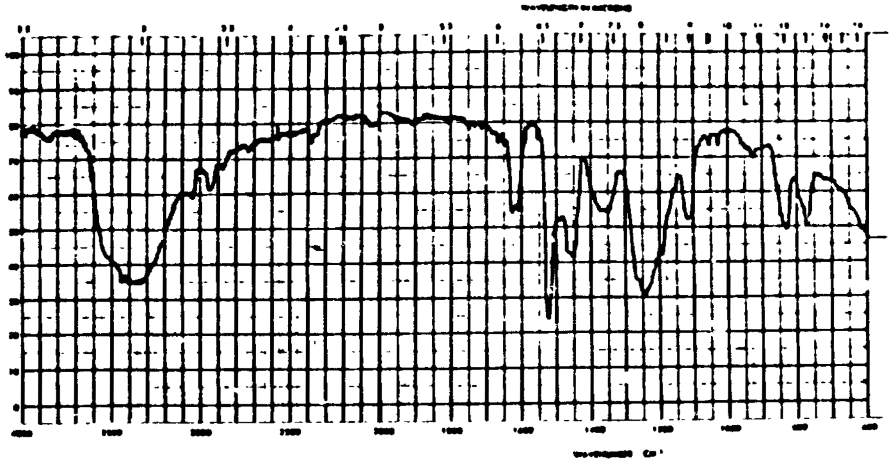
*phr = Parts per hundred of resin.

TABLE 9. PEROXIDES SCREENED FOR ALLYL ETHER POLYMERIZATION

Chemical Name	Source	Trade Name	10 Hour Half Life Temperature
2,5-dimethyl-2,5-bis (t-butylperoxy)hexane	Lucidol	Lupersol 101	119°C
Dicumyl peroxide	Hercules	Di-Cup R	113°C
t-Butyl perbenzoate	Whitco Chemical	Esperox-10	105°C
α,α-bis(t-butylperoxy) diisopropylbenzene	Hercules	Vulcup R	120°C

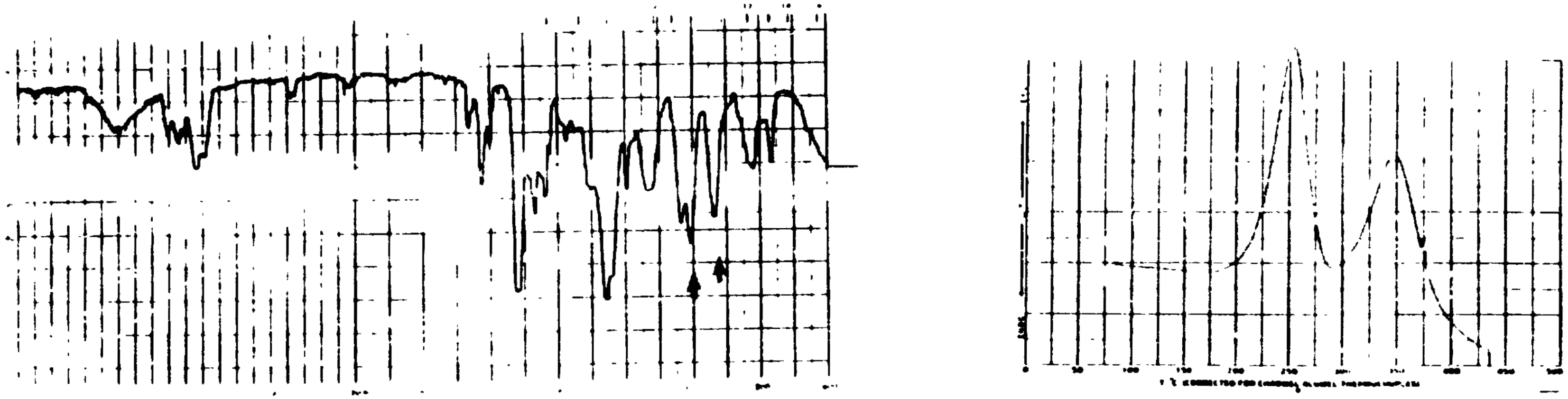
Differential scanning calorimetry (DSC) measurements and infrared spectral analysis of the uncatalyzed allyl derivatives and the catalyzed, 160^{0}C and 200^{0}C cured samples were carried out. The DSC and spectral curves clearly show that the Claisen rearrangement to a allyl substituted benzene species occurs in both the allyl novolac resin and the 9,9-bis(4-allyloxyphenyl) fluorene sample. In the 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene sample where the Claisen rearrangement is blocked, loss of the allyl group occurs.

Figure 23 gives the spectra and DSC curves of the allyl novolac resin. The baseline phenol-formaldehyde novolac is shown in the first spectrum, the allyl derivatized novolac in the second spectrum, the catalyzed allyl novolac after two hour treatment at 160^{0}C in the third spectrum and after treatment for one hour at 200^{0}C in the last spectrum. The novolac used for allyl derivatization clearly shows an absorption at about 3400 centimeters^{-1} and no absorption at about 925 and 1000 centimeters^{-1}. The allyl novolac shows reduction of the 3400 centimeters^{-1} absorption (phenolic hydroxyl) and the appearance of an absorption at 925 and 1000 centimeters^{-1} (allyl). The 160^{0}C treated material shows reappearance of the phenolic hydroxyl absorption at 3400 centimeters^{-1} and very little reduction in the 925 and 1000 centimeters^{-1} absorptions. Very little spectra change is observed for the sample which was treated for one hour at 200^{0}C even though sample hardened at this temperature. The absorption that appears at about 1750 centimeters^{-1} is carbonyl and its



Phenol-formaldehyde Novolac

$\uparrow$ = $-CH_2CH = CH_2$



Allyl Novolac

Allyl Novolac

Figure 23. IR spectra and DSC curves of curing allyl novolac.

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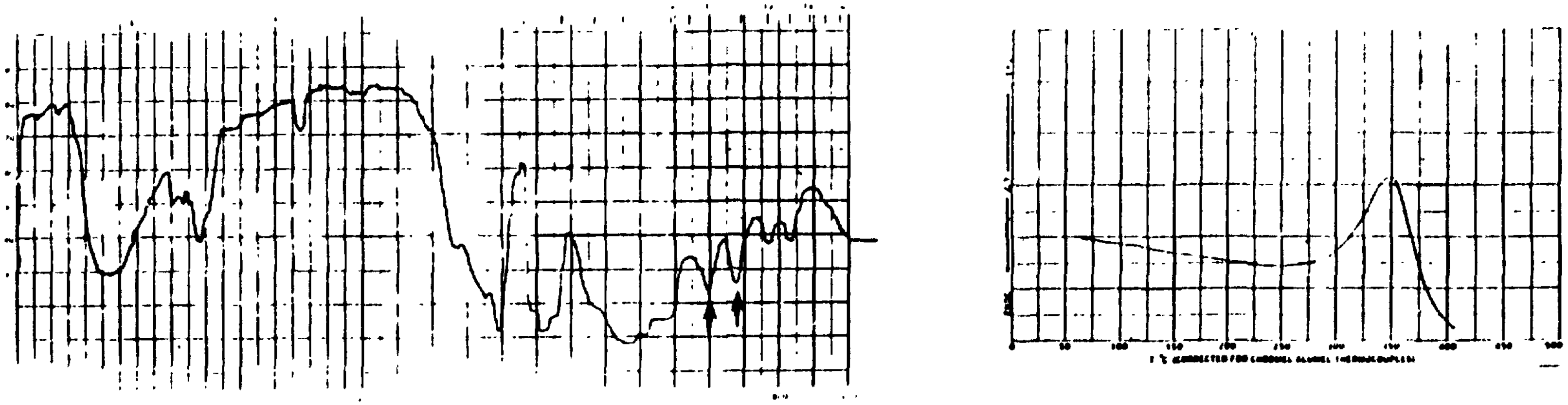
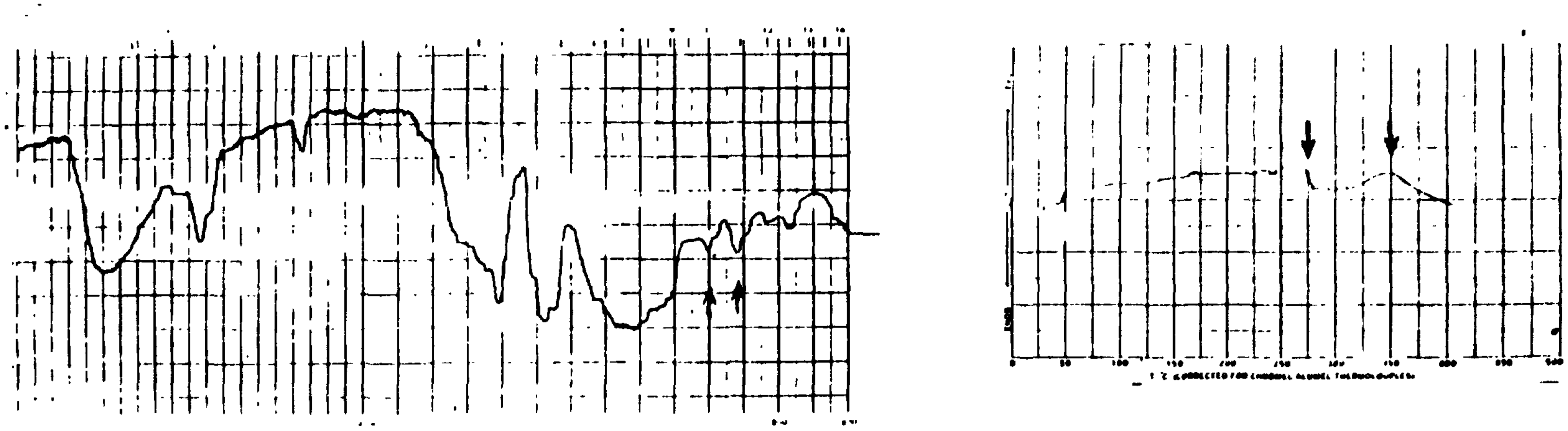


Allyl Novolac after 2 hours at 160°C



Allyl Novolac after 2 hours at 160°C + 1 hour at 200°C

↑ = $-CH_2CH = CH_2$

Figure 23. (Concluded)

origin is not clear. The uncatalyzed resin was also examined spectrally with heating and similar spectra were obtained.

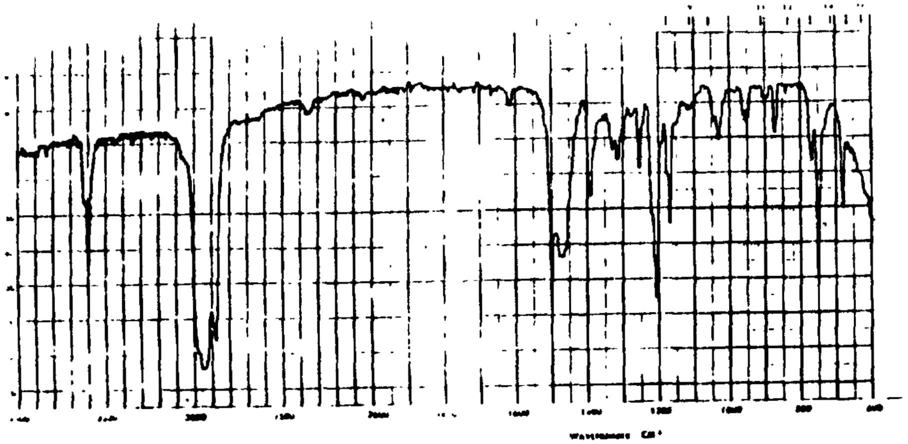
The DSC curves of the allyl novolac show two peaks, one at about 260°C and one at about 350°C. After heat treatment the first exotherm is removed leaving only the 350°C exotherm. Supported by the spectral series described, the first exotherm is clearly due to the Claisen rearrangement and the second exotherm is not assignable.

Several options exist for the assignment of the second exotherm, some are: free radical cure of phenolic moeities, allylic polymerization and sample decomposition. The 9,9-bis(4-allyloxyphenyl)fluorene samples showed identical spectral and DSC phenomena.

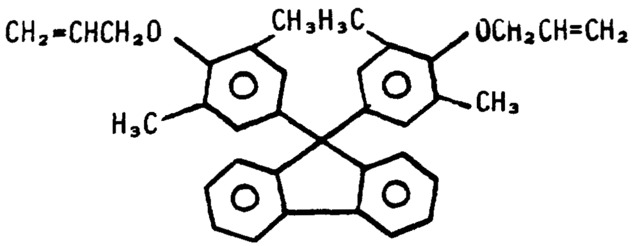
Figure 24 gives a similar spectral and DSC series for the 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene monomer. The first spectrum is of the underivatized phenol, the second spectrum is of the allyl derivatized phenol, the third spectrum is of the 160°C treated ether and the last spectrum of the 200°C treated material. Spectral changes include the loss of phenolic hydroxyl with allyl ether derivatization as seen in the first two spectra. The first two spectra also show the appearance of the 925 and 1000 centimeter^{-1} absorptions due to the presence of the allyl group. Upon treatment at 160°C in the presence of peroxide the allyl absorption essentially disappears. Little spectral change is observed for the one hour at 200°C treated material.

The DSC curve of the 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene monomer shows a single exotherm at about 265°C preceded by a melting endotherm at 172°C. After heat treatment at 160°C the melting endotherm is gone and the exotherm still present but reduced. After heat treatment at 200°C, the 265°C exotherm is essentially absent. Sample decomposition begins to occur in both the 160°C and 200°C treated materials at about 300°C with sublimate occuring on the inside of the DSC cell cover in both cases. The IR spectrum of the sublimate failed to yield its identity.

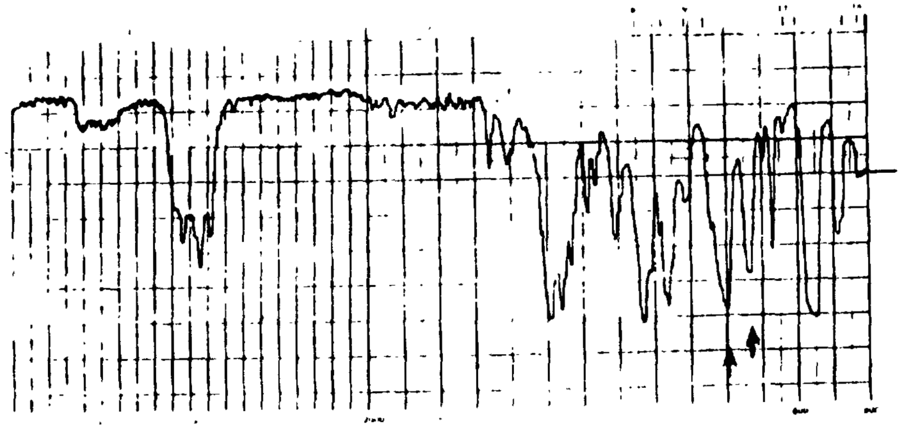
Hurd and Yarnall (Reference 7) identified propylene and 2,6-dipropyl-4-methylphenol as the major decomposition products of 2,6-dipropyl-4-



9,9-Bis(3,5-dimethyl-4-hydroxyphenyl)fluorene (Nujol Mull)



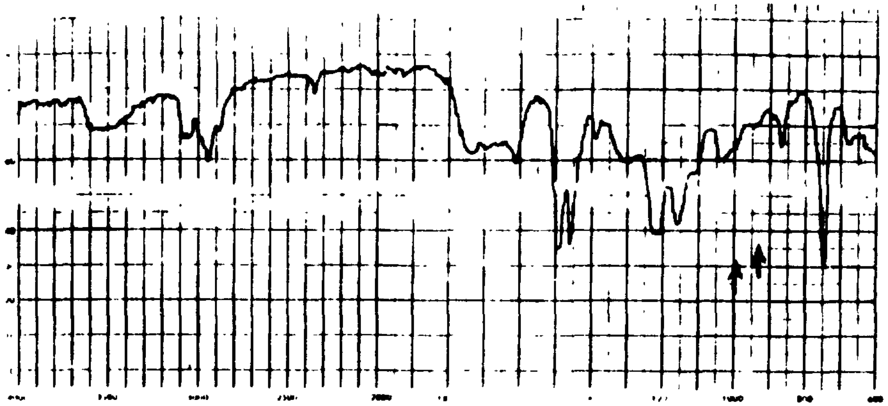
9,9-Bis(3,5-dimethyl-4-allyloxyphenyl) fluorene

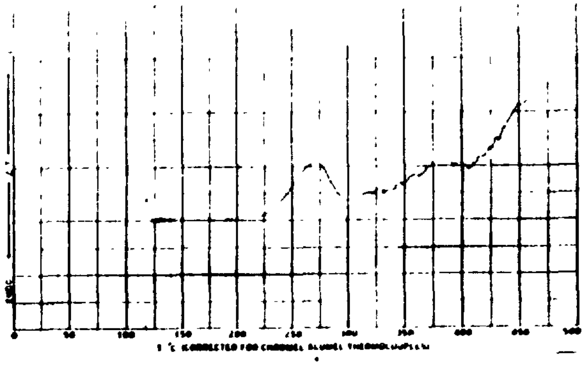


9,9-Bis(3,5-dimethyl-4-allyloxyphenyl)fluorene

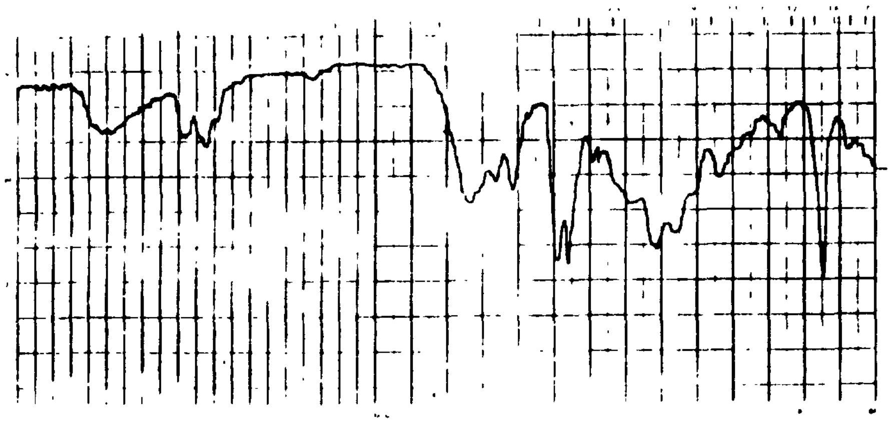
↑ = - $CH_2CH = CH_2$

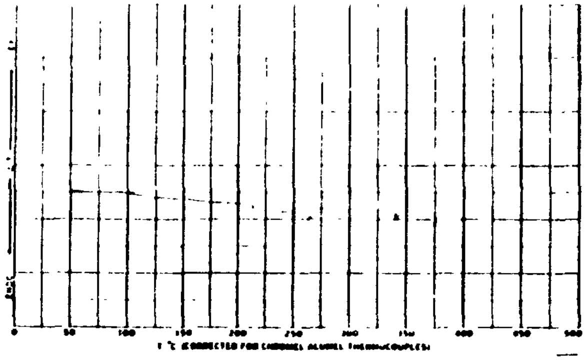
Figure 24. IR spectra and DSC curves of 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene.





9,9-Bis(3,5-dimethyl-4-allyloxyphenyl)fluorene after 2 hours at 160°C





Above: after 2 hours at 160°C and 1 hour at 200°C

↑ = $-CH_2CH=CH_2$

Figure 24. (Concluded)

methylphenylallyl ether. It is concluded that a similar decomposition occurs with 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene rather than polymerization of the allyl group. This conclusion is supported by the weight loss data discussed below.

The weight loss of the three allyl derivatized compounds with time and temperature without peroxide catalyst were measured analytically. Two additional samples were included in this study. They were the allyl novolac and the 9,9-bis(4-allyloxyphenyl)fluorene blended with 10 phr of triallyl phosphite and 5 phr dicumyl peroxide. These results are given in Table 10.

The weight loss data show the following:

1. The uncatalyzed 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene undergoes the Claisen rearrangement with very little weight loss occurring (assumed complete after 50 minutes at 180°C from previous spectral analysis).

2. The 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene undergoes a weight loss equivalent to quantitative loss of the allyl group after 50 minutes at 180°C (theoretical weight loss is 20.8 percent).

3. The uncatalyzed allyl novolac undergoes a weight loss which is greater than either of the fluorene compounds after 60 minutes at 142°C probably due to loss of low molecular weight species from the resin. It undergoes a weight loss less than the fluorene compound wherein the Claisen rearrangement is blocked but more than the fluorene compound where it is not blocked after 50 minutes at 180°C. This is interpreted as continued loss of low molecular weight species from the curing polymer and some loss of the allyl group where its rearrangement to an ortho position in the novolac structure is blocked.

4. Both the catalyzed and uncatalyzed allyl novolac samples were hard at 200°C after the 60 minutes at 200°C treatment. Both samples lost no weight with continued treatment at 200°C (120 minutes).

TABLE 10. WEIGHT LOSS STUDIES OF ALLYL ETHER DERIVATIVES UNDER NITROGEN

Compound	Treatment: Time/Temperature, Weight Loss in Percent			
	60 min/142°C	+ 50 min/180°C	+ 60 min/200°C	+ 120 min/200°C
Allyl novolac	4.6	11.5	14.3	14.3
9,9-bis(4-allyloxyphenyl)fluorene	0.6	2.0	6.1	12.0
9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene	2.5	23.7	29.9	38.1
Allyl novolac with triallylphosphite and dicumyl peroxide	16.3	22.3	25.6	25.5
9,9-bis(4-allyloxyphenyl)fluorene with triallyl phosphite and dicumyl peroxide	11.8	18.4	21.8	28.4

5. The allyl novolac and 9,9-bis(4-allyloxyphenyl)fluorene with triallyl phosphite and dicumyl peroxide showed loss of most of both of these additives with the heat treatment.

The most striking results obtained from this study is the essentially quantitative rearrangement of the allyl group based on the weight loss data from the 9,9-bis(4-allyloxyphenyl)fluorene and cure of the allyl novolac in the absence of radical catalysts.

Anaerobic char yields were determined on several of the compositions. These char yields at 800°C are listed below.

Composition (Final Heat Treatment)	Y_c^0, Percent
Allyl novolac without catalyst (3 hrs @ 200°C)	32
Allyl novolac with 5 phr Lupersol 101 (1 hr @ 200°C)	37
Allyl novolac with 10 phr triallyl phosphite and 5 phr dicumyl peroxide (3 hr @ 200°C)	38
9,9-Bis(4-allyloxyphenyl)fluorene with 5 phr Lupersol 101 (1 hr @ 200°C)	22

All of these anaerobic char yields were less than the program target of 50 percent and triallyl phosphite provided esssentially no char yield benefit.

AA 406 however did show char yield improvement. This compatable blend consisted of 80 parts of the allyl novolac and 20 parts of the AA 406 resin and was cured for 2 hours at 200°C. A nine percent improvement in the anaerobic Y_c^{800} was observed for the allyl novolac/AA 406 blend over the neat allyl novolac resin.

Figure 25 shows the anaerobic TGA curves for both the 200°C cured allyl novolac and 200°C cured allyl novolac blended with AA 406 resin. Both resin systems show initial gradual weight loss beginning about 200°C. The two curves are seen to be essentially congruent up to about 400°C. The T_d onset temperature for the allyl novolac/AA 406 blend is seen to be 428°C whereas the T_d onset temperature for the unblended allyl novolac is 450°C. The lower T_d onset temperature for the allyl novolac/AA 406 blend is due to decomposition of the AA 406 resin. The final Y_c^{800} for the two resin systems are 37 percent for the allyl novolac resin and 46 percent for the allyl novolac/AA 406 blend.

TGA measurements in both static and flowing air were carried out on powdered allyl novolac resin samples. Figure 26 shows the static air weight loss curves for the 200°C cured allyl novolac resin and the allyl novolac/AA 406 blend. The curves are superimposed up to 400°C and an almost indiscernible weight gain occurs in both systems at about 225°C. This is probably due to oxygen uptake by the residual allyl groups. At 400°C both resin systems have lost only two percent during oxidative char testing. Anaerobically the allyl novolac and the allyl novolac/AA 406 resins lost five and four percent respectively.

At about 410°C the allyl novolac/AA 406 blend begins its rapid oxidative weight loss, whereas the allyl novolac does not begin rapid weight loss until approximately 446°C is reached. This difference as previously discussed is due to decomposition of AA 406 resin. As the temperature increases, the

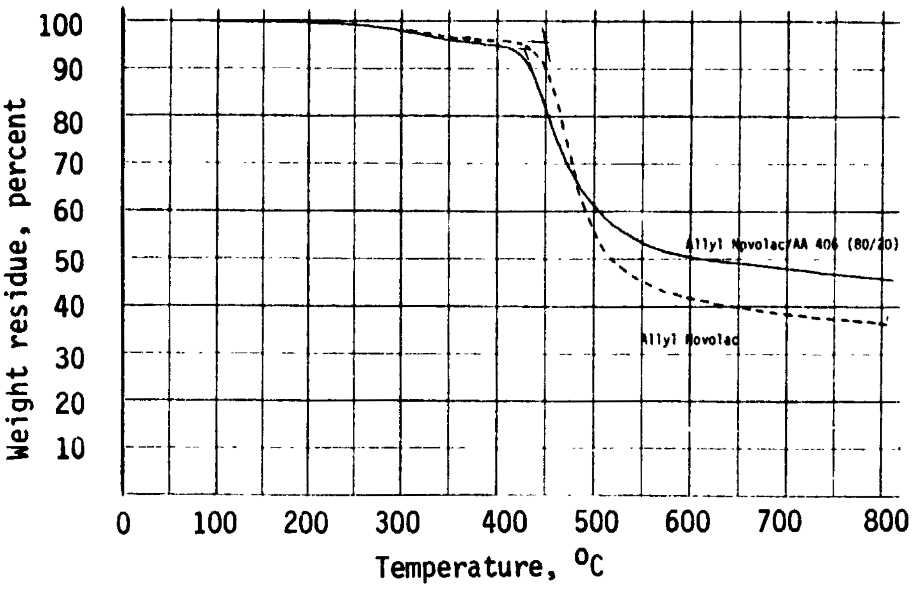


Figure 25. Weight loss curves of allyl novolac and allyl novolac/AA 406 in nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

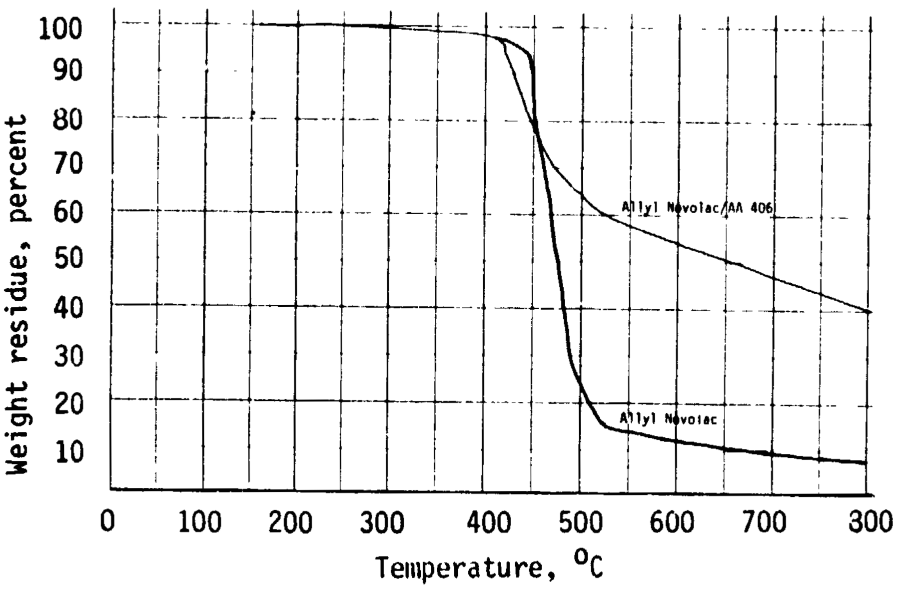


Figure 26. Weight loss curves of allyl novolac and allyl novolac/AA 406 in static air (15°C/min, -60 mesh).

allyl novolac undergoes nearly a 70 percent weight loss between 450 and 500°C. The final char yield is found to be only eight percent. The allyl novolac/AA 406 resin after an initial rapid loss due to decomposition of the AA 406 resin undergoes a more gradual loss and eventually a char yield of 40 percent at 800°C is recorded. This is a 32 percentage point improvement over the unmodified allyl novolac resin.

Figure 27 shows the flowing air weight loss curve for the allyl novolac/AA 406 blend. The general shape of the curve is consistent with the expected result for oxidative testing of polymers in general. Its shape is much like the earlier curves seen for the phenolic and novolac cyanate resins which were tested in static air. The oxidative weight loss curve is above the anaerobic curve for a span of 130°C. This is like the behavior of the previously discussed epoxy novolacs. Deviation from expected behavior is not judged significant in view of the evidence that the polymer gains weight in the early stages of oxidative testing.

Its shape is markedly different however from the shape of its weight loss curve obtained in static air testing seen in Figure 26. With the allyl novolacs this appears to be a combination of both oxygen uptake by the sample and localized oxygen concentration dilution by volatile decomposition products. The second cause is melting of the powdered sample to give a single lump of polymer leading to reduced available surface area for oxidation.

Inspection of the char residues in the platinum boat showed that both resins melted during anaerobic and aerobic char yield determinations to give a single lump of polymer. This molten char behavior is different from the non-melting chars obtained on the previously discussed phenolics, novolac-cyanate, and epoxy novolac resins. The phenolics and novolac-cyanate resins showed no signs of fusion or melting and the epoxy novolacs during oxidative char yield measurement showed only partial melting and fusion.

From the standpoint of obtaining reduced fiber release from composites in a fire, it can be visualized that melting and good oxidative resistance as demonstrated by the allyl novolac/AA 406 resin system could very well

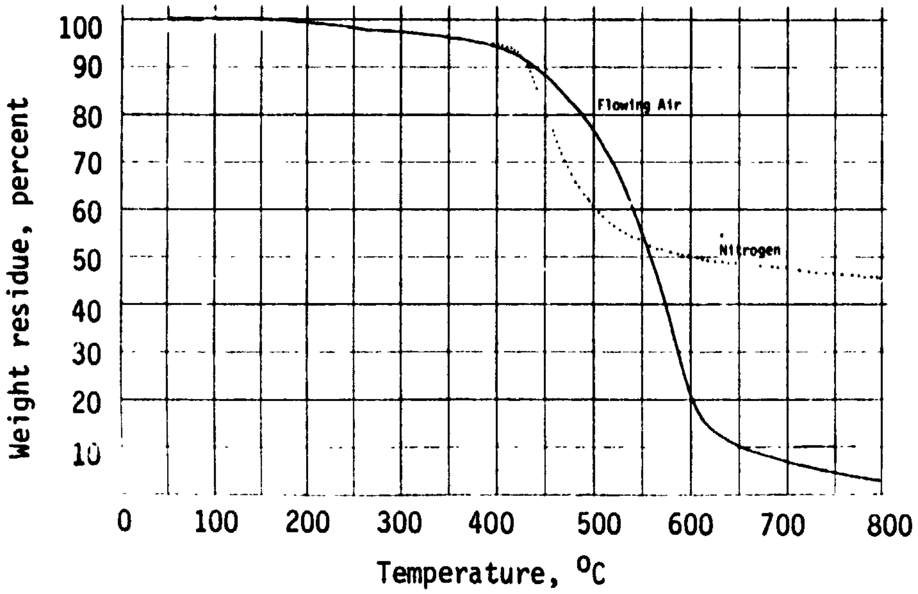


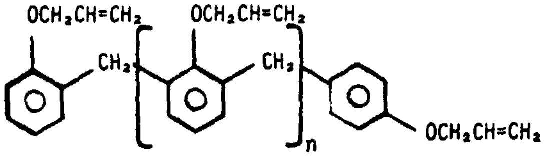
Figure 27. Weight loss curves of allyl novolac/AA 406 in flowing air and nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

reduce fiber release from composites in a fire. Even though the composite structure would melt in most fire scenarios, it is expected that it would behave much like molten, dripping plastics wherein the resin would continually offer minimum surface area for continued thermal and oxidative degradation as opposed to the non-melting novolacs and novolac cyanates.

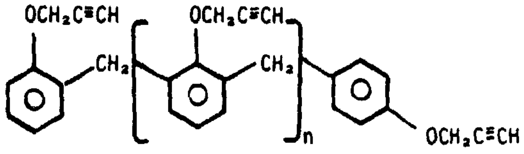
DTUL measurement on the 200°C cured unmodified allyl novolac resin gave a value of only 73°C. Clearly, even for their most interesting char yield behavior they seem to have little promise as a graphite support matrix resin for elevated temperature applications.

3.6 PROPARGYL ETHER DERIVATIVES

The ability of the ethynyl group to provide addition cure and high char yields was investigated. Originally planned was use of an ethynyl group directly attached to an active phenolic monomer which would be required to survive novolac condensation conditions. Due to the reasonable cost and ready availability of the propargyl halides and ability to introduce the propargyl group after novolac condensation, the propargyl novolacs were investigated. Basically, a twenty percent point improvement in char yield was obtained with use of propargyl bromide in place of allyl bromide as described in detail below. The similarity between the allyl novolac and propargyl novolac structures can be seen below.



Allyl novolac



Propargyl novolac

The propargyl ethers of two compounds were prepared in a manner similar to that used for the preparation of the allyl ethers. Thus propargyl bromide was reacted with the previously described novolac and 9,9-bis(4-hydroxyphenyl) fluorene to provide their respective ethers. The reactions were run under mild conditions to minimize possible side reactions and moderate yields were obtained. Slightly more severe reaction conditions should provide much higher yields of the ethers. Infrared analysis of the products verified that the propargyl ethers had been obtained.

Three formulations were investigated for cure and char yield determinations. The formulations were cured for 2 hours at 160°C (propargyl novolac nearly gelled) and for 2 hours at 204°C in an inert environment. All three compositions were hard to spatula probe at the final cure temperature. The propargyl novolac formulations were tough while the 9,9-bis(propargyloxyphenyl) fluorene was very brittle. The formulations and weight loss data through final cure are given in Table 11.

The hardening mechanism of the propargyl ether derivatives is not clear. The spectral series through cure show loss of the acetylenic hydrogen (3310 cm^{-1}),

TABLE 11. PROPARGYL ETHER FORMULATIONS

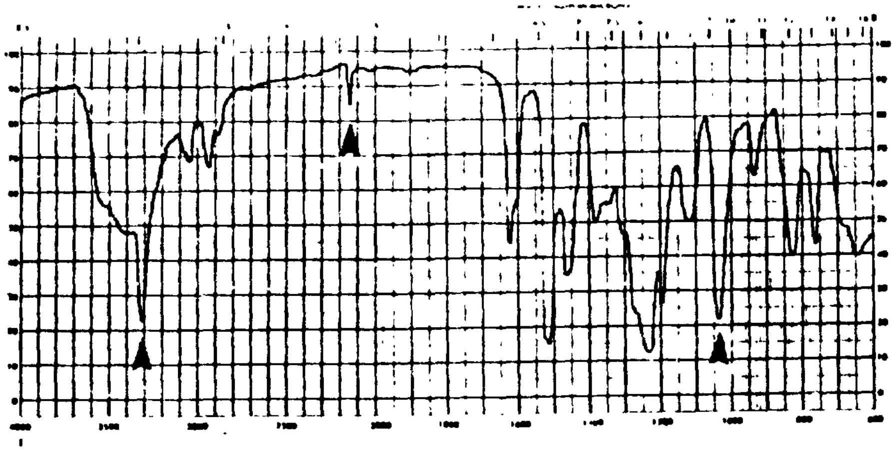
Formulation Number	Compound	Weight Percent	Weight Loss through 204°C Cure*
1	Propargyl Novolac	95	17.1
	Dicumyl Peroxide	5	
2	Propargyl Novolac	75	
	AA 406	20	20
	Dicumyl Peroxide	5	
3	9,9-bis(4-propargyloxyphenyl) fluorene	95	8.6
	Dicumyl Peroxide	5	

*Peroxide loss probably included in weight losses.

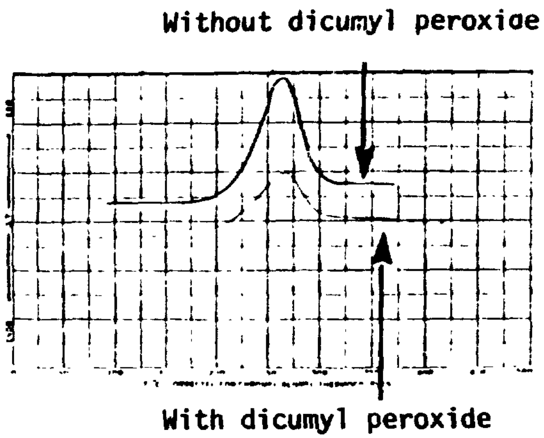
the triple bond (2140 cm^{-1}) and loss of a strong absorption at 1040 cm^{-1}. This later absorption may be due to ether linkage, ($-CH_2-O-$). This absorption is also in the allyl novolac spectra but is masked by the strong allyl absorption. The spectra of the 204°C cured propargyl novolac and allyl novolac are very similar. DSC analysis of the propargyl derivatives shows only one exotherm compared to the allyl derivatives. In the later case, allylic rearrangement followed by allyl cure was thought to be the origin of the two exotherms. Since propargyl ethers would be expected to rearrange, two exotherms were also expected. Figures 28 and 29 give the spectra and DSC curves of the propargyl novolac, the 9,9-bis(4-propargyloxyphenyl)fluorene and their cured products.

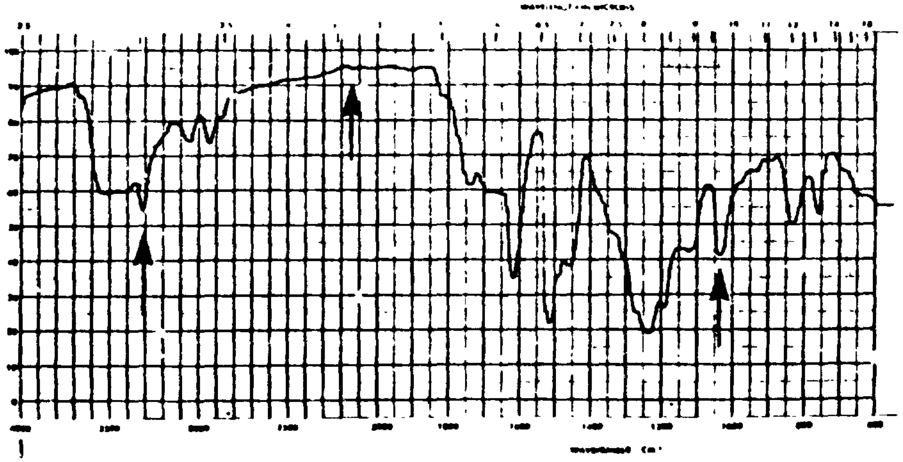
Following nitrogen and air (1 SCFH) TGA curves showed that the propargyl derivatives provided much better char yields than the allyl derivatives. Anaerobic char yields of the propargyl and allyl derivatives are compared in Table 12.

A twenty percent benefit to anaerobic char yield is observed for the propargyl ethers over the allyl ethers for both the novolac and the 9,9-bis substituted fluorene compounds. The use of the AA 406 with the propargyl novolac gives slight benefit (3 percent) over the unmodified propargyl novolac.



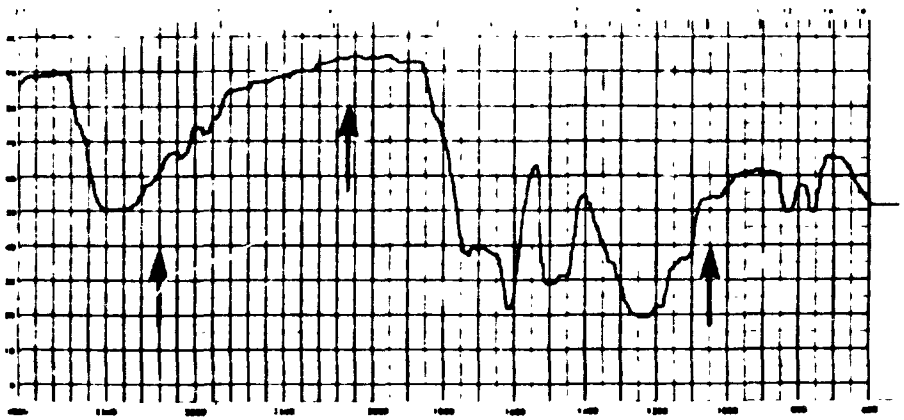
Propargyl novolac





Propargyl novolac after 2 hours at 160°C

Figure 28. IR spectra and DSC curves of propargyl novolac with cure.



Propargyl novolac after 2 hours
at 160°C and 2 hours at 204°C

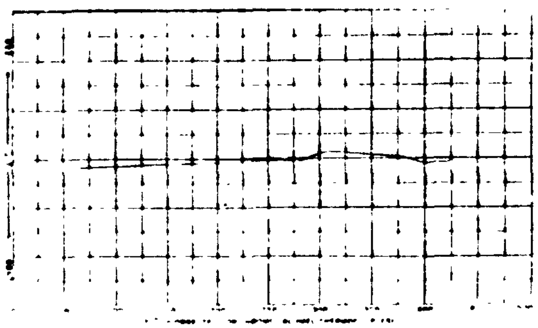
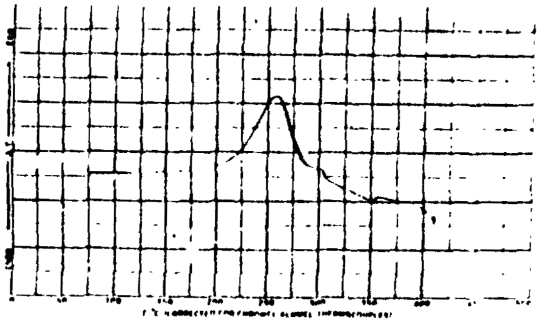
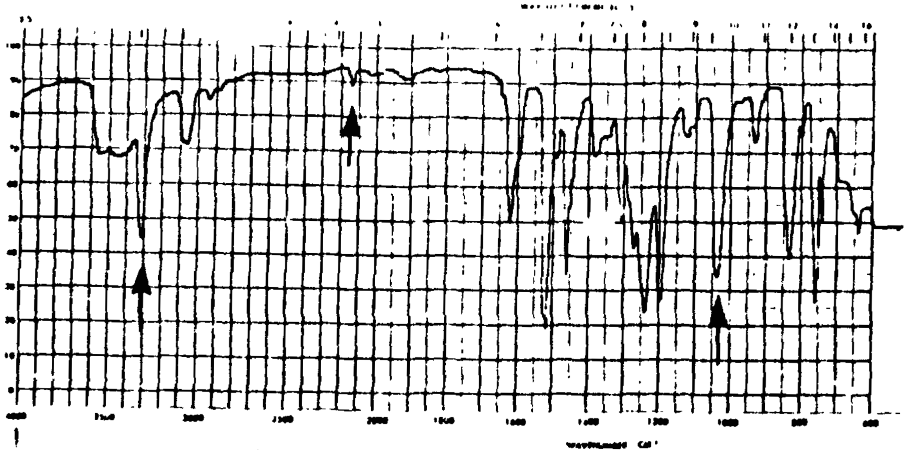
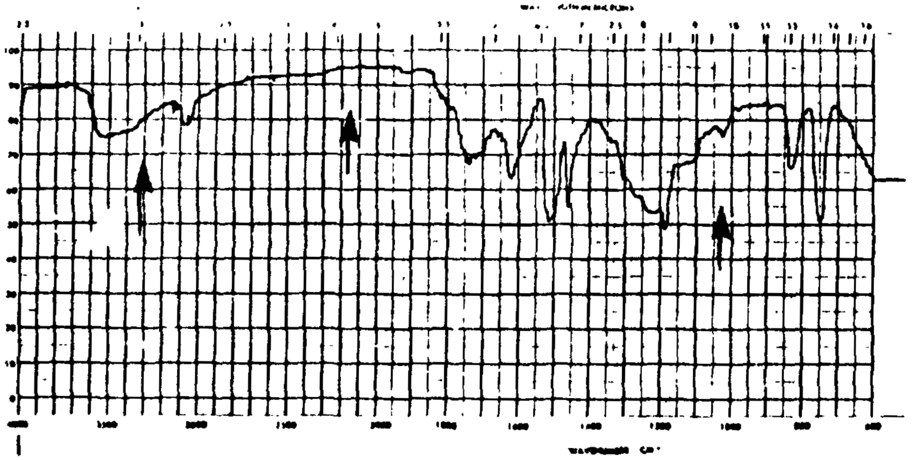


Figure 28. (Concluded)





9,9-Bis(4-propargyloxyphenyl)fluorene



9,9-Bis(4-propargyloxyphenyl)fluorene after
2 hours at 160°C and 2 hours at 204°C

Figure 29. IR spectra and DSC curves 9,9-bis(4-propargyloxyphenyl) fluorene with cure.

TABLE 12. PROPARGYL AND ALLYL ETHER CHAR YIELDS IN NITROGEN

	Y_c^{800}, Percent
Allyl Novolac	38
Propargyl Novolac	58
Allyl Novolac/AA 406 (80/20)	46
Propargyl Novolac/AA 406 (79/21)	61
9,9-Bis(4-allyloxyphenyl)fluorene	22
9,9-Bis(4-propargyloxyphenyl)fluorene	42

Anaerobic char yield curves for the propargyl derivatives are shown in Figure 30.

Flowing air TGA measurement was carried out on the powdered propargyl novolac/AA 406 blend. This curve is given in Figure 31. The propargyl novolac with its high anaerobic char yield and air weight loss retention equivalent to the best phenolic resin met program char yield goals.

DTULs of the 204°C cured propargyl novolac and 9,9-bis(4-propargyloxyphenyl)fluorene were 100°C and 202°C respectively. The allyl novolac provided a DTUL of 75°C. Both the propargyl and allyl novolacs require development of much higher DTULs to be useful. The DTUL of the 9,9-bis(4-propargyloxyphenyl) fluorene is good but this system was very brittle. The prognosis for sought composite mechanical performance being obtained with either of these systems is speculative.

3.7 ACRYLATE-ESTER DERIVATIVES

A method which could be most economical in the development of addition cureable phenolic resins would be to include the addition cureable group as a part of one or both of the raw materials - the phenolic substrate or the aldehyde. Several possibilities exist; however, if cure is to occur through vinyl groups, this group will be sensitive to the condensation conditions employed as well as the potential of cure inhibition by the presence of the phenolic

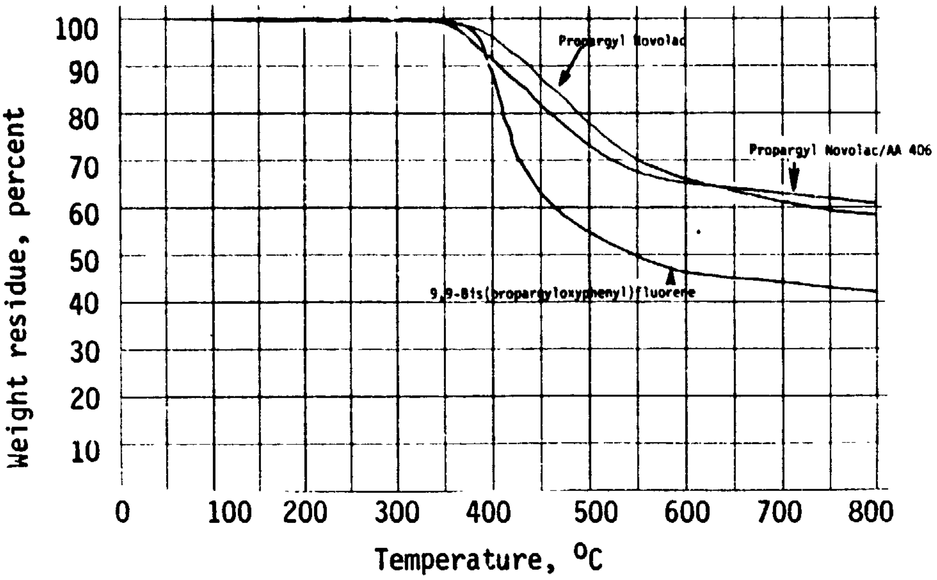


Figure 30. Weight loss curves of propargyl novolac, propargyl novolac/AA 406 and 9,9-bis(4-propargyloxyphenyl) fluorene in flowing nitrogen (15°C/min, 0.5ℓ/min, -60 mesh).

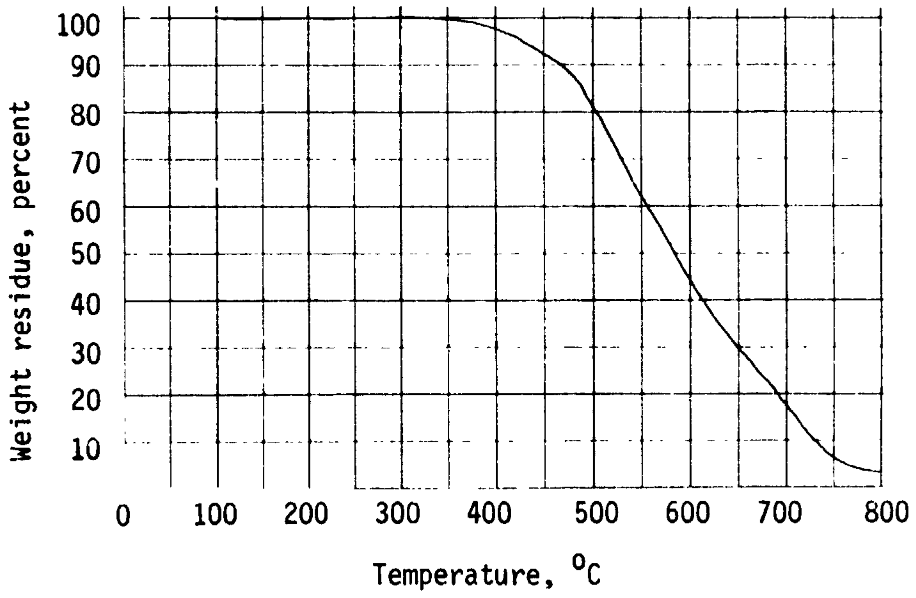
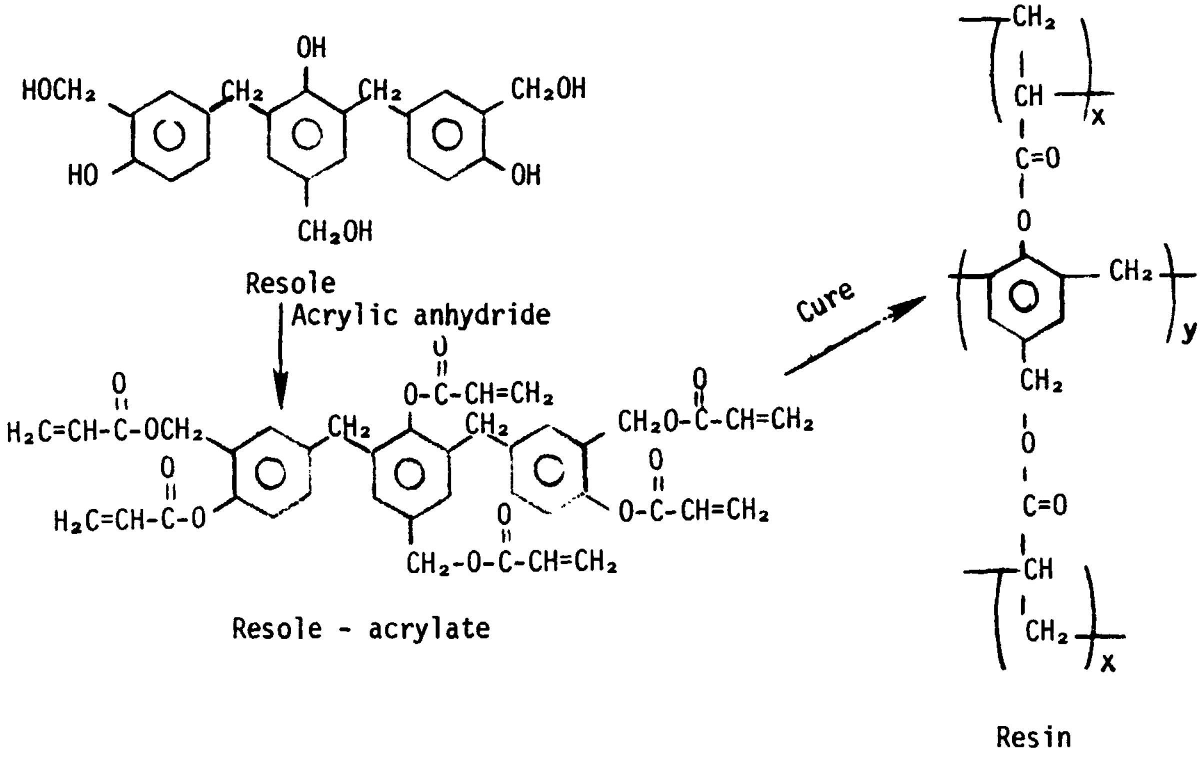


Figure 31. Weight loss curve of propargyl novolac/AA 406 in flowing air (15°C/min, 0.5ℓ/min, -60 mesh).

structure in the prepolymer. Post esterification or etherification of the prepolymer should eliminate the latter problem.

Due to the high reactivity of many vinyl structures with acids frequently used in novolac preparation, resoles were selected for the investigation of unsaturated aldehydes to provide addition cureable systems. The hydroxyl groups in the resole (methylol, phenolic) were esterified with acrylic anhydride. If successful, this approach could also lead to resins with final crosslink densities more nearly approaching that of conventional phenolic resins. The resin structure shown below has a calculated hypothetical crosslink density of 68.5 molecular weight units (compare to Section 3.8).



Acrolein, furfural and formaldehyde were condensed with phenol using the resole preparative method given by Sorenson and Campbell (Reference 3). This procedure is given in the experimental section of this report. The baseline novolac was also treated with acrylic anhydride and characterized for comparative purposes.

All of the resole-acrylate resins were liquids at room temperature.

The novolac-acrylate resin was a solid with a melting point approximately the same as the baseline novolac. The condensation conditions employed were possibly somewhat severe for the furfural based resole since a few lumps of insoluble resin were present in the prepolymer.

The systems were catalyzed with the mixed catalyst system which was successfully used for the Derakane 470-36 system (butylperbenzoate and cumene hydroperoxide 50/50). Weight loss data through polymerization and gel data are provided in Table 13. AA 406 was blended with the formaldehyde based resole-acrylate for eventual char yield determination and is included in the table.

As noted in Table 13, all of the resins cracked at some cure stage except for the acrolein based resole-acrylate resin. Weight losses of the resin castings through final cure were high and were not studied in detail. Resin cracking however is likely due to cure shrinkage rather than volatile loss from the resin systems. All of the resins were somewhat brittle. Due to the cracking phenomena, these systems could not be seriously considered further. The acrolein based resole-acrylate was slightly "tougher" than the other systems however it foamed during cure suggesting that void formation during composite fabrication would occur.

Infrared analysis of the starting resoles and resole-acrylates through cure are typified by the formaldehyde based resole-acrylate spectral series given in Figure 32. The strong hydroxy absorption at 3 microns is lost upon derivatization with acrylic anhydride with appearance of a strong carbonyl absorption at 1740 centimeters^{-1}. Cure of the vinyl groups is indicated by loss of the appropriate absorptions and is indicated in the figure by arrows.

Anaerobic char yields at 800°C and DTUL measurements were carried out on the cured systems. These data are given in Table 14.

The resole-acrylate and novolac-acrylate provided essentially equivalent char yields of 30 and 31 percent respectively. AA 406 provided a 19 percentage point increase to the char yield of the resole-acrylate and furfural may have also contributed to the char yield but the weight loss of this system

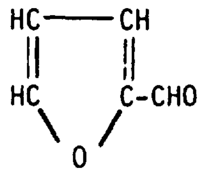
TABLE 13. CURE AND WEIGHT LOSS OF RESOLE-ACRYLATE PREPOLYMERS

Aldehyde	Formaldehyde	Formaldehyde[a]	Acrolein	Furfural	Baseline Novolac-Acrylate
Catalyst[b], phr	2.0	1.7	2.0	5.3	4.0
Weight loss, percent after:					
1 hour at $60^{\circ}C$	4.8	3.8 gelled	1.9	6.3	0.0
1 hour at $90^{\circ}C$	8.6 gelled	5.1	7.7	16.5	2.9 gelled
16 hours at $120^{\circ}C$	14.3 cracked[c]	14.1 cracked[c]	23.1 blown/gelled	32.9 gelled	7.7
2 hours at $160^{\circ}C$	14.3	14.5	23.1	38.0 cracked[c]	8.7
2 hours at $204^{\circ}C$	17.8	18.4	30.8 not cracked	41.8	15.4 cracked[c]

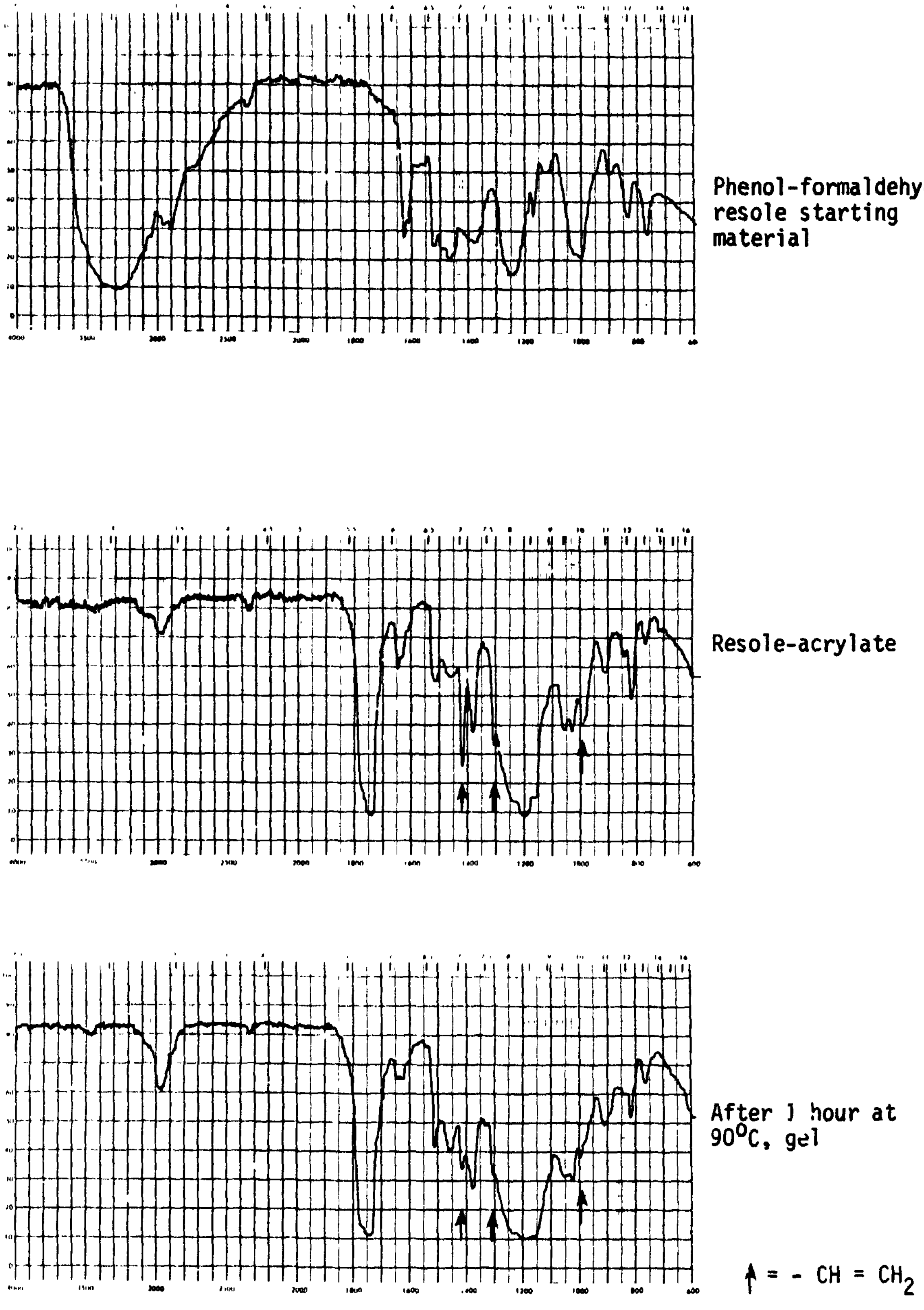
[a] 88/12 Parts by weight resole-acrylate and AA 406.
[b] Equal parts of butyl perbenzoate and cumene hydroperoxide.
[c] Casting developed several cracks due to cure shrinkage.

$H_2C{=}CHCHO$

Acrolein



Furfural



Phenol-formaldehyde resole starting material

Resole-acrylate

After 1 hour at 90°C, gel

↑ = - CH = CH_2

Figure 32. Infrared spectra of the phenol-formaldehyde resole through cure.

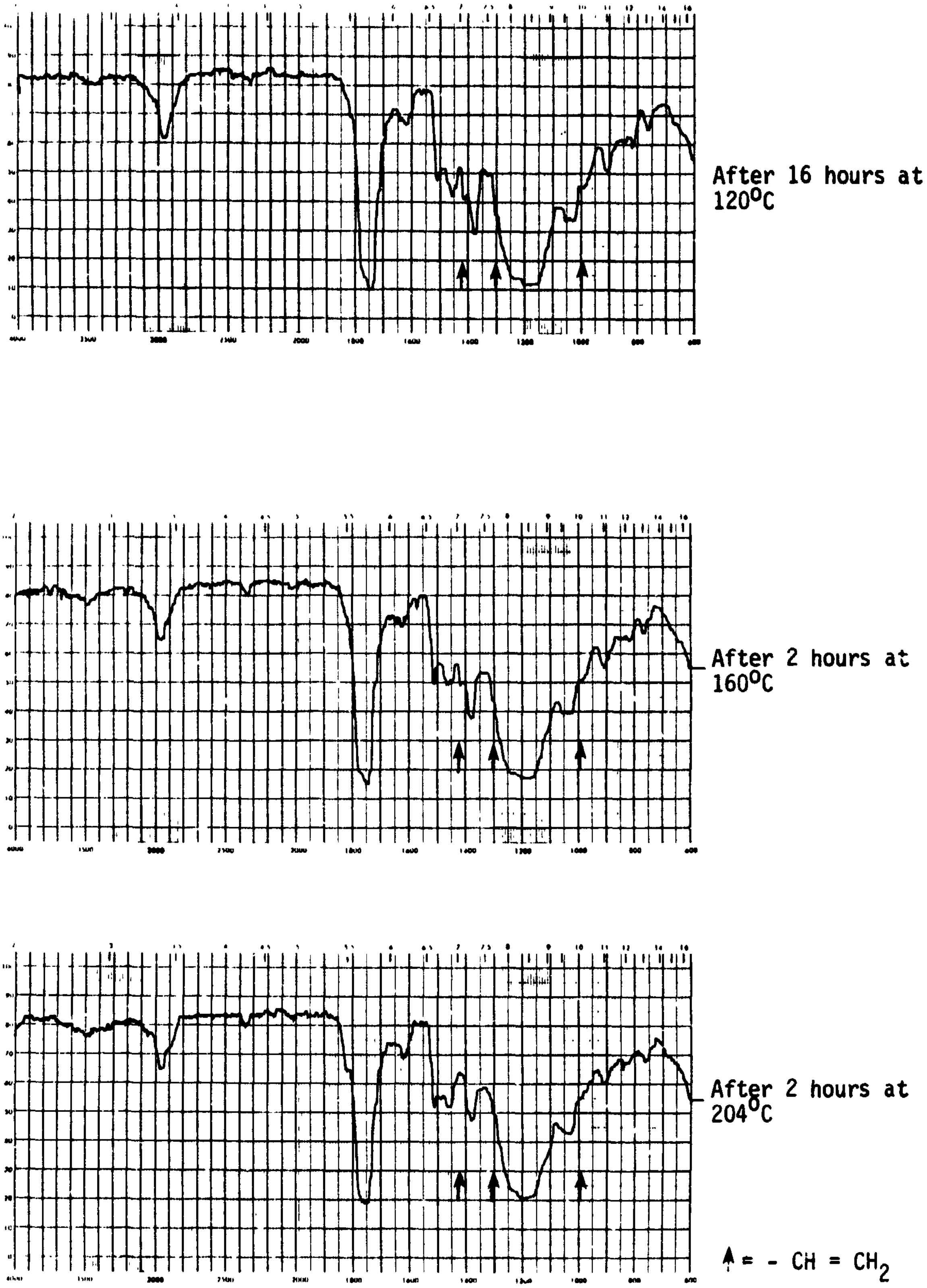


Figure 32. (Concluded)

TABLE 14. TGA AND DTUL CHARACTERIZATION OF RESOLE-ACRYLATES

Number		Y_C^{800}, Percent	DTUL, °C
1	Formaldehyde based resole-acrylate	30	78
2	Formaldehyde based resole-acrylate with AA 406 (88/12)	49	68
3	Acrolein based resole-acrylate	28	40
4	Furfural based resole-acrylate	37	86
5	Novolac-acrylate	31	114

through cure was very high which makes such a conclusion dubious. Char yield benefit would be expected from use of this aldehyde however, in view of Mackay's work (Reference 8). The DTULS of all of the systems were too low for 177°C performance.

In view of the resin cracking problem experienced in this investigation, it is difficult to make a positive statement about the systems investigated. Clearly, other phenols or aldehydes as well as other esterification or etherfication reagents should be investigated before a final prognosis is made.

3.8 SELECTION OF PROMISING RESINS FOR COMPOSITE EVALUATION

As stated under the objectives of this program in Section 2, processability of the developed resins as well as high char yield demonstration were key items. Fortunately, processability of the derivatized novolac and resole prepolymers was in general excellent. With this benchmark in hand, mechanical performance of composites fabricated from promising resins became critical, particularly at elevated temperatures. This section describes our resin selections and rationale for their selection for evaluation in graphite composites.

Only two resin systems investigated, the novolac-cyanates and the propargyl ether novolacs provided the program's target anaerobic char yield of 50 percent at 800°C. The remainder of the derivatized phenolic prepolymers showed anaerobic char yields at 800°C of about 25 percent and more typically 30 percent. With the AA 406 additive 15-20 percent increases in char yield occurred with many of the systems to give nearly the program target anaerobic char yield of 50 percent. Consequently, neat or with selected additives char yields equivalent to state-of-the-art phenolics seem assured for addition cured phenolic prepolymers.

As with the anaerobic char yields discussed above, oxidative weight loss testing of the many derivatives showed that only minor variations in oxidative stability are to be expected from addition cure derivatized novolacs. Table 15 compares the flowing air char yields of the best phenolic resin to the best of several resin classes investigated. Large variations in oxidative

TABLE 15. FLOWING AIR CHAR YIELD COMPARISON
(-60 MESH POWDERS)

	Compound Percent Weight retained:	500°C	600°C	700°C	800°C
1.	Phenol/9,9-bis(4-hydroxyphenyl) fluorene phenolic (75/25) (Hexa cure)*	78	44	4	0
2.	9,9-Bis(4-cyanatophenyl)fluorene*	80	56	10	0
3.	Allyl Novolac/AA 406 (80/20)	77	20	8	3
4.	Formulated DEN 438 Epoxy	82	58	18	0
5.	Propargyl Novolac/AA 406 (79/21)	81	44	17	∼3

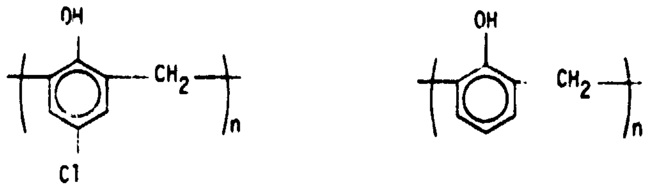
*Static Air.

resistance are not evident from the data presented.

Accordingly, our attention was then directed toward upper temperature mechanical performance capability of the derivatives investigated based on DTUL measurements. Only the cyanate resins with DTULs in excess of 200°C showed promise to easily meet the target 177°C (350°F) to 204°C (400°F) performance capability. The novolac cyanate resin was selected as the first candidate. As described below, the next two candidates were selected for the reasons cited.

To achieve 177°C mechanical performance, addition cured resins based on novolac structures require that a high crosslink density be achieved in the cured resin and/or that a rigidizing (Tg elevating) structure be incorporated into the resin. Phenols such as 2,7-dihydroxynapthalene and aldehydes such as benzophenone or fluorenone should lead to novolac polymers with Tgs above 204°C but at possibly significant expense to the melt processability of their prepolymers.

Linear high molecular weight phenol-formaldehyde polymers (o,o substituted) with the structures indicated below have melting points of 170-185°C and 160-180°C respectively.



mp 170-185°C   mp 160-180°C

Linear High Molecular Weight Phenol-formaldehyde Polymers

Isomers of (o, p substituted) linear phenol-formaldehyde polymers as well as use of mixed phenols such as p-chlorophenol and p-cresol influence the melting points of the polymers (see Reference 9). It was concluded however, that essentially all isomers and mixtures of substituted phenols polymerized with formaldehyde to provide linear prepolymers will result in polymers with glass transition temperatures below 204°C.

Hypothetical structures, calculated molecular weight between crosslinks (M_c) and DTUL data obtained for several novolac prepolymers are given in Figure 33.

The DTUL results given in the figure clearly show that only highly crosslinked phenol-formaldehyde novolac based addition polymers will produce sufficiently high HDT's (DTUL's) to meet the target 177-204°C (350-400°F) composite mechanical performance temperature. Low polymerization efficiencies, intramolecular looping and impurities all have the effect of lowering potentially high DTULs of resin systems and the calculated M_cs shown in the table are certainly much lower than the values actually achieved in the polymerized systems.

Molecular weight between crosslinks was calculated from the relationship: mer molecular weight divided by the number of bonds to the mer minus two for polymer linearity. Anaerobic char yields were obtained at the 15°C/minute heatup rate as previously described. DTUL measurements were taken as the intercept of any softening event (curve) with the expansion curve. DTUL

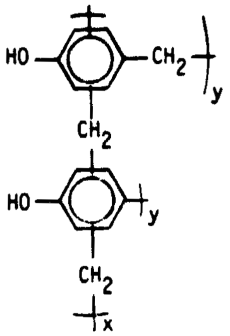
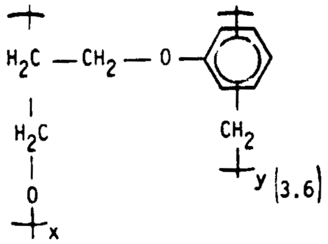
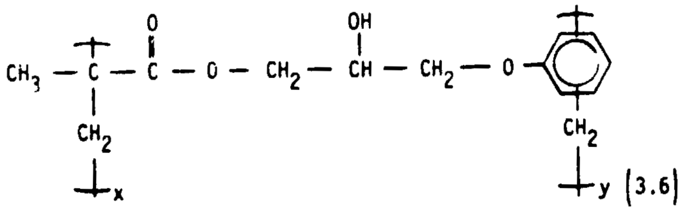
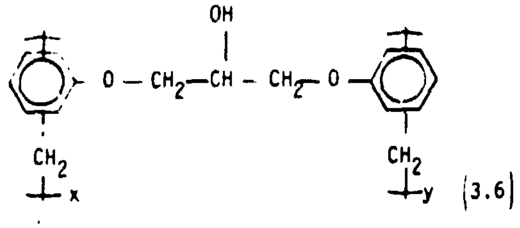
Number	Polymer System	Calculated Mc	Anaerobic Char Yield at 800°C	DTUL
1	 Phenolic Resin	112	50-60%	--
2	 Homopolymerized DEN 438	81	30%	235°C
3	DADS Cured DEN 438	112.5	--	212°C
4	 Derakane 470-36	124	19%	145°C*

Figure 33. Hypothetical structures of novolac based polymers.

Number	Polymer System	Calculated Mc	Anaerobic Char Yield at 800°C	DTUL
				
5	Novolac cured DEN 438	134	33%	150°C
6	Same as above when y = 2.2 (DEN 431)	--	--	100°C
7	Aniline cured DEN 438	208.5	--	60°C

*Up to 5 percent by weight styrene in the cured system.

Figure 33. (Concluded)

measurement of DADS cured DEN 438 illustrate the technique used. This is shown in Figure 34. Even though penetration did not occur until 250+°C, sample softening occurred between 200° and 250°C and the sample was rated as having a DTUL of 212°C. In lightly crosslinked and linear polymers complete penetration occurs and the intercept of the penetration curve with the expansion curve is the DTUL.

When softening occurs without penetration, the depth of sample penetration during softening appears to correlate well with the calculated M_cs and DTULs given in Figure 33. Lower M_cs and higher DTULs give less penetration during DTUL measurement. Homopolymerization of available epoxy novolac resins with EMI 24 illustrate this behavior well. DEN 431, DEN 438 and ERE 1359 were polymerized with 2 and 4 phr of EMI 24 catalyst.

Figure 35 shows the DTUL measurements conducted on these castings. DEN 438 clearly gives superior DTUL results to DEN 431 and ERE 1359. This

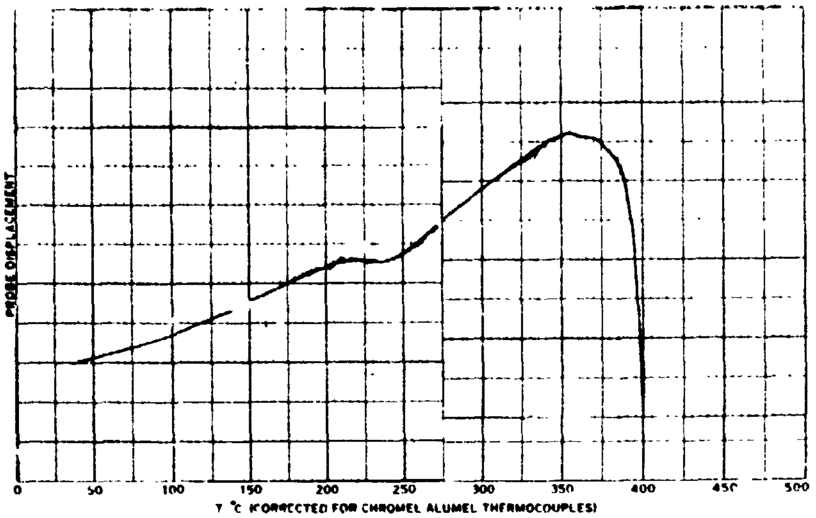


Figure 34. DTUL of DADS cured DEN 438.

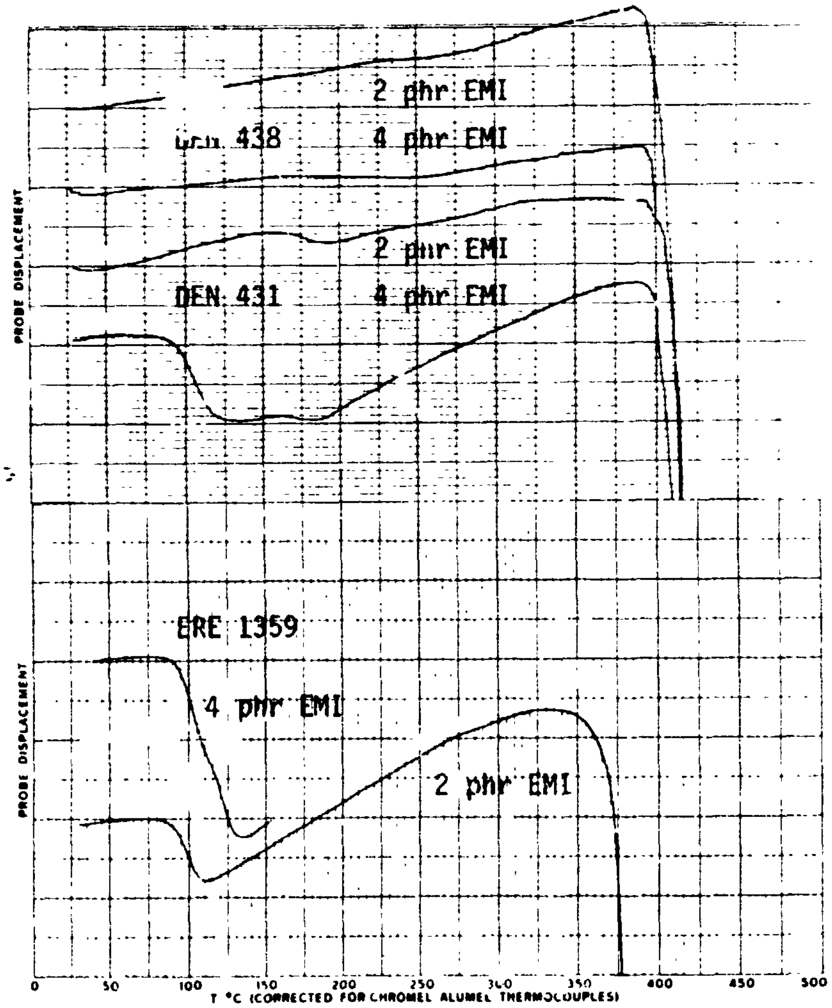


Figure 35. DTUL measurements on homopolymerized epoxy novolacs.

is due to its high functionality and in all cases the DTUL results obtained with 2 phr of the EMI 24 catalyst gives superior DTUL results to the DTUL results obtained with 4 phr. These results can be interpreted in terms of both impurity level (EMI 24) and D.P. The lower the catalyst concentration the higher the DP of the polyether reaction (and lower hydroxyl concentration). All of the tested samples were cured simultaneously (2 hours at 90^{o}C + 4 hours at 218^{o}C). All samples were between 110 and 120 mils thick.

In addition, the purity of novolacs used to cure epoxy novolacs appears to be sensitive to this test. DEN 431 cured with the previously described 80^{o}C melting baseline novolac and the room temperature melting novolac gave the results shown in Figure 36 (0.5 phr BDMA catalyst). The lower melting novolac contains more free phenol and consequently has a lower functionality. Based on the concept of penetration depth at softening as an index of crosslink density, the high melting novolac produces a more highly crosslinked system.

In view of the above, it became clear that cure schedule and catalyst variations would basically lead to little improvement in the DTUL of the vinyl ester or allyl ether derivatives. The acrylate esters had been discarded due to resin cracking. This left the propargyl ether and glycidyl ether derivatives. Both systems had good features as well as deficiencies. The propargyl ether derivatives with their high char yields were brittle particularly the 9,9-bis(4-propargyloxyphenyl)fluorene resin (DTUL 202^{o}C) and were only obtained in low yields. Additional efforts are expected to improve preparative yields, however the "tougher" propargyl ether novolac only had a DTUL of 160^{o}C. Since the cure mechanism is unknown and possibly involves an allylic type rearrangement, new monomer design to improve the DTUL performance would largely be on a trial and error basis. The glycidyl ether derivatives however even though an approach appeared to exist to achieve high DTULs, were far below the program's target char yield.

Anaerobic char yield, (Y_c^{800}) and DTUL characterization of DEN 438 (1.8 phr EMI 24) and DEN 438 with phosphorus additives was carried out to maximize the char yield of this system. Two phr of AA 406, Phos Chek P/30

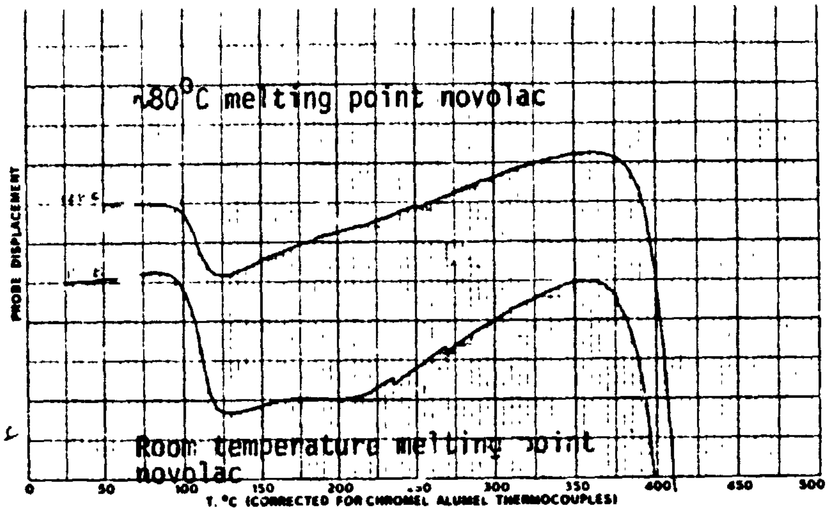


Figure 36. DTUL curves for DEN 431 cured with two novolacs with different melting points.

and Phosgard C-22-R were mixed with precatalyzed DEN 438 and cured for two hours at 90°C and overnight at 218°C (425°F). Anaerobic char yield and DTUL results on these systems are given in Table 16 and Figures 37 and 38.

All of the phosphorus additives affected the DTUL and char yield measurements. The AA 406 additive (not all soluble) completely eliminated the slight softening tendency of the resin whereas both the Phos Check and Phosgard modified samples showed some softening at lower temperatures than the unmodified DEN 438. Anaerobic char yields for all of the phosphorous-containing resins were approximately 10 percentage points above the unmodified resin.

The DTUL and char yield values obtained for the homopolymerized DEN 438 containing char promoter additives made this system attractive for further evaluation. Its ready availability, low cost and reduced hydroxyl content are also good features. It was selected over the propargyl ether derivatives as the second candidate.

TABLE 16. ANAEROBIC CHAR YIELDS AND DTULs OF DEN 438 WITH PHOSPHORUS ADDITIVES

ADDITIVE, 2 phr	DTUL	800°C CHAR YIELD, %
AA 406*	None**	41
Phos Check P/30*	162°C	45
Phosgard C-22-R	170°C	42
No additive	230°C	30

* Not homogeneous

** Possible Tg at ~202°C

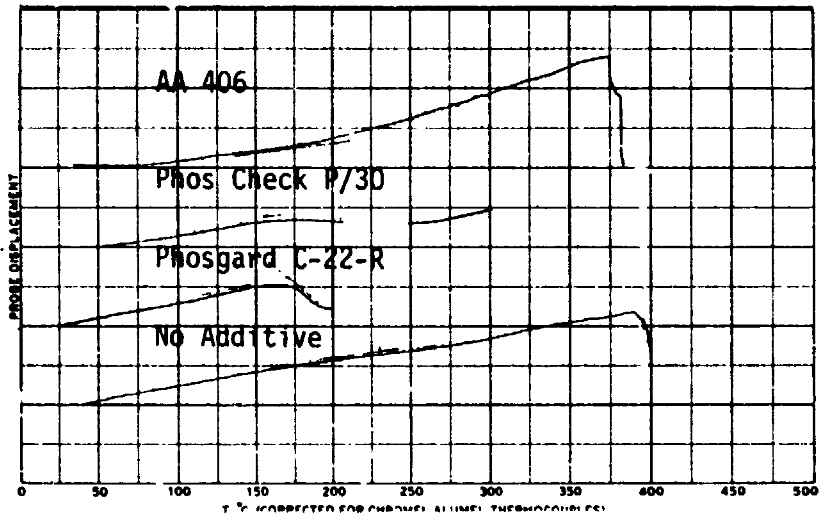


Figure 37. DTUL curves of DEN 438 with phosphorus additives.

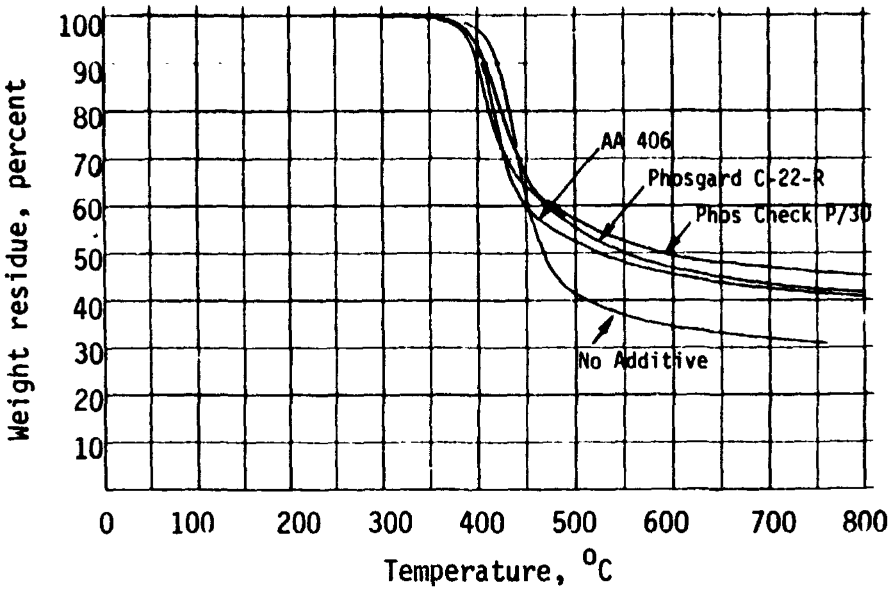


Figure 38. Anaerobic char yields of DEN 438 with phosphorus additives.

The third candidate, Derakane 470-36 was selected for composite evaluation for the reasons listed below.

- Commercial availability
- Low cost
- Known and documented cure chemistry
- The immediate application of this system if acceptable composite strengths could be demonstrated

A sufficient quantity (132 g) of the novolac cyanate resin was prepared to investigate the fabrication of graphite composites. It differed from the previously (5.5g) preparation described in that the melting points of the starting novolacs were 80°C (5.5g prep) and slightly above room temperature (132g prep). The as prepared larger batch of novolac cyanate had a slightly lower viscosity than the smaller batch, however after treatment under high vacuum overnight at 60°C its viscosity was slightly greater than the smaller batch. The 20g weight loss incurred by the vacuum-heat treatment probably consisted largely of phenyl cyanate.

The DEN 438 and Derakane 470-36 resins were used as received from the manufacturer.

Four small unidirectional graphite composites were fabricated using the three resin matrices with Thornel 300 graphite fibers.

● DEN 438/1.8 phr EMI-24	1 Composite
● Novolac Cyanate	2 Composites
● Derakane 470-36*	1 Composite

The prepregs for these composites were all prepared by hot melting a film of resin onto Mylar film, drum winding the fibers into the resin film and finishing the fiber impregnation on a vacuum hot table. The DEN 438 and novolac cyanate prepregs had very good tack properties and ambient flow lives of one week and 4+ weeks respectively. The Derakane 470-36 prepreg had high tack and continued to be sticky, 8 weeks after preparation.

Vacuum bag, trap mold processing was used to prepare all of the composites. Pressure application was consistent with resin thickening and approaching gel for both the DEN 438 and novolac cyanate systems. The Derakane 470-36 (majority of styrene removed) gelled rapidly from the liquid state and a precise time to apply pressure was not discernable. The Derakane laminate was fabricated using more of a casting type technology used for unsaturated polyester composites. The layup was vacuum degassed at room temperature, heat applied and after the resin thinned, pressure was applied. The downward movement of the top caul plate was arrested by 0.10 inch stops on each side of the laminate.

The physical properties of the composites are given in Table 17.

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*Styrene vacuum stripped from resin, 14 percent by weight styrene estimated retained in the resin (0.5 phr butyl perbenzoate and 0.75 phr cumene hydroperoxide catalysts.)

TABLE 17. PHYSICAL PROPERTIES OF ADDITION CURED NOVOLAC GRAPHITE COMPOSITES

Laminate No.	Resin System	Resin Content, Weight Percent	Fiber Volume Percent	Void Content, Percent
DD 44-5	DEN 438/ 1.8 pbw EMI-24	46.8	45.0	0.5
DD 17-146	Novolac Cyanate	41.5	51.0	6.0
DD 17-147	Novolac Cyanate	25.8	68.0	2.0
DD 17-152	Derakane 470-36	39.2	52.6	0.8

Table 18 provides the short beam shear strengths (SBS) of the four laminates at test temperatures up to 204°C (400°F). The ambient short beam shear strengths of the four composites ranged from 74.2 to 93.3 MPa (10.7 to 13.5 Ksi). SBS strengths seen in the table for the DEN 438 and novolac cyanate resin systems are only fair in view of state-of-the-art. The SBS value for the Derakane 470-36 however, is considered excellent. Apparently, this vinyl cured system is compatible with the epoxy size on the T-300 fibers and further has at least moderate tensile strength and elongation.

The two novolac cyanate composites show 72 and 76 percent strength retention of room temperature short beam shear strengths at 177°C (350°F). 5208/T-300 composites show approximately a 57 percent retention of room temperature strength at 177°C (350°F) (Reference 10). The epoxy novolac had a 48 percent retention of its room temperature strength at 177°C (350°F). The Derakane laminate had unacceptable properties at 177°C (350°F) but should be useful to temperatures up to 121°C (250°F).

Table 19 provides the flexural properties of the four laminates with test temperatures up to 204°C (400°F). 5208/T-300 Shows approximately an 80 percent retention of room temperature flexural strength at 177°C (350°F) (Reference 10). Only the novolac cyanate resin system equals this percentage

TABLE 18. SHORT BEAM SHEAR PROPERTIES OF ADDITION CURED NOVOLAC GRAPHITE COMPOSITES

Laminate No.	Resin System	Short Beam Shear Strength, MPa (psi)			
		Test Temperature, °C (°F)			
		Ambient	121 (250)	177 (350)	204 (400)
DD 44-5	DEN 438/1.8 phr EMI-24	81.5 (11,828)	52.6 (7643)	38.9 (5641)	31.3 (4545)
DD 17-146	Novolac Cyanate	75.6 (10,970)	61.4 (8798)	54.3 (7890)	44.1 (6392)
DD 17-147	Novolac Cyanate	74.2 (10,760)	63.5 (9122)	56.2 (8151)	45.8 (6650)
DD 17-152	Derakane 470-36	93.3 (13,540)	53.4 (7752)	31.5 (4564)	Not tested

TABLE 19. FLEXURAL PROPERTIES OF ADDITION CURED NOVOLAC GRAPHITE COMPOSITES

Laminate No.	Resin System	Flexural Strength, MPa (Ksi)/Modulus, GPa (Msi)			
		Test Temperature, °C (°F)			
		Ambient	121 (250)	177 (350)	204 (400)
DD 44-5	DEN 438/1.8 phr EMI-24	1103(160)/ 96.5(14.0)	737(107)/ 86.2(12.5)	53.7(78)/ 85.5(12.4)	46.9(68)/ 86.2(12.5)
DD 17-146	Novolac Cyanate	931(135)/ 78.6(11.4)	Not Tested	758(110)/ 73.8(10.7)	696(101)/ 78.6(11.4)
DD 17-147	Novolac Cyanate	1441(209)/ 122(17.6)	1613(231)/ 131(19.0)	1661(241)/ 125(18.2)	1420(206)/ 130(18.9)
DD 17-152	Derakane 470-36	1241(180)/ 88.9(12.9)	854(124)/ 91.7(13.3)	455(66)/ 74.5(10.8)	Not Tested

strength retention. In fact, with the second novolac cyanate laminate shown in Table 19, the flexural strength is seen to increase with increasing temperatures through 177°C (350°F). The DEN 438 system showed a 49 percent retention of room temperature flexural strength at 350°F and the Derakane system a 37 percent retention.

Based principally on the high temperature composite strengths, the novolac cyanate and epoxy novolac resins were selected for the final composite evaluation efforts described below.

3.9 FINAL COMPOSITE EVALUATION

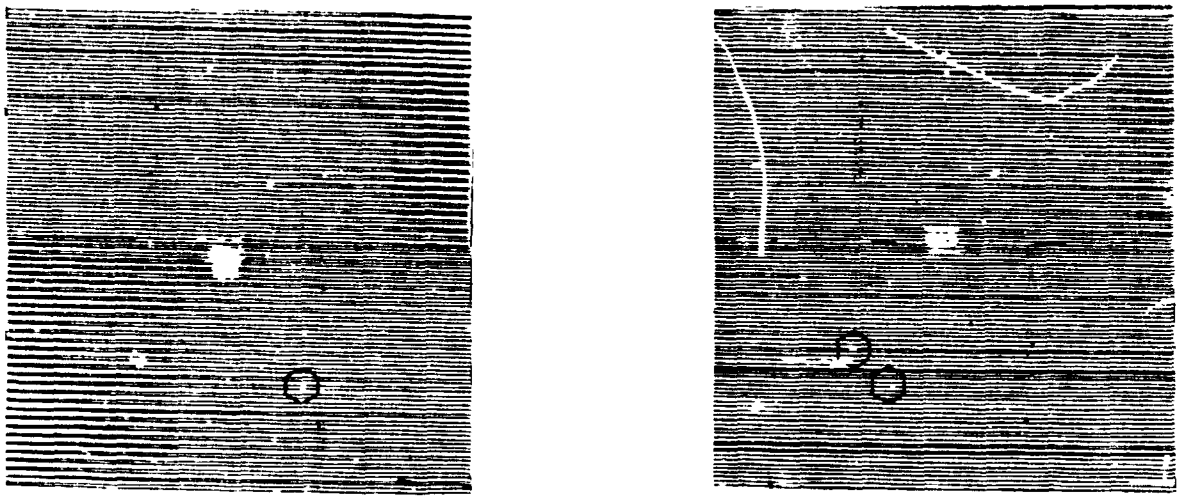
Twelve 20.3 cm x 20.3 cm x 0.254 cm (8" x 8" x 0.10") Thornel 300 composites were fabricated. Six used the epoxy novolac for the matrix and six the novolac-cyanate. C-scan data showed that high quality composites were obtained and four composites from each resin system were transmitted to the NASA Project Monitor. Typical C-scans are shown in Figure 39. Two composites from each resin system were cut into flexural and short beam shear specimens and tested.

In an attempt to render the AA 406 resin soluble in the DEN 438, it was predissolved in triglycidyl-p-aminophenol (Ciba-Geigy 0510) prior to blending with the DEN 438. The final formulation for the epoxy novolac was:

DEN 438	88 parts
0510	8 "
AA 406	4 "
Total	100 parts
EMI-24	1.6 phr

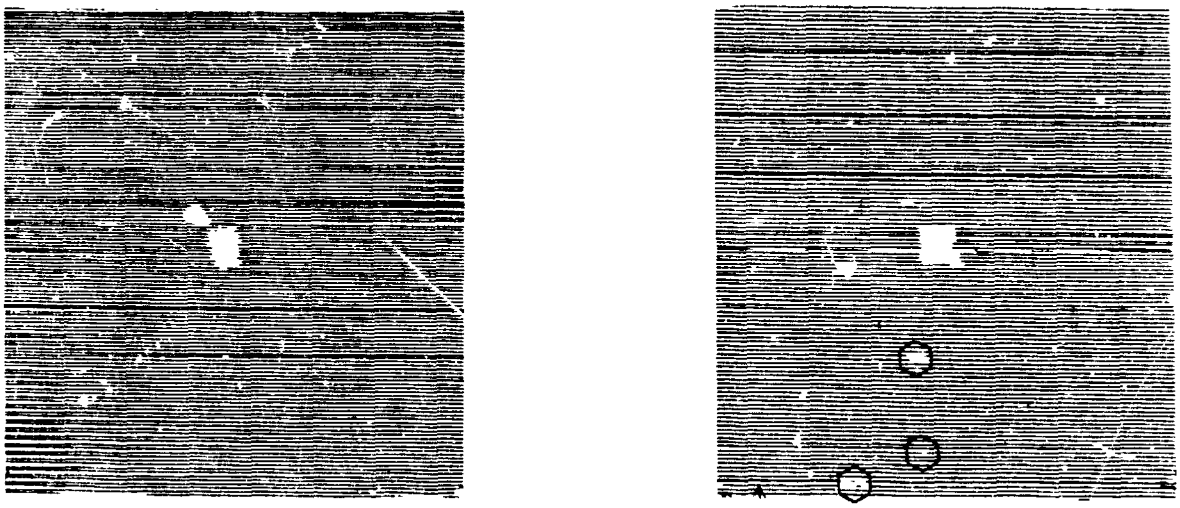
Upon cooling after mixing at 60°C, the blend became slightly turbid probably due to the AA 406 prepolymer becoming insoluble in the DEN 438.

Typical fabrication procedures used for each laminating resin are given in the experimental section of this report. Table 20 gives the physical



Novolac-cyanate graphite composite

Novolac-cyanate graphite composite



Epoxy novolac graphite composite

Epoxy novolac graphite composite

Notes:

1. Nonbond areas are indicated with hexagons.
2. White areas in center of composites are lead references.
3. Fiber direction is perpendicular to scan lines.

Figure 39. Typical C-scans of large novolac-cyanate and epoxy novolac unidirectional composites

properties of the 12 laminates and Tables 21 and 22 the short beam shear and flexural properties of the two laminates retained for testing.

The epoxy novolac systems show slight improvement in mechanical properties over these previously reported in Tables 18 and 19. Initial dry short beam shear strengths were 92.4 MPa (13.4 ksi) under ambient conditions and 45.8 MPa (6.64 ksi) at 177°C (350°F). Flexural strengths were 1289 MPa (187 ksi) under ambient conditions and 665 MPa (96.4 ksi) at 177°C (350°F). Of interest are the strength increases which occur with aging at 204°C (400°F). The absolute strengths even of the heat aged specimens are less than state-of-the-art values.

The novolac-cyanate systems show excellent strength retention to 204°C (400°F). On a percentage basis, the strength retention exceeds state-of-the-art values. The absolute values of shear and flexural strength in the initial dry tested condition are below state-of-the-art values except at 177°C (350°F) where the short beam shear strength is equal to state-of-the-art values. After heat aging in air at 204°C (400°F), the flexural strength has increased to the point where state-of-the-art flexural values are now equalled. The short beam shear strengths after heat aging at 177°C (350°F) remain equal to state-of-the-art short beam shear strengths.

Both the epoxy novolac and novolac-cyanate systems demonstrate excellent thermal stability at the aging temperature 204°C (400°F).

TABLE 20. PHYSICAL PROPERTIES OF ADDITION CURED NOVOLAC/T300 COMPOSITES

Laminate No.	Resin System	Resin Content, Weight Percent	Specific Gravity g/cc	Fiber Content, Volume Percent	Calculated Void Content, Volume Percent
DD 44-17	Epoxy novolac	39.5	1.51	52.2	0
DD 44-18	↓	38.0	1.52	53.8	↓
DD 44-19		39.0	1.52	52.7	
DD 44-20		38.4	1.54	53.5	
DD 44-21		36.8	1.53	55.0	
DD 44-22		37.4	1.52	54.4	
DD 44-29	Novolac cyanate	30.0	1.55	63.3	1.6
DD 44-30	↓	36.5	1.53	56.4	1.0
DD 44-31		36.8	1.55	56.8	0
DD 44-32		31.4	1.55	61.8	1.1
DD 44-33		30.6	1.56	62.7	1.0
DD 44-34		34.3	1.53	58.7	1.9

TABLE 21. SHORT BEAM SHEAR STRENGTHS OF NOVOLAC CYANATE AND EPOXY NOVOLAC/T300 COMPOSITES

Laminate Number	Specimen Conditioning	Short Beam Shear Strength MPa (Ksi) Test Temperature, ^{o}C (^{o}F), 3 Specimens per Test Ambient	121 (250)	177 (350)	204 (400)	Comments
Epoxy Novolac						
DD 44-20	Initial, dry	82.7 (12.0)		44.2 (6.41)	39.0 (5.65)	
DD 44-21	Initial, dry	92.4 (13.4)	61.6 (8.97)	45.8 (6.64)	37.2 (5.40)	
DD 44-20	500 Hrs, 204°C Air	88.2 (12.8)		49.3 (7.28)		0.7 percent weight loss
DD 44-20	1000 Hrs, 204°C Air	91.7 (13.3)		49.2 (7.13)		1.7 percent weight loss
DD 44-20	2000 Hrs, 204°C Air	84.8 (12.3)/		50.7 (7.35)		2.6 percent weight loss
DD 44-21	2000 Hrs, 204°C Air	76.5 (11.1)		66.9 (7.71)		4.3 percent weight loss
Novolac-Cyanate						
DD 44-31	Initial, dry	109.0 (15.8)	85.5 (12.4)	73.8 (10.7)	67.1 (9.73)	
DD 44-32	Initial, dry	95.1 (13.8)		64.6 (9.37)	60.4 (8.76)	
DD-44-32	500 Hrs, 204°C Air	82.0 (12.0)		68.9 (10.0)		0.3 percent weight loss
DD 44-32	1000 Hrs, 204°C Air	82.8 (12.0)		68.3 (9.91)		0.5 percent weight loss
DD 44-31	2000 Hrs, 204°C Air	86.2 (12.5)		54.2 (7.87)		2.2 percent weight* loss
DD 44-32	2000 Hrs, 204°C Air	71.7 (10.4)		56.5 (8.19)		0.8 percent weight loss

*Comparison to Table 22 flexural specimen weight loss data suggests error in this data point

TABLE 22. FLEXURAL PROPERTIES OF NOVOLAC CYANATE AND EPOXY NOVOLAC/T300 COMPOSITES

Laminate Number	Specimen Conditioning	Flexural Strength, MPa (Ksi)/Modulus GPa (Msi)				Comments
		Test Temperature, °C (°F)				
		Ambient	121 (250)	177 (350)	204 (400)	
		Epoxy Novolac				
DD 44-20	Initial, dry	1289 (187)/ 98.6 (14.3)		665 (96.4)/ 91.0 (13.2)	576 (83.5)/ 100 (14.5)	2 Specimens
DD 44-21	Initial, dry	1268 (184)/ 101 (14.7)	917 (133)/ 95.1 (13.8)	689 (100)/ 89.6 (13.0)	592 (85.9)/ 91.7 (13.3)	3 Specimens
DD 44-20	500 hrs, 204°C Air	1261 (183)/ 99.3 (14.4)		775 (116)/ 97.9 (14.2)		2 Specimens 0.5 percent weight loss
DD 44-21	1000 Hrs, 204°C Air	1365 (198)/ 101 (14.7)		867 (126)/ 97.4 (13.7)		2 Specimens 1.2 percent weight loss
DD 44-20	2000 Hrs, 204°C Air	1572 (228)/ 114 (16.6)		854 (124)/ 101 (14.7)		2 Specimens 2.0 percent weight loss
		Novolac Cyanate				
DD 44-31	Initial, dry	1206 (175)/ 91.0 (13.2)	1172 (170)/ 91.0 (13.2)	1138 (165)/ 88.9 (12.9)	1075 (156)/ 101 (14.6)	3 Specimens
DD 44-32	Initial, dry	1324 (192)/ 96.5 (14.0)		1124 (163)/ 93.8 (13.6)	1117 (162)/ 107 (15.5)	2 Specimens
DD 44-32	500 Hrs, 204°C Air	1551 (225)/ 92.4 (13.4)		1302 ([illegible])/ 96.5 ([illegible])		2 Specimens 0.3 percent weight loss
DD 44-31	1000 Hrs, 204°C Air	1530 (222)/ 93.8 (13.6)		1255 (182)/ 93.1 (13.5)		2 Specimens 0.6 percent weight loss
DD 44-32	2000 Hrs, 204°C Air	1433 (208)/ 108 (15.8)		1234 (179)/ 103 (14.9)		2 Specimens 0.8 percent weight loss

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

1. Cyanate and propargyl ether derivatives of novolacs exhibited anaerobic char yields at 800°C comparable to those of state-of-the-art phenolics.

2. A phosphonitrillic derivative (AA 406) was effective in increasing char yields of glycidyl ether derivatives.

3. The allyl novolacs, epoxy novolac acrylates and methacrylates, and resole acrylates exhibited low heat distortion temperatures (DTUL) values.

4. Novolac cyanate/T300 graphite composites exhibited excellent mechanical properties at 204°C. Further studies are recommended to increase the flexibility and moisture resistance of the novolac cyanates.

5. Novolac glycidyl ether/T300 graphite composites exhibited excellent processability, equivalent to that of state-of-the-art epoxies. Further work is recommended to increase DTUL and mechanical properties at elevated temperatures.

SECTION 5

EXPERIMENTAL

PREPARATION OF PHENOL-FORMALDEHYDE NOVOLAC (BASELINE NOVOLAC)

To a round bottom flask was added 28.2 grams (0.30 mole) of phenol, 19.5 grams (0.24 mole) of 37 percent aqueous formaldehyde and 0.05 grams oxalic acid dihydrate. The flask was placed into a 100°C oil bath. During the first two hours the flask was shaken vigorously every 10-15 minutes. The reaction was allowed to proceed overnite and the bath temperature increased to 140°C.

The yield of novolac was 28.2 grams and its melting point was approximately 80°C.

PREPARATION OF NOVOLAC-CYANATE RESIN

Five grams of the phenol-formaldehyde novolac described above were dissolved in 40 milliliters of reagent acetone and 25 milliliters of reagent methylene chloride. Cyanogen bromide (8 grams; 0.075 mole) was dissolved in the solution and the flask equipped with magnetic string bar immersed in an alcohol/dry ice bath. When the temperature of the stirring solution reached 0°C, 7 grams (0.07 mole) of triethylamine was added dropwise maintaining the temperature between 0° and 5°C. Upon completion of triethylamine addition, the reaction was allowed to stir at 0°C for 30 minutes. At this time 150 milliliters of ice water was added to the flask and stirring continued for 5 minutes.

The contents of the flask were poured into a separatory funnel, the methylene chloride drained into the reaction flask, a fresh portion of ice water stirred with the methylene chloride solution for five minutes and this process repeated to give a total of 3 aqueous washings. The methylene chloride after treatment with 5g of $MgSO_4$ was removed with gentle warming under vacuum. The flask was placed under high vacuum overnight at room temperature to give a yield of 5.5 grams of novolac-cyanate prepolymer. Upon placing the viscous liquid product on a 204^oC hotplate a few bubbles formed in the product prior to gel which occurred in 4 minutes. These bubbles may represent a trace amount of methylene chloride or other volatile material. The weight loss of a small film of the prepolymer in TGA measurement was 2 percent to 100^oC and 10 percent to 200^oC where the temperature was held for 10 minutes and no further weight loss occurred. This weight loss data suggests the loss of higher boiling compounds such as phenyl cyanate rather than methylene chloride. The cured resin had an anaerobic char yield of 54 percent at 800^oC.

A second, 132g preparation of novolac-cyanate resin was carried out. No difficulties were encountered in its preparation. The resin after 4 hour cure at 204^oC (400^oF) had a density of 1.29g/cc, and an anaerobic char yield of 58 percent at 800^oC. The aerobic char yield curve was slightly better than the aerobic char yield curve of the first 5.5g preparation.

A final preparation of novolac cyanate resin was carried out. The novolac prepolymer used in this preparation was obtained from a 10 fold scale up of the procedure described by Sorenson and Campbell (Reference 3). Additional vacuum treatment of the novolac occurred for 16 hours at 150^oC to remove much of the free phenol in the product. Eight hundred grams of this novolac was treated with 1000 grams of cyanogen bromide as described above. The gel properties of the product were 1.5 hours at 200^oC and about 24 hours at 100^oC. The explanation for the increased gel time over the products described above is the product has less impurities in it due to better aqueous extraction on the 22 liter scale. This product was used in the fabrication of six large composites.

PREPARATION OF 9,9-BIS(3,5-DIMETHYL-4-HYDROXYPHENYL)FLUORENE

Fluorene (36g; 0.2 mole), 2,6-dimethylphenol (54g; 0.44 mole) were dissolved with stirring in 80 milliliters of acetic acid. Upon attaining a homogeneous solution, 40 milliliters of 30 percent hydrogen bromide in acetic acid and 3 milliliters of thiolactic acid was added. In a few minutes a precipitate formed and the reaction was allowed to proceed for 3 hours at room temperature. The precipitate was filtered away from the reaction mixture and washed with two 10 milliliter portions of acetic acid. The product was slurried with 100 milliliters of water, filtered, the operation repeated and dried overnight at 150°C to give 60 grams of crude 9,9-bis(3,5-dimethyl-4-hydroxyphenyl)fluorene.

The 60 grams of crude product was recrystallized from 800 milliliters of ethyl alcohol using 10g of charcoal to give 45 grams of dried product (56.5 percent yield). mp 285-6°C (corr.)

PREPARATION OF 9,9-BIS(3,5-DIMETHYL-4-ALLYLOXYPHENYL)FLUORENE

9,9-Bis(3,5-dimethyl-4-hydroxyphenyl)fluorene (4.06g; 0.01 mole) and sodium hydroxide (1.00g; 0.025 mole) were dissolved in 50 milliliters of refluxing ethyl alcohol. Allyl bromide (3.03g; 0.025 mole) was added to the refluxing solution and in a few minutes sodium bromide began to precipitate. Samples were removed from the reaction mixture every hour and worked up with aqueous potassium carbonate (∿10 ml of 10 percent solution) and chloroform (∿3 ml). When the infrared spectrum of the chloroform residue showed no further reduction in hydroxyl absorption at $\sim 3400 cm^{-1}$, the reaction was worked up.

The reaction mixture was poured into 150 milliliters of a 10 percent potassium carbonate water solution with 100 milliliters of chloroform. The chloroform was separated from the water layer and washed with a second portion of potassium carbonate solution (150 milliliters). The chloroform layer was then washed with 100 milliliters of water, dried over magnesium sulfate, filtered and the chloroform removed with heat under vacuum. Final conditions were 16 hours at 80^{o}C at less than one millimeter pressure. Thus obtained was 4.1g (84 percent yield) of 9,9-bis(3,5-dimethyl-4-allyloxyphenyl)fluorene. mp 182^{o}C by DSC.

PREPARATION OF 9,9-BIS(4-ALLYLOXYPHENYL)FLUORENE

Using the molar ratios and procedure described in the previous preparation and starting with 9,9-bis(4-hydroxyphenyl)fluorene (9.0 grams; 0.026 mole), 9.5 grams (84 percent yield) of 9,9-bis(4-allyloxyphenyl)fluorene was obtained. The product was glassy with a softening point of about 35^{o}C.

PREPARATION OF THE ALLYL ETHER OF THE BASELINE NOVOLAC

Five grams of the phenol-formaldehyde novolac (mp 80^{o}C) described previously was treated as described above with allyl bromide. Required molar ratios of allyl bromide and sodium hydroxide were calculated on the basis of the weight of novolac as equivalent to phenol. No difficulty was encountered in the aqueous potassium carbonate washings of the chloroform solution of the allyl novolac, however when water was used in the last wash of the chloroform solution an emulsion formed which required the addition of a small amount of potassium carbonate solution to break. The yield of allyl novolac was 4.5g (62.5 percent yield based on phenol). It was a viscous liquid at room temperature.

PREPARATION OF 2,7-DICYANATONAPHTHALENE

2,7-Dihydroxynaphthalene (8.0 grams; 0.05 mole) and cyanogen bromide (11.7 grams 1.1 mole) were dissolved in 50 ml of reagent acetone. The flask with magnetic string bar, acetone and reactants were placed into an alcohol/dry ice bath. When the temperature reached 0^{o}C, triethylamine (11.0 grams; 1.1 mole) was added dropwise maintaining the temperature between 0^{o} and 5^{o}C. Upon completion of triethylamine addition, the reaction was allowed to continue for 1/2 hour, the triethylamine hydrobromide filtered from the reaction and the filtrate poured slowly into 200 ml of ice water. The solid product was dried overnite under vacuum to give 12 grams of crude product which was crystalized from 75 ml of methylene chloride to give 6 grams of product, mp 138-139^{o}C (corr.).

PREPARATION OF 9,9-BIS(4-CYANATOPHENYL)FLUORENE

The procedure used to prepare the 2,7-dicyanatonaphthalene was essentially repeated to provide 17.5 grams of crude 9,9-bis(4-cyanatophenyl) fluorene. Crystallization occurred from 50 milliliters of methylene chloride with 30 milliliters of hexane to provide purified crystals of product, mp 158.5-159°C (Corr.). Literature melting point 158°C, (CA 75 49610m).

PREPARATION OF 9,9-BIS(4-GLYCIDYLOXYPHENYL)FLUORENE

To a 250 milliliter round bottom flask was added 9,9-bis(4-hydroxyphenyl) fluorene (11.0 grams; 0.031 mole), epichlorohydrin (27.8 grams; 0.30 mole) and water (0.15 gram). The mixture was heated to 80°C in an oil bath with stirring. Sodium hydroxide (2.52 grams; 0.063 mole) was added in six portions. When the reaction temperature reached 99°C, the reaction was removed from the oil bath and placed in a cold water bath. When the reaction temperature fell to 95°C, another portion of the sodium hydroxide was added. Temperature control was maintained between 95 and 100°C by sodium hydroxide additions and intermittent heating and cooling as described above. When the exothermic reactions subsided (about 30 minutes), the excess epichlorohydrin was distilled from the reaction mixture at a pressure of about 50 millimeters. The pot temperature was not allowed to exceed 150°C. The residue was then cooled to about 70°C and 100 milliliters of benzene was added to precipitate the salt present. The salt was removed by vacuum filtration and washed with two 5 milliliter portions of benzene. The benzene solutions were combined and the benzene was distilled. Some difficulty was encountered with the foaming of the product during benzene removal and this was alleviated by heating the flask and contents to 150°C and removal of the benzene at that temperature. Final conditions for removal of the epicnlorohydrin and benzene was one hour at 150°C and less than one milliliter pressure.

Obtained was 12.7 grams of product whose melting point was about 110°C. During product isolation a portion of the product was lost by the benzene solution boiling out of the flask. The recovered yield was 83 percent of theory.

PREPARATION OF ACRYLATE ESTER OF DEN 438 EPOXY NOVOLAC

To a side arm test tube was added 8.9 grams of DEN 438, 3.6 grams of acrylic acid, 0.2 gram of triethylbenzylammonium chloride and 0.2 grams of hydroquinone. The test tube with thermometer was immersed into a 110°C oil bath and the contents kept under nitrogen purge. Gentle stirring during heat up provided a homogeneous reaction. The mixture thickened slowly over its 1.5 hour reaction time at 100°C. After cooling 4.15 grams of styrene was added to the very viscous acrylate ester resin. Gel particles were removed by filtration through polypropylene felt.

PREPARATION OF 9,9-BIS(4-PROPARGYLOXYPHENYL)FLUORENE

9,9-Bis(4-hydroxyphenyl)fluorene (3.50g; 0.01 mole) and sodium hydroxide (1.00g; 0.025 mole) were dissolved in 50 milliliters of ethyl alcohol at R.T. Propargyl bromide (2.99g; 0.025 mole) was added to the solution and after one hour when no sodium bromide appeared, the solution was heated to reflux. In a few minutes sodium bromide began to precipitate. After two hours at reflux, the reaction mixture was poured into 150 milliliters of a 10 percent potassium carbonate water solution with 100 milliliters of chloroform. The chloroform was separated from the water layer and washed with a second portion of potassium carbonate solution (150 milliliters). The chloroform layer was then washed with 100 milliliters of water, dried over magnesium sulfate, filtered and the chloroform removed with heat under vacuum. Final conditions were 3 hours at 60°C at less than one millimeter pressure. Thus obtained was 2.4g (56 percent yield) of 9,9-bis(4-propargyloxyphenyl) fluorene mp $< 45^{\circ}$C.

PREPARATION OF THE PROPARGYL ETHER OF THE BASELINE NOVOLAC

Five grams of the phenol-formaldehyde novolac (mp 80°C) was treated as described above with propargyl bromide. Required molar ratios of propargyl bromide and sodium hydroxide were calculated on the basis of the weight of the novolac as equivalent to phenol. The yield of propargyl novolac was 1.5g (22 percent yield based on phenol). It was a viscous, sticky liquid at room temperature.

PREPARATION OF A RESOLE - ACRYLATE

To an erlenmeyer flask was added 9.4g (0.1 mole) of phenol, the selected aldehyde* and 14g of a 10 percent aqueous solution of potassium hydroxide (0.025 mole). The reaction was stirred and heated at 70°C for 2 hours. Sufficient 10 percent sulfuric acid was added to bring the PH to 6-7. Vacuum was applied and the water was removed. The temperature was not allowed to exceed 70°C. The dehydration was continued until free phenol was distilled from the reaction indicating essentially complete water removal.

The product was dissolved in 50 milliliters of acetone and 5 milliliters of pyridine was added. Acrylic anhydride, 50.4g (0.4 mole) was then added and after the exotherm subsided the reaction was refluxed for 1 hour. Upon cooling, 25 milliliters of water was added slowly to hydrolyze the excess acrylic anhydride and the mixture again was briefly refluxed. 50 Milliliters of methylene chloride was added to the mixture and 3 extractions with 150 milliliter portions of distilled water of the methylene chloride solution occurred. A final wash with a 10 percent aqueous solution of sodium bicarbonate was carried out, the methylene chloride solution was dried with 10g of $MgSO_4$ and filtered. Removal of the solvent under high vacuum provided the neat syrup-like resin.

The acrylation step was carried out on the baseline novolac as described above for the resoles to give a product with a melting point of about 80°C.

Infrared spectral analysis of the products showed that complete acrylation had occurred in all of the products.

THORNEL 300 PREPREG PREPARATION

Prepregs were prepared in all cases by hot melt coating a film of the resin onto Mylar, taping the coated Mylar onto the drum, overwinding the resin with fibers (40 tows per inch) and completion of the impregnation step on a hot table with a squeegee. Resin contents of the prepregs varied from 45 to 50 percent by weight.

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*12.3g Aqueous formaldehyde; 14.4g furfural; 8.4g acrolein.

TYPICAL PREPARATION OF NOVOLAC CYANATE UNIDIRECTIONAL GRAPHITE COMPOSITES

Thirteen plies of prepreg were laid into a steel trap mold with TX 1040 on both sides of the stack of novolac cyanate graphite prepreg. Two plies of 7781 glass fabric were placed on each side of the TX 1040 sheets. The layup was placed in a vacuum bag and full vacuum applied for 30 minutes at room temperature. The mold containing the layup was removed from the vacuum bag and placed in a press preheated to 65°C (150°F). The temperature controller was set for 135°C (275°F) and the gel-thickening properties noted with time and increasing temperature. Thirty five minutes after start, 0.7 MPa (100 psi) was applied (138°C). The laminate was held at 135°C for 1 hour and the temperature raised to 177°C (350°F) and held there for 1 hour. The laminate was cooled under pressure to room temperature. After demolding the composite was post cured with the five other composites fabricated by the above procedure. Application of 0.7 MPa (100 psi) to the composite stack occurred in a cold press. The composites were then heated to 218°C (425°F) for 6 hours and cooled.

TYPICAL PREPARATION OF EPOXY NOVOLAC UNIDIRECTIONAL GRAPHITE COMPOSITES

The epoxy novolac graphite prepregs were laid up in the manner described above for the novolac cyanate composites. Due to the low flow characteristics of the prepreg however, additional bleeder plies were added to each side of the composite such that with the bleeder plies completely impregnated the composite would have the proper final resin content.

The trap mold containing the layup was placed into a vacuum bag and held under full vacuum for 1 hour. This assembly was then placed into a cold press and the controller set for 121°C (250°F). When the temperature reached 90°C, 0.4 MPa (50 psi) was applied and the vacuum vented to the atmosphere. The controller was set for 107°C (225°F) and the composite was cured for 2 hours at that temperature.

Post cure of the epoxy novolac cyanate graphite composites occurred as described above for the novolac-cyanate graphite composites.

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APPENDIX A

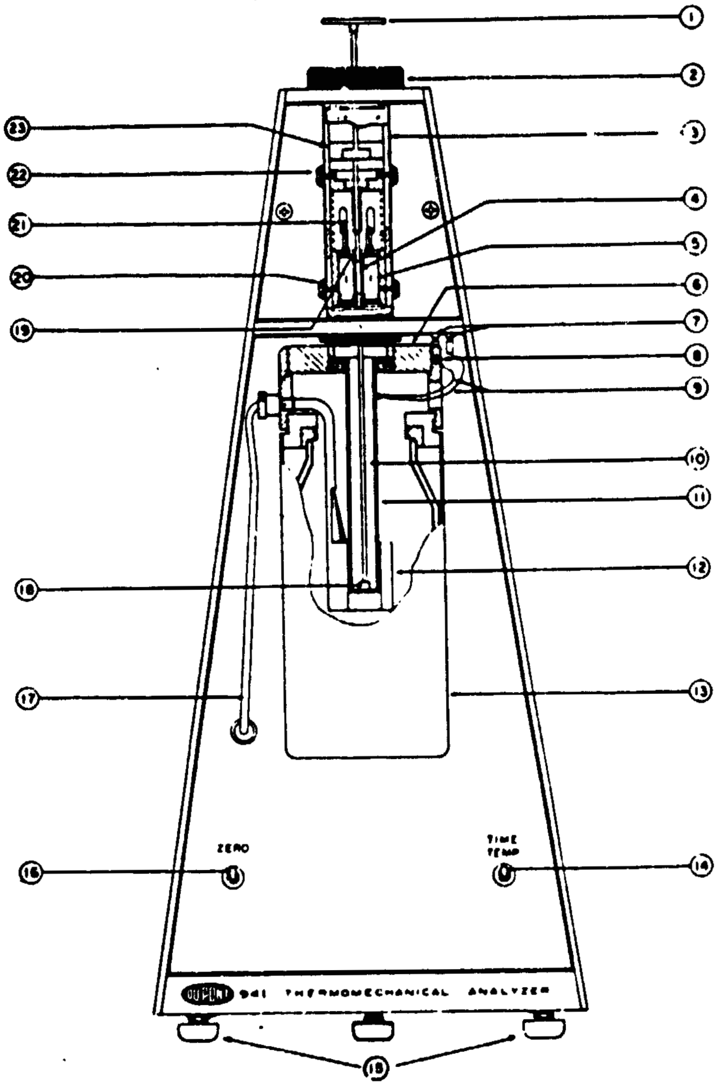
DISTORTION TEMPERATURE UNDER LOAD

Distortion temperature under load (DTUL) is carried out on a cured sample of resin with essentially parallel faces as sketched in Figure A-1. The intercept of the expansion curve with the softening curve or a change in slope of the expansion curve is taken as the temperature at which the sample will no longer support the compressive load placed upon it.

Figure A-2 shows the epoxy-novolac, DEN 438 cured with several curing agents and how DTUL's relate to the target performance temperature. In the case shown, 177°C (350°F) is the target performance temperature and 227°C is the suggested minimum DTUL to be obtained on the experimental resin system to match state-of-the-art/177°C (350°F) performing epoxy resin systems. See Reference 10.

FIGURE A-1

SKETCH OF SET-UP TO DETERMINE DISTORTION TEMPERATURE UNDER LOAD (DTUL)



Item	Description	Item	Description
1	Weight tray	12	Heater assembly
2	Retainer nut	13	Dewar
3	Head assembly	14	Time-Temp switch
4	LVDT core	15	Adjustable legs
5	LVDT	16	Zero switch
6	Dewar cap	17	Heater lead wire
7	Thermocouple connectors	18	Sample
8	Set screws	19	Shaft assembly (upper)
9	Thermocouple wires	20	Transducer Position control
10	Shaft assembly (lower)	21	Zero spring
11	Sample holder tube	22	Probe Position control
		23	Upper Bearing guide

DTUL experiments are conducted using a 0.025 inch diameter probe and a 100g weight on the weight tray. This places a 449 psi load on the sample.

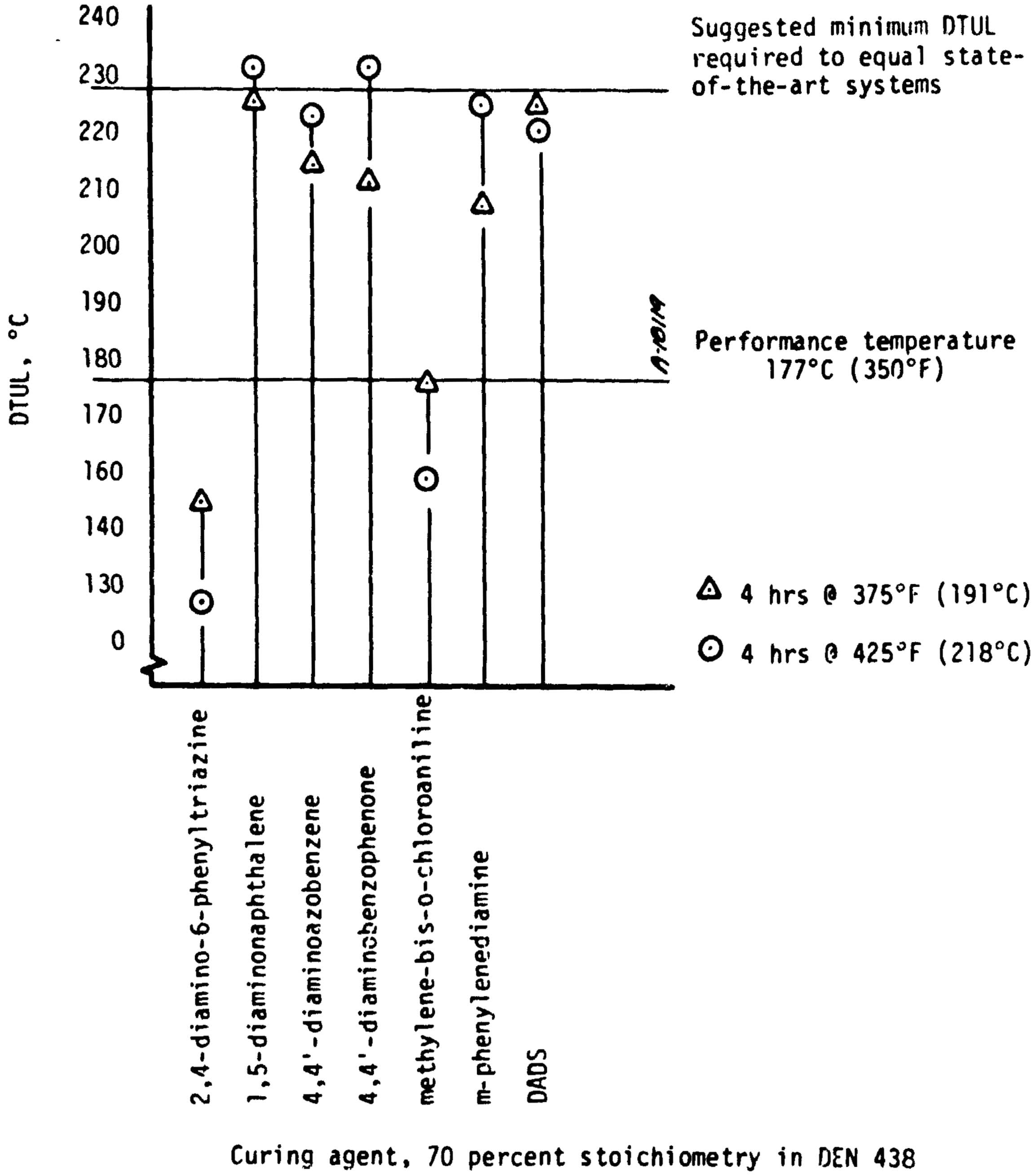


Figure A-2. Distortion temperature under loads for various curing agents with DEN 438, at two final cure temperatures.

APPENDIX B

AA 406

AA 406 is a hydrolytically stable, semi-inorganic, polymer intermediate derived from phosphonitrillic chloride and hydroquinone. It is a dry, free flowing powder, which softens upon heating but does not melt. The properties imparted by cured AA 406 are flame resistance, heat stability, structural strength and excellent environmental existence by finished products based on either AA 406 alone or coreacted with any of a variety of other resins or polymeric systems. In addition, the cured AA 406 exhibits good electrical properties and resistance to nuclear radiation.

AA 406 is soluble in a number of types of organic polar solvents including alcohols, ketones, esters, amides, acids and cyclic ethers such as tetrahydrofuran and dioxane. It is insoluble in hydrocarbons and chlorinated hydrocarbons; however some of these solvents may be used as diluents in conjunction with other solvents.

AA 406 may be reacted with phenolic resin curing agents, such as hexamethylenetetramine and monomeric and polymeric materials containing groups reactive to the hydroxyphenyl system. Examples of such reactants include isocyanates, isothiocyanates, epoxies, acids, acid halides, and active halogen and ester compounds.

Because of its polar nature, AA 406 is compatible with a number of other resin systems, such as phenolics, polyesters, epoxies, polyamides, and many elastomers. Blends may be prepared from dry powders, by dissolution, or by mixing with liquid or semisolid resin systems. AA 406 as produced is a solid, soluble, thermoplastic material and must be cured to fully realize its favorable properties. This may be accomplished by heat alone, or by the addition of phenolic curing agent such as hexamethylenetetramine and heat.

When curing by means of heat alone, AA 406 is heated for one hour at 425°F during which time the resin undergoes a characteristic color change from tan to dark brown or black. Curing may also be accomplished by heating it at higher temperatures for shorter periods of time, i.e., 15 minutes at 500°F.

Hexamethylenetetramine may be used to cure AA 406 at somewhat lower temperatures. Mixtures of resin containing one to 15 percent by weight of hexamethylenetetramine cure in one hour at 250°F. The best values of heat resistance and strength have been obtained from AA 406 systems containing five percent hexamethylenetetramine, cured partially at 250° to 300°F, then finally at 425°F.

The structure of this resin system is given below.