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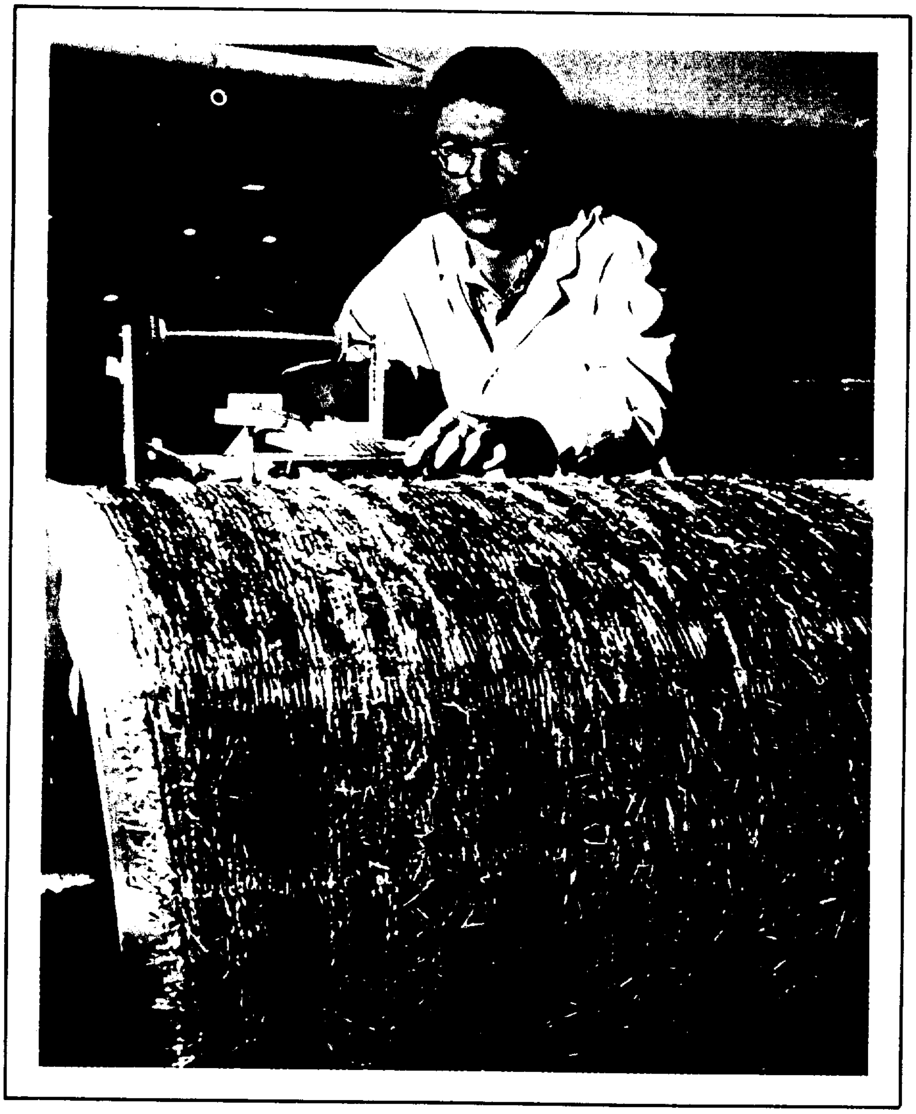
PLASTICS DESIGN & PROCESSING



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RESINS AND ADDITIVES

Performance Properties Of Graphite Reinforced Composites With Advanced Resin Matrices

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Graphite-reinforced composites have potential applications in advanced aircraft due to their weight savings and performance characteristics (figure 1 and table 1). Performance characteristics of composites depend on the properties of the materials comprising the composite and the process by which they are combined. This is particularly true of graphite-reinforced composites where the mechanical strengths are dependent on the type, amount, and orientation of the fibe well as the type of the resin m used. The contribution of the resin trix to the ultimate performance o composite has been studied, with ticular emphasis on the thermal, f mability, and some mechanical p erties.

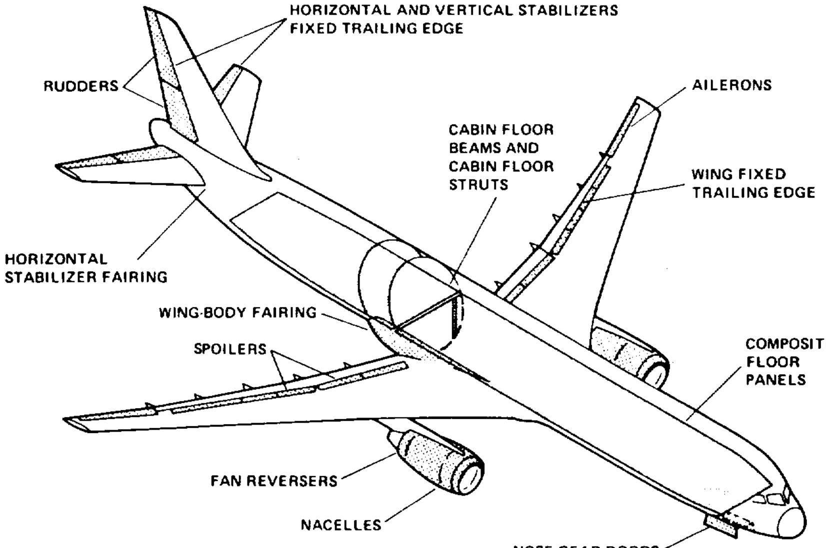

Fig. 1, Composite material application.

Table 1 — Metal vs. C

	M Weig
Wing	1
Fixed trailing edge	
Aileron	
Spoiler	
Wing-to-fuselage fairing	
Tail	
Elevator	
Rudder	
Horizontal stabilizer fairing	
Fuselage	
Cabin floor beams and supports and cargo floor beams	
TOTAL	2

This article looks at the effect o ferent resin matrices on thermal mechanical properties of gra composites, and relates the the and flammability properties to anaerobic char yield of the resins. processing parameters of gra composites utilizing graphite f and epoxy or other advanced resi matrices are presented. Therm resin matrices studied were: ar cured polyfunctional glycidyl an type epoxy (baseline), phen novolac resin based on condens of dihydroxymethyl-xylene and ph cured with hexamine, two type polydismaleimide resins, phe resin, and benzyl resin. The the plastic matrices studied were ethersulfone and polyphenylen fone.

Table 1 — Metal vs. Composite Weight-Saving Summary

	Metal Weight (kg)	Composite Weight (kg)	Differences	
			Weight (kg)	Percent
Wing	1214	992	−222	−18.3
Fixed trailing edge	477	381	−95	−20.0
Aileron	98	73	−24	−25.0
Spoiler	251	226	−24	−10.0
Wing-to-fuselage fairing	389	311	−78	−20.0
Tail	464	349	−115	−24.8
Elevator	184	138	−101	−25.0
Rudder	241	181	−133	−25.0
Horizontal stabilizer fairing	40	31	−20	−22.5
Fuselage	708	531	−177	−25.0
Cabin floor beams and supports and cargo floor beams	708	531	−177	−25.0
TOTAL	2386	1872	−514	−21.6

amount, and orientation of the fiber, as well as the type of the resin matrix used. The contribution of the resin matrix to the ultimate performance of the composite has been studied, with particular emphasis on the thermal, flammability, and some mechanical properties.

This article looks at the effect of different resin matrices on thermal and mechanical properties of graphite composites, and relates the thermal and flammability properties to the anaerobic char yield of the resins. The processing parameters of graphite composites utilizing graphite fabric and epoxy or other advanced resins as matrices are presented. Thermoset resin matrices studied were: amine-cured polyfunctional glycidyl amine-type epoxy (baseline), phenolic-novolac resin based on condensation of dihydroxymethyl-xylene and phenol cured with hexamine, two types of polydismaleimide resins, phenolic resin, and benzyl resin. The thermoplastic matrices studied were polyethersulfone and polyphenylenesulfone.

Properties evaluated in the study included anaerobic char yield, limiting oxygen index, smoke evolution, moisture absorption, and mechanical properties at elevated temperatures including tensile, compressive, and short-beam shear strengths. Generally, it was determined that graphite composites with the highest char yield exhibited optimum fire-resistant properties.

Resin Chemistry — Thermoset Matrices

The chemistry of the resin matrices studied is outlined in figure 2. The baseline epoxy resin is amine-cured polyfunctional glycidyl amine-type epoxy resin.

The phenolic resin is essentially the product of the condensation of dihydroxymethyl-xylene and a phenol (1). These phenolic novolac-type resins are usually cured with hexamine to yield thermally stable, cross-linked polymers possessing good long-term performance to 230 °C.

Two types of bismaleimide resins were studied. Bismaleimide A is a solvent resin system. Prepregs from this resin are prepared from a resin solution containing N-methylpyrrolidinone as the solvent. Bismaleimide B is a hot-melt maleimide-type resin which forms a low-viscosity fluid after being molten. This resin is processed by hot-melt coating techniques into graphite prepreg with excellent tack and drape.

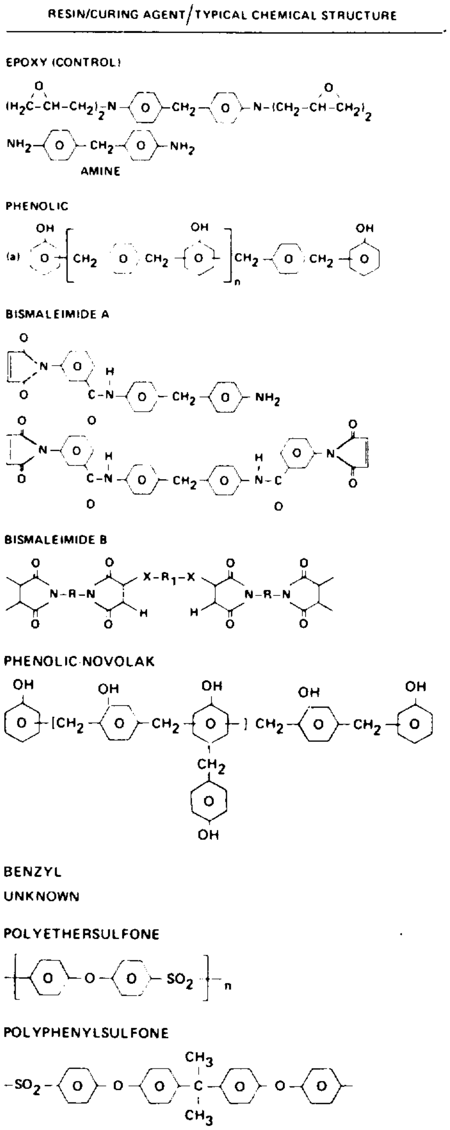

Fig. 2, Resin matrices for graphite composites.

The bismaleimide A resin is produced by reacting m-maleimidobenzoic acid chloride with an aromatic diaminocompound in the molar proportion of difunctional amine acid halide 1.4:2. The resin consists of a mixture of a bismaleimide and an aminoterminated monoimide. This mixture, close to the eutectic mixture, is cured by melting at 120-140 °C, which causes polymerization by addition of the free-amino groups to maleimide double bonds followed by a vinyl polymerization of the terminating maleimide double bonds. The advantage of this material is that the bismaleimide obtained in the first reaction provides a cured resin with a higher elongation to break as compared with other state-of-the-art bismaleimide-type resins reported previously. (2, 3).

Bismaleimide B is a eutectic ternary mixture of bismaleimides. Cure is accomplished by both chain extension and polyaddition. This resin mixture is capable of "B" staging by prepolymerization to provide a suitable high melt viscosity on the prepreg.

The fourth resin was a conventional phenolic-novolak resin. Its chemistry has been described previously (1). This phenolic resin is compounded for nonflammability and low smoke emission.

The fifth resin was a benzyl-type resin. The exact chemistry of this commercial resin system is not known.

Resin Chemistry — Thermoplastic Matrices

The thermoplastic resin matrices studied included polyethersulfone and

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polyphenylsulfone. The chemist these thermoplastics has been scribed previously in detail (4, 5) sulfone resins consist of the diary phone and benzoxy groups and propylidenyl linked together in va configurations (figure 2). Tl linkages are present in both polyr They permit rotation about the lin which imparts inherent toughne: the resins. Similar to other the plastics that have predomin aromatic nuclei in their backbone. of these resins should be hydrolyt stable, though no actual testing conducted on these resins in this to confirm this speculation.

Processing of Composites

All composites were fabric utilizing 8-harness satin-w graphite* designated as style fabric weighing 360.9 g/m². Prep were prepared utilizing this gra cloth as a standard reinforceme order to assess the effect of matrix on the flammability and chanical properties of the compo

Prepreg Preparation

The prepregs were prepare follows:

Epoxy/graphite — The preprec prepared by passing the graphite through a solution of the epoxy The coated fabric then was p through a vertical drying tower, provided a programmed drying p dure for the prepreg. Drying wa complished at 120 °C for 10 min.

Phenolic/graphite, phen novolak/graphite, and benzyl/gra — The prepreg preparation was e tially the same as the epoxy/gra

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*"Thornel" graphite yarn, Union Carbide New York.

polyphenylsulfone. The chemistry of these thermoplastics has been described previously in detail (4, 5). The sulfone resins consist of the diaryl sulphone and benzoxy groups and isopropylidenyl linked together in various configurations (figure 2). These linkages are present in both polymers. They permit rotation about the linkage which imparts inherent toughness to the resins. Similar to other thermoplastics that have predominantly aromatic nuclei in their backbone, both of these resins should be hydrolytically stable, though no actual testing was conducted on these resins in this study to confirm this speculation.

Processing of Composites

All composites were fabricated utilizing 8-harness satin-weave graphite* designated as style 133 fabric weighing 360.9 g/m². Prepregs were prepared utilizing this graphite cloth as a standard reinforcement in order to assess the effect of resin matrix on the flammability and mechanical properties of the composites.

Prepreg Preparation

The prepregs were prepared as follows:

Epoxy/graphite — The prepreg was prepared by passing the graphite cloth through a solution of the epoxy resin. The coated fabric then was passed through a vertical drying tower, which provided a programmed drying procedure for the prepreg. Drying was accomplished at 120 °C for 10 min.

Phenolic/graphite, phenolic-novolak/graphite, and benzyl/graphite — The prepreg preparation was essentially the same as the epoxy/graphite prepreg. The benzyl/graphite prepreg was staged at 135 °C for 10 min. in order to reduce volatile content to 3-4%.

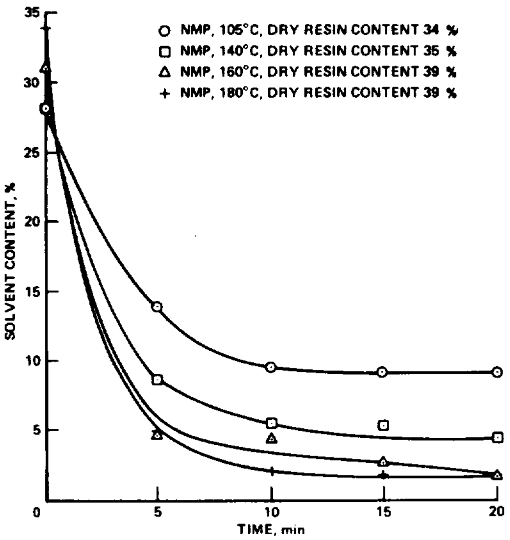

Fig. 3, Drying cycles for bismaleimide A prepregs.

Bismaleimide A/graphite — A resin solution consisting of 16 part-by-weight (pbw) of resin, 16 pbw of NMP, and 8 pbw toluol, was prepared by heating the components in a glass-enamelled vessel to 90 °C under constant stirring. The solution is further diluted, providing a 35%-by-weight solution. The prepregs are fabricated by use of standard prepregging equipment. Dip-coating techniques are used for wetting the fabric, followed by drying in a vertical drying tower with a temperature range of 150° to 170 °C. The prepregging speed is 0.6 cm/min. The resin solution is further diluted to provide a 30-32%-by-weight solution. The prepreg is passed through the drying tower twice at a speed of 0.6 cm/min. The effect of drying temperature on solvent content in the prepreg is shown

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*"Thornel" graphite yarn, Union Carbide Corp., New York.

in figure 3. Only a small amount of solvent loss was achieved by increasing the drying cycle from 160–180 °C. The optimum temperature for minimizing the amount of residual solvent was 170 °C.

Bismaleimide B/graphite — A resin solution consisting of 17.4 pbw of resin, 5.2 pbw of resin, 5.2 pbw diethyleneglycolmonoethylether, and 12.2 pbw of dioxane was prepared by heating the components at 100 °C for 2 hr. The prepreg is fabricated in the same manner as bismaleimide A. The impregnation bath is heated to 40 °C to prevent the resin from crystallizing.

Polyethersulfone/graphite — The polyethersulfone was dissolved in 12% methylene chloride solution which was used for the prime coat, and a 20% solution for prepregging. The prepreg was dried for 15 min. at 150 °C.

Polyphenylsulfone/graphite — The resin was dissolved in NMP. A 12% solution was used for the prime coat, and a 20% solution for prepregging. The prepreg was dried at 288 °C for 1 hr.

The resin content and the residual solvent (volatile content) from the above prepregs was determined by extracting them with dimethylacetamide (DMAC). The resin and volatile content was determined by the equation:

$$\frac{W}{O} = \frac{W_1 - W_2}{W_1} \times 100$$

(W_1 = weight of prepreg and W_2 = weight of fibers).

The resin content

$$\left(\frac{W}{O}\right) = \frac{W_1 - W_2}{W_1} \times 100$$

$$- \text{ volatile content } \left(\frac{W}{O}\right).$$

The resin, solvent, and fiber content for the above prepregs is indicated in table 2.

Table 2 — Resin/Solvent Content For Prepregs

Composite Resins	Content — %, Weight Resin	Fiber	Volatile
Epoxy	39.9	59.2	0.9
Phenolic	39	50.9	10.1
Bismaleimide A	38	45.5	16.5
Bismaleimide B	42.4	49.4	8.2
Phenolic-Novolak	51	40.7	8.3
Benzyl	39.4	48	12.6
Polyethersulfone	~35	—	—
Polyphenylsulfone	~35	—	—

Composite Fabrication

The prepregs containing the resins described above were laminated using the pressures, curing, and postcuring conditions outlined in table 3. All laminates fabricated consisted of 10 plies of graphite cloth.

Characterization Studies

Flammability, thermochemical, and mechanical tests were conducted to characterize the properties of both the neat resins and the laminates consisting of resin with the 133 graphite cloth. Measurements were conducted to evaluate the following properties of the materials: thermal stability, ease of ignition and propensity to burn, smoke emission, moisture absorption, and mechanical properties at ambient and elevated temperatures.

The thermal stability was measured by thermogravimetric analysis. The char yields of the various composites and neat resins were investigated by thermogravimetry (table 4). Thermal analyses of the composites were conducted on a thermogravimetric analyzer (TGA)** using nitrogen atmosphere. The TGA data for a heating rate of 10 °C/min. in nitrogen are shown in table 4. The TGA behavior of the bismaleimide A and B resins are quite different, as indicated by the char yield and the temperature at which the maximum weight loss occurs in the thermogram. Bismaleimide B, which is a highly cross-linked resin, seems to be more stable because of the higher decomposition temperatures. The higher

Table 3 — Processing and Curing

Resin Matrix	Cu
Epoxy	30 min @ 23 °C, 15 min @ 116 °C, 45 min @ 116-124 °C 160-200 min @ 177-1 Cool,
Phenolic	1 hr @ 82 °C, 1 hr @ 121 °C, 4 hr @ 232 °C, 4 hr @ 246 °C, In autoclave
Bismaleimide A	30 min @ 121 °C, 4 hr @ 177 °C, In autoclave
Bismaleimide B	15 min @ 9 °C, 80 min @ 150 °C, 315 min @23 °C, In autoclave
Phenolic-Novolak	1 hr @ 93 °C, 1 hr @ 93 °C, 4 hr @ 149 °C, Cool
Benzyl	20 min @ 59 °C, 20 min @ 79 °C, 40 min @ 104 °C, 4 hr @ 129 °C,
Polyethersulfone	15 min @ 149 °C, 30 min @371 °C,
Polyphenylsulfone	60 min @ 288 °C, 30 min @ 343 °C,

** "Thermographic analyzer" (TGA) 950, E.I. DuPont de Nemours & Co., Wilmington, Del.

Table 3 — Processing and Curing Conditions for Graphite Composites

Resin Matrix	Cure		Postcure
Epoxy	30 min @ 23°C,	Vacuum	
	15 min @ 116°C,	Vacuum	
	45 min @ 116-124°C,	690 kn/m^2	None
	160-200 min @ 177-182°C,	690 kn/m^2	
	Cool,	Vacuum	
Phenolic	1 hr @ 82°C,	1380 kn/m^2	6 hr @ 175°C
	1 hr @ 121°C,	1380 kn/m^2	4 hr from 175-200°C
	4 hr @ 232°C,	1380 kn/m^2	13 hr from 200-250°C
	4 hr @ 246°C,	1380 kn/m^2	Slow cool down to
	In autoclave		ambient in air oven
Bismaleimide A	30 min @ 121°C,	Vacuum only	2 hr @ 154°C
	4 hr @ 177°C,	690 kn/m^2	2 hr @ 182°C
			15 hr @ 210°C
			Slow cool down to
	In autoclave		ambient in air oven
Bismaleimide B	15 min @ 9°C,	Vacuum	15 hr @250°C
	80 min @ 150°C,	Vacuum	In air oven
	315 min @23°C,	400 kn/m^2	
	In autoclave		
Phenolic-Novolak	1 hr @ 93°C,	Vacuum	
	1 hr @ 93°C,	690 kn/m^2	
	4 hr @ 149°C,	690 kn/m^2	None
	Cool	690 kn/m^2	
Benzyl	20 min @ 59°C,	172 kn/m^2	4 hr @ 121°C
	20 min @ 79°C,	172 kn/m^2	
	40 min @ 104°C,	172 kn/m^2	
	4 hr @ 129°C,	345 kn/m^2	
Polyethersulfone	15 min @ 149°C,		
	30 min @371°C,	1380 kn/m^2	None
Polyphenylsulfone	60 min @ 288°C,		
	30 min @ 343°C,	1380 kn/m^2	None

shown in table 4. The TGA behavior of the bismaleimide A and B resins are quite different, as indicated by the char yield and the temperature at which the maximum weight loss occurs in the thermogram. Bismaleimide B, which is a highly cross-linked resin, seems to be more stable because of the higher decomposition temperatures. The higher char yield of the bismaleimide A resin is an indication that this resin has higher aromaticity.

The calculated char-yield values indicated are based on the fact that the graphite fiber has 100% char yield in an anaerobic environment (actual char yield approximately 98–99% at 900°C). Also, the resin removal is

Table 4 — Char Yield of Graphite Composites and Resins

Composite Resins	Resin Content %, Wt.	Composite Char Yield %, Wt.	Resin Char Yield %, Wt.	Neat Resin Char Yield,%, Wt.,*	PDT** °C dT/dt = 10 °C/min.	Max dW/dt At °C
Epoxy	33.2	79	37	38	360	425
Phenolic	24.6	83	31	46	430	525
Bismaleimide A	25.6	82.5	32	50	420	382
Bismaleimide B	43.3	71.5	34	46	425	470
Phenolic-Novolak	25.7	86	46	46	380	550
Benzyl	26	84.5	40	53	330	545
Polyethersulfone	36	77.5	38	40	545	595
Polyphenylsulfone	36	81	47	47	556	595

*Char yield at 900°C, N_2.
**Polymer decomposition temperature
***Calculated values

100% when the samples are subjected to the nitric acid immersion procedure to determine fiber and resin content in the laminate. The actual char yield of the neat resin samples is higher in most of the resins (table 4).

The ease of ignition was measured by the oxygen index. The oxygen index $OI = O_2/(O_2 + N_2)$ of the composite was determined per ASTM D-2863. Table 5 is the oxygen index of the graphite composites at ambient temperature. The polyethersulfone/graphite composite exhibited the highest oxygen of all the composites tested. This is in agreement with previous studies (6) which have shown that polyethersulfone has a high oxygen index when tested as a neat resin.

Table 5 — Limiting Oxygen Index For Graphite Composites

Composites	LOI,%
Epoxy	41
Phenolic	46
Bismaleimide A	47
Phenolic-Novolak	50
Bismaleimide B	—
Polyethersulfone	54
Polyphenylsulfone	52

Note: Data unavailable for bismaleimide B and benzyl.

The smoke evolution from the graphite composites was determined using the NBS-Aminco smoke-density chamber. The specific optical density (D_S) values were obtained from individual test data and then averaged. The test results obtained are presented in figures 4 and 5. It can be seen that a significant smoke reduction was achieved in the thermoset-graphite composites with the phenolic and bismaleimide resins when compared with the epoxy/graphite composites. The phenolic exhibited high smoke evolution. In the case of the thermoplastic-graphite composites (figure 5), both polyethersulfone and polyphenylsulfone exhibited extremely low smoke evolution.

The moisture absorption of three of the composites was determined by water immersion. Previous studies (7) have shown moisture has a detrimental effect on the physical propertie composites. In this study, mois equilibrium studies were conducte the epoxy and the neat bismaleir resins and composites. Before e sure, the samples were dried i

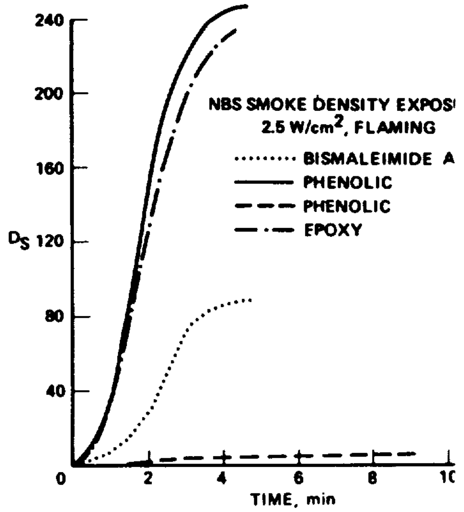


Fig. 4, Smoke evolution history of moset/graphite composites.

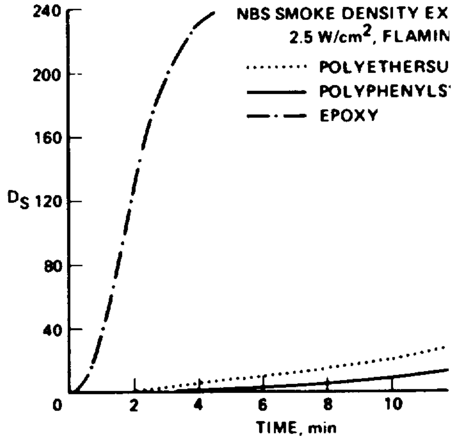


Fig. 5, Smoke evolution history of moplastic/graphite composites.

tal effect on the physical properties of composites. In this study, moisture equilibrium studies were conducted on the epoxy and the neat bismaleimide resins and composites. Before exposure, the samples were dried in a vacuum oven at 110°C for 4 hr. The sample was immersed in distilled water, and the water take-up was measured over a period of 28 days.

Simultaneously, equivalent values were measured for neat resin samples and laminates. The moisture equilibrium data on the bismaleimide resins as well as the epoxy are shown in figure 6. Bismaleimide B has a water absorption of around 5% after 28 days immersion in water. Since the composite fabricated with this resin contains 50% by volume of resin, the laminate absorbs approximately 2.5%. The absorption of both the neat resin and the composites is almost complete after 28 days. Bismaleimide A absorbs approximately 4.3% by weight after 28 days. The composite with this resin shows a slow water take-up. Equilibrium conditions are not reached after 28 days of water immersion. In all cases, the bismaleimide resin exhibited lower moisture absorption than the baseline epoxy resin.

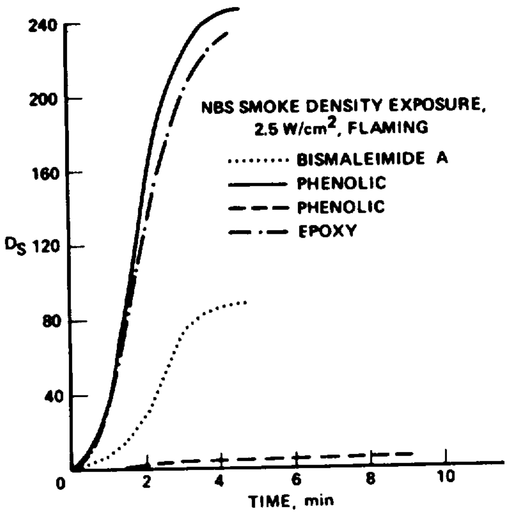


Fig. 4, Smoke evolution history of thermoset/graphite composites.

Mechanical Properties

Flexural, tensile, compressive, and

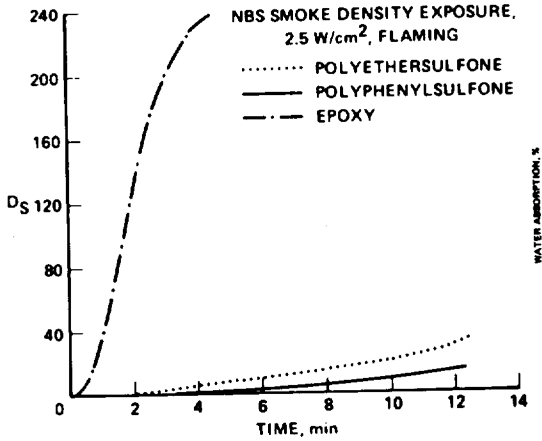


Fig. 5, Smoke evolution history of thermoplastic/graphite composites.

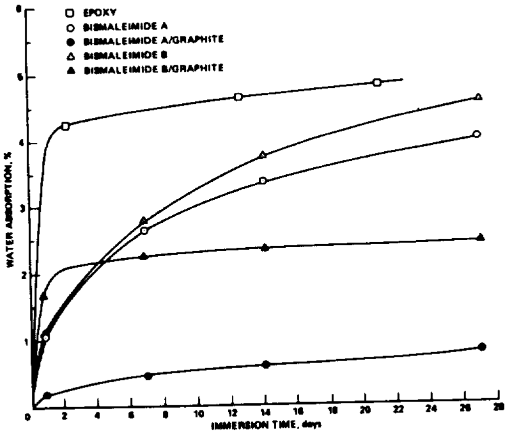
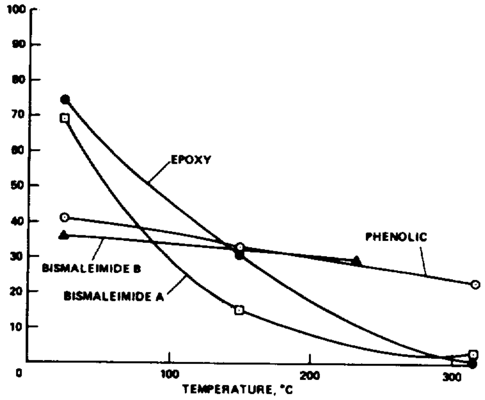


Fig. 6, Moisture equilibrium data on neat resins and composites.



ig. 7, Effect of temperature on short-beam hear strength of graphite composites.

short-beam shear-strength tests were conducted on graphite fabric-reinforced laminates prepared with four different matrix resins: epoxy, phenolic, bismaleimide A, and bismaleimide B. The effect of temperature on these mechanical properties is shown in figures 7-13. The samples were heated for 30 min. at the temperatures indicated prior to testing at these temperatures. The highest mechanical values at 23 °C were obtained with the epoxy/graphite composite followed by the bismaleimide A/graphite composite. The short-beam shear, flexural, tensile, and compressive strength of the bismaleimide A/graphite is very close to that of the epoxy/graphite at 23 °C (figures 7-10). However, a significant degradation of these properties occurs at 150 °C. This property loss for bismaleimide A is the consequence of residual solvent.

It is well known (11) that residual solvent acts as a plasticizer for the composites. The prepregs used for molding contain approximately 3.5% of n-methylpyrrolidone which cannot be dried off quantitatively during cure and postcure. Previous studies (8,9,10) have shown that it is very difficult to dry off residual prepregging solvent from cured laminates, and in many cases the solvent forms complex structures with the polymer. The bismaleimide A system was primarily designed as a low-temperature resin matrix possessing excellent fire-resistant properties.

The bismaleimide B resin was designed as a high-temperature resin, and it retains its mechanical properties up to 250 °C without any significant degradation (figures 7 and 8).

Figure 10 illustrates the rigidity retention of bismaleimide B at elevated temperatures. The modulus is almost constant over the entire temperature

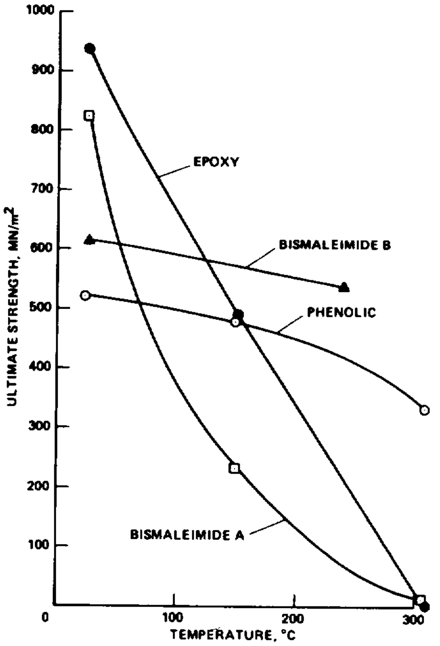


Fig. 8, Effect of temperature on flexural strength of graphite composites.

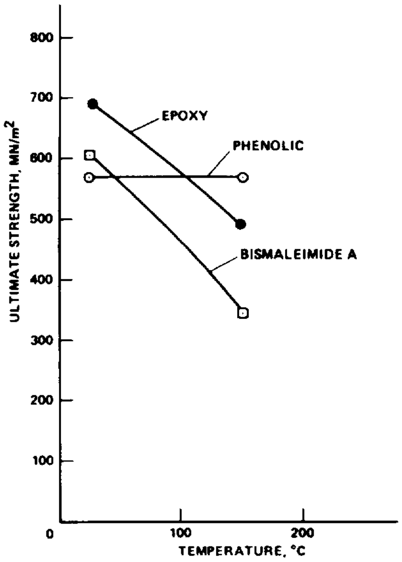
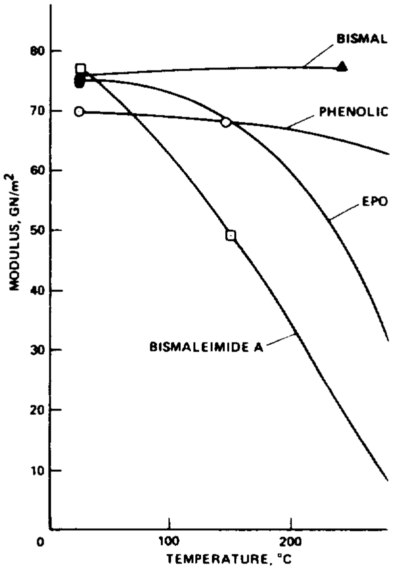


Fig. 9, Effect of temperature on te strength of graphite composites.

Fig. 11, Effect of temperature on ural modulus of graphite composit



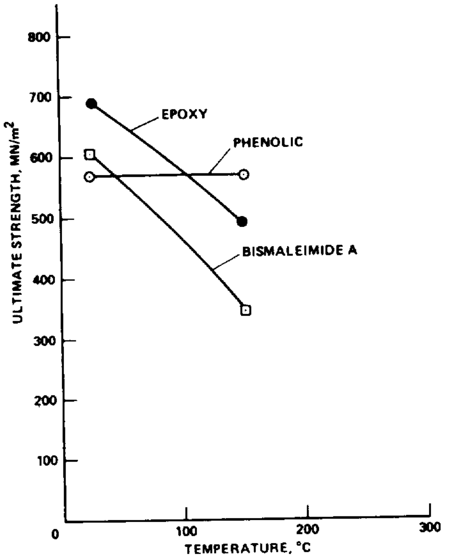
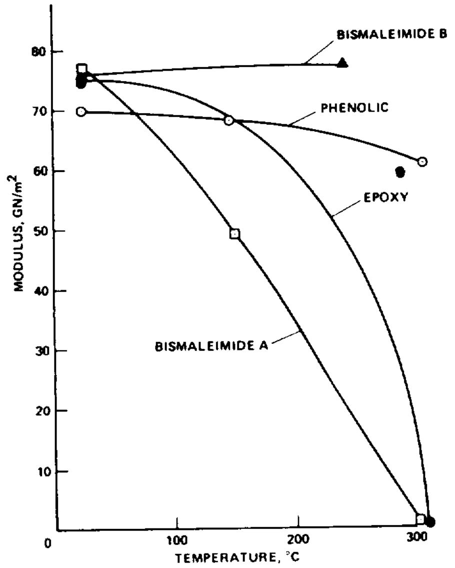


Fig. 9, Effect of temperature on tensile strength of graphite composites.

Fig. 11, Effect of temperature on flexural modulus of graphite composites.



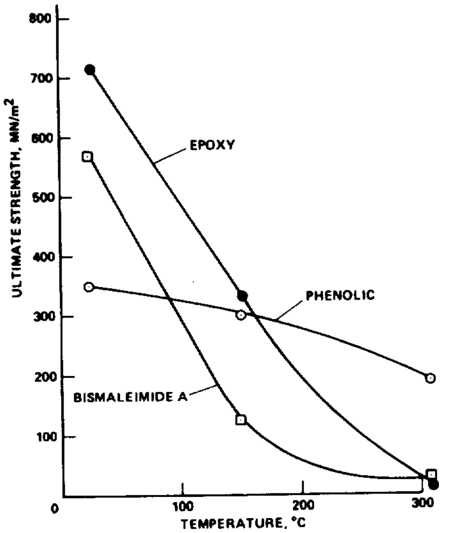
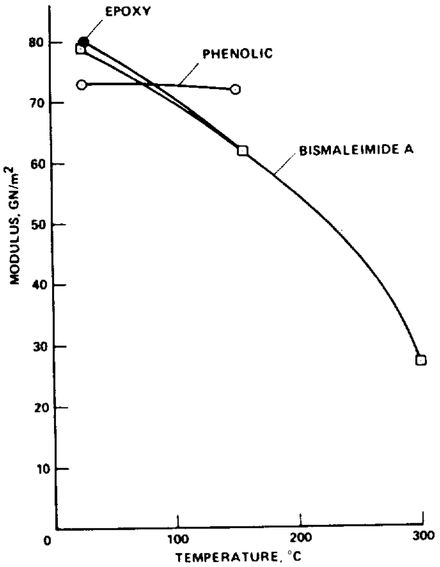


Fig. 10, Effect of temperature on compressive strength of graphite composites.

Fig. 12, Effect of temperature on tensile modulus of graphite composites.



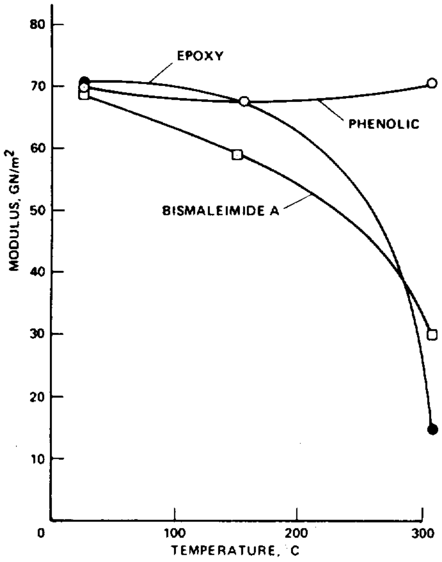


Fig. 13, Effect of temperature on compressive modulus of graphite composites.

range for this composite. Figures 12 and 13 illustrate the tensile and compressive modulus for the epoxy, phenolic, and bismaleimide A composites. The phenolic retains its compressive modulus up to 300°C (figure 13), however, its tensile modulus (figure 12) was lower than that of the epoxy and bismaleimide A at 23°C.

Conclusions

Improved fire-resistant properties were demonstrated with advanced thermoset and thermoplastic matrices in the graphite composites. This is evidenced by the high oxygen index and low smoke evolution from these composites. Among the highlights of this preliminary study are the following:

- Epoxy composites demonstrate the lowest fire-resistant properties of all composites tested.
- Bismaleimide A composites exhibit excellent fire-resistant properties, low moisture absorption, and ambient temperature mechanical properties. This bismaleimide resin is primarily designed as a fire-resistant, high char-yield resin.
- Bismaleimide B and phenolic retain their mechanical properties at elevated temperatures, however, they have lower mechanical properties at ambient temperatures than the epoxy composites. The bismaleimide B is primarily designed as a high-temperature resin.
- Phenolic-novolac, polyethersulfone, and polyphenylsulfone composites exhibit high oxygen index and low smoke evolution. •

Footnotes

1. W. Collins and T. Villani, SPE RETEC, Tech. Papers, p. 1 (1977).
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