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Ablative Resins for Hyperthermal Environments

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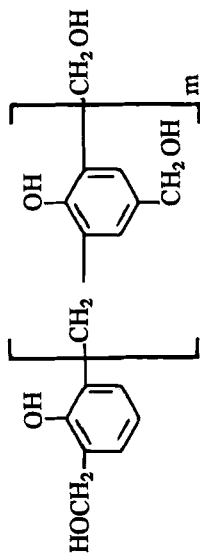
SUMMARY

Thermogravimetric analyses (TGA) appear to have marginal value in correlating the relative performance of resin laminates under hyperthermal ablative environments. The mechanical property (four-point flexural) test appears to have a more general correlation with ablation performance than TGA measurements. A qualitative ranking of the evaluated resins is tabulated.

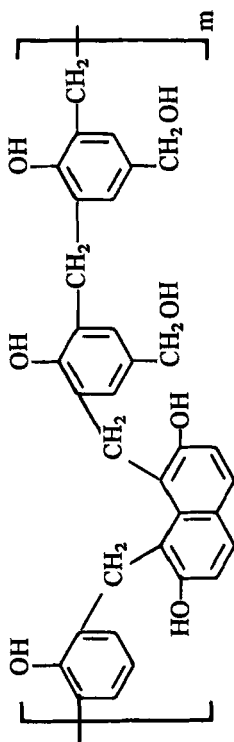
INTRODUCTION

Ablation is the process of thermal protection whereby a material achieves heat absorption by expending mass, which, in essence by energy absorption, helps block heat or the dissipation of heat into the unexpended mass of material. Thermal protection has been provided by this means for vehicles in hypersonic atmospheric flight and high-temperature exhaust nozzles of chemical propulsion systems.

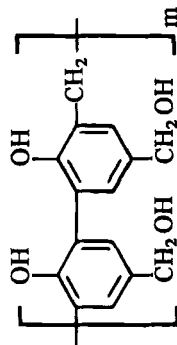
A. Phenol-formaldehyde

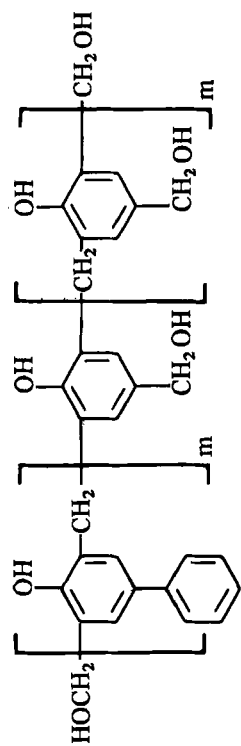


B. 2,7-Naphthalenediol-phenol-formaldehyde

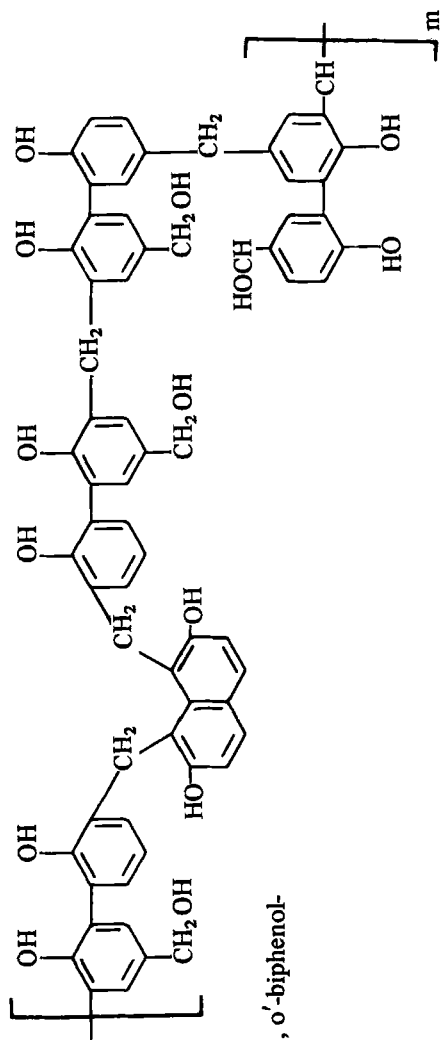


C. o, o'-Biphenol-formaldehyde



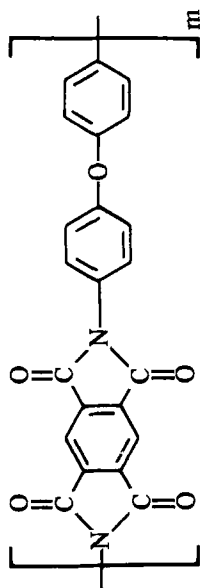


D. p-Phenylphenol-phenol-formaldehyde

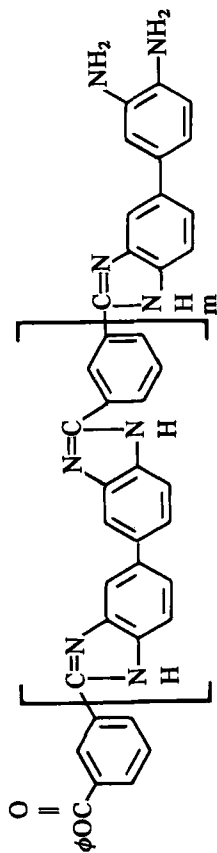


E. 2,7-Naphthalenediol-o'-biphenol-formaldehyde

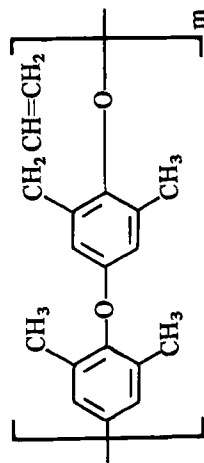
Fig. 1. Resin structures.



F. Polyimide



G. Polybenzimidazole



H. Polyphenylene oxide copolymer

Since the generation of major interest in ablative materials little over a decade ago, much work has been directed toward ablators which would yield thermal protection with the least recession as well as mass erosion for the severe enthalpy, heat flux, and aerodynamic shear environments of re-entry requirements and the high temperature and corrosive atmosphere of newer solid-propellant motors.

Reinforced plastics constitute the largest class of materials for such ablative applications and a great deal of effort has gone into the screening of individual resins, reinforcements, and fabrication methods to arrive at optimum materials and constructions for specific requirements. As experimental data and performance analyses have been accumulated, it has become increasingly apparent that although certain fundamental properties of resins and reinforcements are desirable for good ablation performance, these do not necessarily relate to an equivalent ablation performance of the composite. This has been re-emphasized, in part, by the results of the work described here.

This study was undertaken as part of an overall program for development of advanced ablative composites. It was anticipated that much of the sought-for improvement would derive from the development of unique composite construction techniques, but recent availability in pilot plant or larger quantities of many new high-temperature-resistant resins made it desirable to evaluate these as a prelude to fabrication development of composites. The criteria for inclusion of resins in this study were polymer structures of sufficient carbon content and aromaticity to assure high-temperature thermal stability and the ultimate formation of a thermally and mechanically stable char upon pyrolysis in the ablative process. Reasonably developed processing characteristics and availability in workable quantities were other selection criteria.

The initial selection of resins for comparative evaluation is shown in Table 1, and their chemical structures are illustrated in Fig. 1.

It should be noted that all the resin systems chosen are largely aromatic in structure. The first five are phenolic resin types, four of which have more aromatic phenolic moieties than phenol itself. Aromatic resins in the form of heterocyclic compounds are included with the polyimides, polyamide-imides, polybenzothiazole, and the polybenzimidazole resins. An all-aromatic structure is noted in the branched polyphenylene resin, and an aromatic polyether is included with the polyphenylene oxide copolymer. Factors weighed and studied in this resin selection included: physical, chemical, and thermal properties; mechanical properties of both cured resin and char; thermal conductivity of cured resin and char; char

Table 1. Resins Chosen for Comparison

Resin type	Supplier
A. Phenol-formaldehyde	Monsanto (SC-1008)
B. 2,7-Napthalenediol-phenol-formaldehyde	Hughes
C. o, o'-Biphenol-phenol-formaldehyde	Evercoat Chemical
D. p-Phenylphenol-phenol-formaldehyde	Ironsides (DP-25-10)
E. 2,7-Napthalenediol-o, o'-biphenol-formaldehyde	Evercoat Chemical
F. Polyimide	Dupont (PI-4701)
G. Polybenzimidazole (PBI)	Narmco (Imidite 2801)
H. Polyphenylene oxide copolymer (2,6 dimethyl and 2-methyl-6-allyl)	Rocketdyne
I. Polybenzothiazole	Abex Corp.
J. Polyphenylene (branched)	Hughes (Abchar 412B)
K. Polyamide-imide	Amaco (AI-11)

permeability and yield; thermal shock resistance; and pyrolysis gas properties. Space does not permit a discussion of all the factors studied; however, examination of certain of these is still worthwhile. Problems in correlation of these factors with ablative performance of the resin in a composite structure may then be more meaningful.

THERMAL PROPERTY COMPARISON

A readily available comparison test for the thermal properties of the resins is thermogravimetric analysis (TGA). The three evaluation criteria derived from this test are initial decomposition temperature, temperature at which a 10% weight loss occurs, and per cent weight loss at 1000°C. The values obtained for the various resins are compared in Fig. 2. All the TGAs were run under helium at a rate of 6°C/min. Before considering the significance of these values and their order, it should be realized that these resins were cured and postcured under various temperature-time schedules which can affect the values shown. The curing schedules used were those generally recommended by the supplier or the literature. In certain cases, however, these were changed (upgraded) to better the resin performance.

The values shown in Fig. 2 are representative of the thermal performance of the resins. The best resins, on the basis of TGA, would appear to be

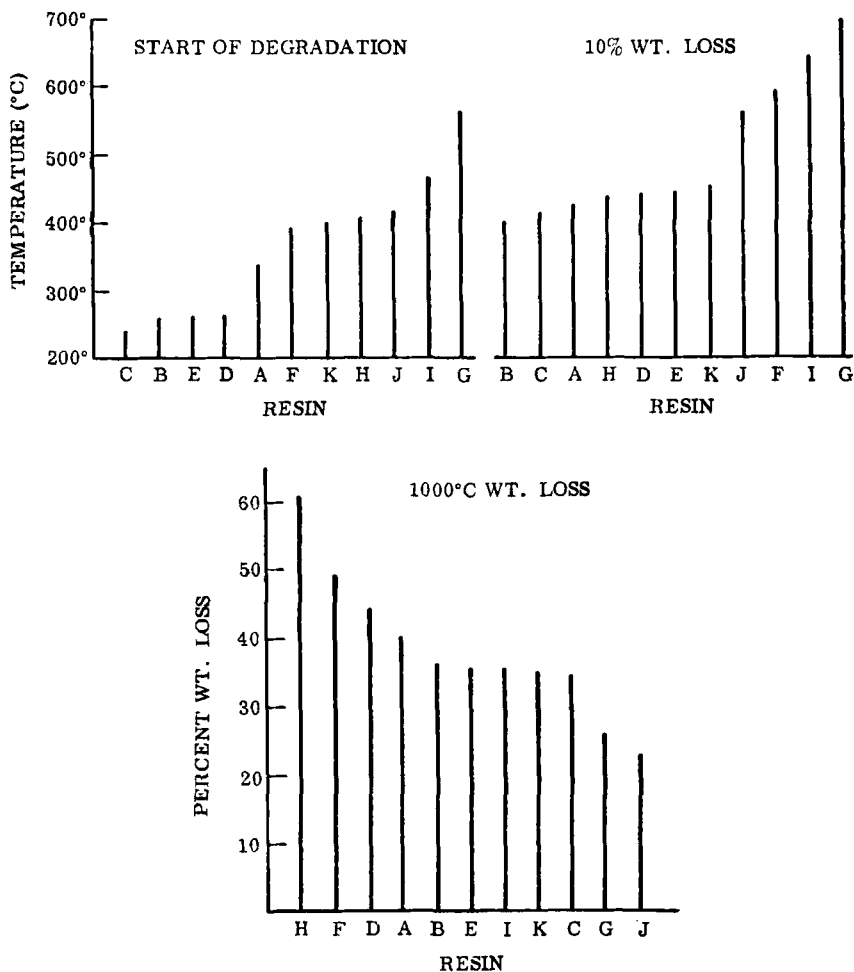


Fig. 2. TGA data summary.

polybenzimidazole, followed by polyphenylene and polybenzothiazole. On the basis of this test alone, the phenolic types, as a group, appear to be the least thermally stable. Considering the four best resins (approximately the upper one-third) for each TGA test criterion, it can be seen that the polybenzimidazole is consistently among the most stable for each test category. The polyphenylene resin appeared to undergo some initial decomposition and weight loss at somewhat lower temperatures than PBI, but

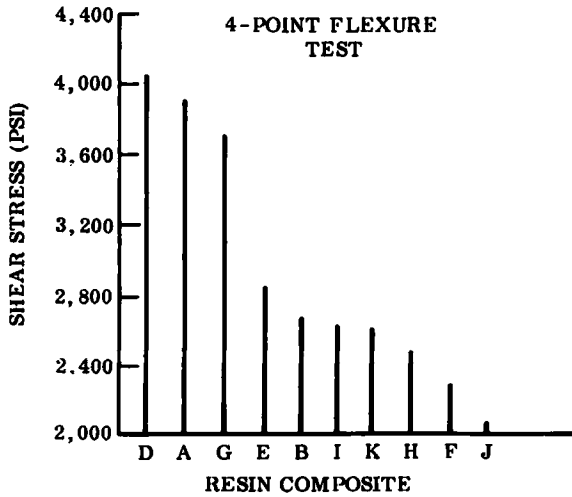
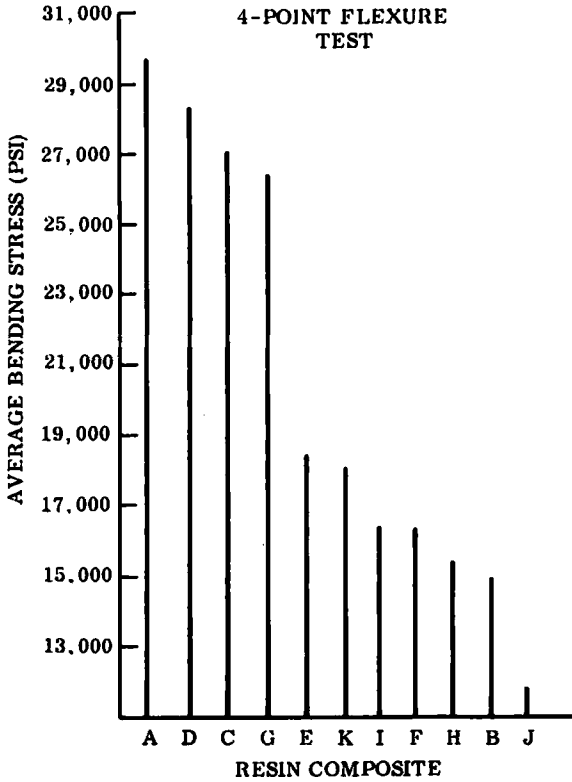


Fig. 3. Mechanical property ranking.

yielded a greater residue at 1000°C. This could possibly be attributed to a less than optimum cure cycle. Polybenzothiazole exhibited the second-highest temperature required for initial decomposition and weight loss, but it proved slightly less thermally stable at 1000°C than either PBI or polyphenylene.

MECHANICAL PROPERTIES COMPARISON

Each of the resins being studied was impregnated on a reinforcement of Pluton B-1 (high purity) carbon cloth and laminated to form a 0.375-in.-thick panel. Physical, thermal, ablation, and mechanical property tests were run with specimens obtained from these panels. A simple mechanical property test was desired to demonstrate the structural integrity and soundness of each composite prior to ablation testing; a four-point flexural test was selected as the most significant. This test yielded values for composite bending stress and shear stress.

It was also recognized that material loss by ablation in a high-pressure or high-aerodynamic-shear environment is accomplished by a combination of mechanical effects as well as thermochemical effects. An attempt at correlation of composite mechanical properties with ablation results thus appeared to be in order. The wedge flow ablative test used in this study included not only the thermochemical ablative capability of the laminate, but the mechanical strength capability of the material under the high-shear conditions. Estimation of the degree of chemical erosion [1] under this wedge ablation test indicates that approximately 60% of the total erosion is chemical and the remaining 40% would be mechanical in nature. Admittedly, the mechanical testing of the material at ambient temperature is not the same as the mechanical erosion contribution at 6000°R. However, the question examined was what correlation these mechanical tests had when compared with the ablation performance or erosion. Figure 3 shows the mechanical test results. The ranking of the resins is also indicated and it should be noted that in general the phenolic resin types appear to be superior to the other resins.

ABLATIVE TEST RESULTS

Ablation testing was carried out using the Arnold Engineering Development Center's 5-MW air arc heater facility, under conditions of 4-10 atm

sample surface pressure and 5000-10,000 Btu/ft²-sec sample surface heat flux. The stream at the nozzle had an enthalpy of 4500 Btu/lb with an arc chamber pressure of 26 atm.

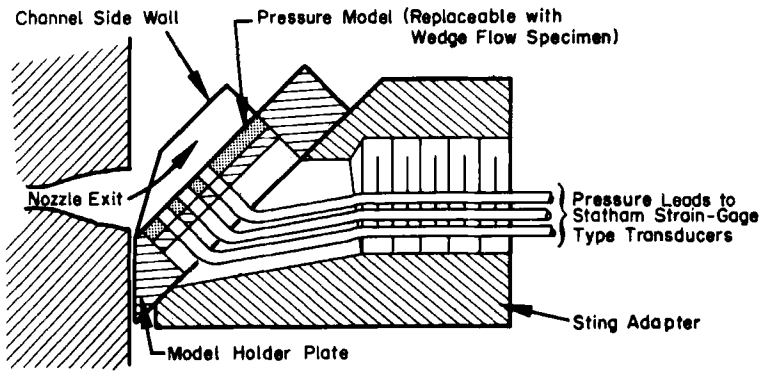


Fig. 4. AEDC 45° wedge flow pressure model.

A yawed wedge sample configuration was chosen for testing because it offered a combination of both a high heat flux as well as high surface shear stress. By this method the flow impinges on the sample at a 45° angle to the surface. This can be seen in Figs. 4 and 5, which demonstrate the test apparatus configuration and how the specimen is mounted for this ablation test. Weight loss of the laminate was determined. The ablated test samples were sectioned and photographs taken so that the erosion profile and char layer might be evaluated and the maximum erosion depth measured. Analysis of these data yielded: \dot{S} , the surface erosion rate (in./sec); $\rho_v \dot{S}$, the mass erosion rate at the maximum erosion point (lb/ft²-sec); and \dot{M} , total mass loss rate (g/sec). Dividing these gross ablation results by the dwell time in the arc yielded rates per unit time and eliminated dwell time variations in the analysis. It was assumed that the extreme thermal environments of this test virtually eliminated any transient rate periods; in consequence, the rates were considered steady-state values.

The ablation samples were prepared from portions of the same laminated composites used for the mechanical testing described earlier. The laminates consisted of 35 plies of Pluton B-1 (high purity) carbon fabric (3M Company) with resin contents that varied between 39 and 44% by weight of the various resins. The specimens themselves, however, were cut at a 20° angle through the thickness of the parallel ply laminate so that the resulting specimen presented a shingle effect with the edges of each fabric ply

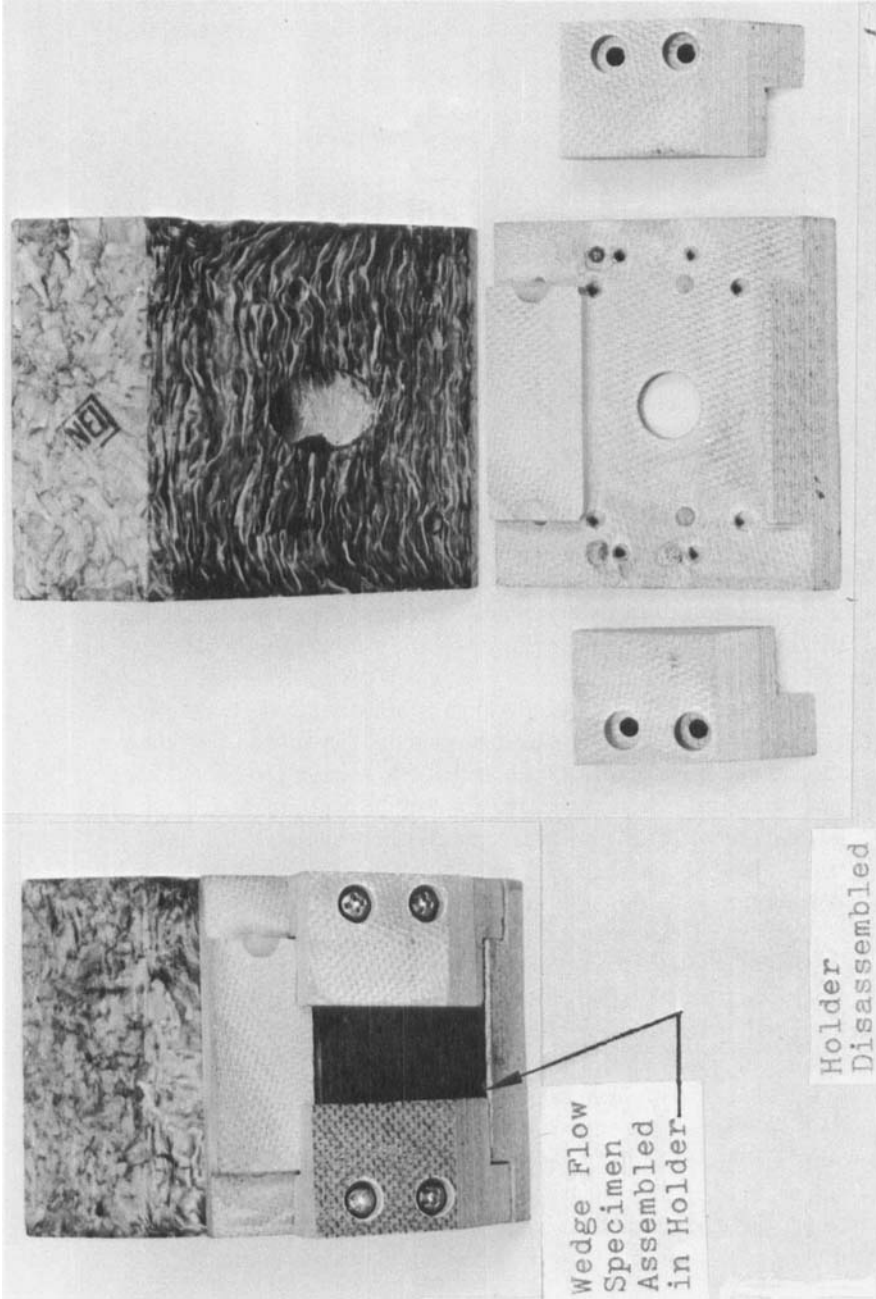


Fig. 5. Wedge flow holder.

oriented 20° to its surface. The specimens were positioned so that the plasma flow was in the direction of the shingle angle.

The specimen, mounted in a holder, was positioned at an angle of 45° from the plane of the plasma arc nozzle. The ablation test results, for nominal 1-sec runs, are summarized in Figs. 6(a), 6(b), and 6(c). As with the TGA tests, if the four best resins (approximately the upper one-third) are considered for each ablation test criterion, it is seen that polybenzimidazole shows the best performance overall. A phenol formaldehyde resin (SC1008) also appears in the upper group for each ablation ranking category. The polyamide-imide and 2,7-naphthalenediol-*o,o'*-biphenol formaldehyde both appear in the upper performance group in terms of recession rate and mass erosion rate at the maximum erosion point. After the PBI resin, total mass loss rate was least for *p*-phenylphenol-phenol-formaldehyde resin followed by polybenzothiazole.

The char thickness measured in the area of maximum erosion ranged from 0.013 to 0.035 in. formed/sec. A high charring rate and thick, strong char formation have generally been considered desirable for good ablative performance. The greatest char formers were the polyimide, polyphenylene, and polybenzothiazole resins. The three resins forming the least char were polyamide-imide, *p*-phenylphenol-phenol-formaldehyde, and the polyphenyleneoxide copolymer.

DISCUSSION AND CONCLUSIONS

Thermogravimetric analyses have generally been used as a first indication of resins worthy of consideration as ablaters. The analysis appears to have marginal value, however, in correlating relative performance of the resin laminates under the hyperthermal ablative environments reported in this work. Indeed, some of the phenolic resin types with relatively poorer TGA results gave superior ablative performance and it was only the polybenzimidazole that showed a consistent correlation of performance.

The mechanical property (four-point flexural) test appears to have a more general correlation than TGA with the ablation performance, as shown in Table 2. This can only be ascribed to the hyperthermal environment and the mechanical erosion portion of the total erosion experienced. This does not, of course, predicate that a mechanically strong resin will be a good ablator; it only indicates that mechanical strength plays a part in obtaining better ablation performance. While a strong char has generally been recognized as a desirable or even necessary attribute of a good ablative

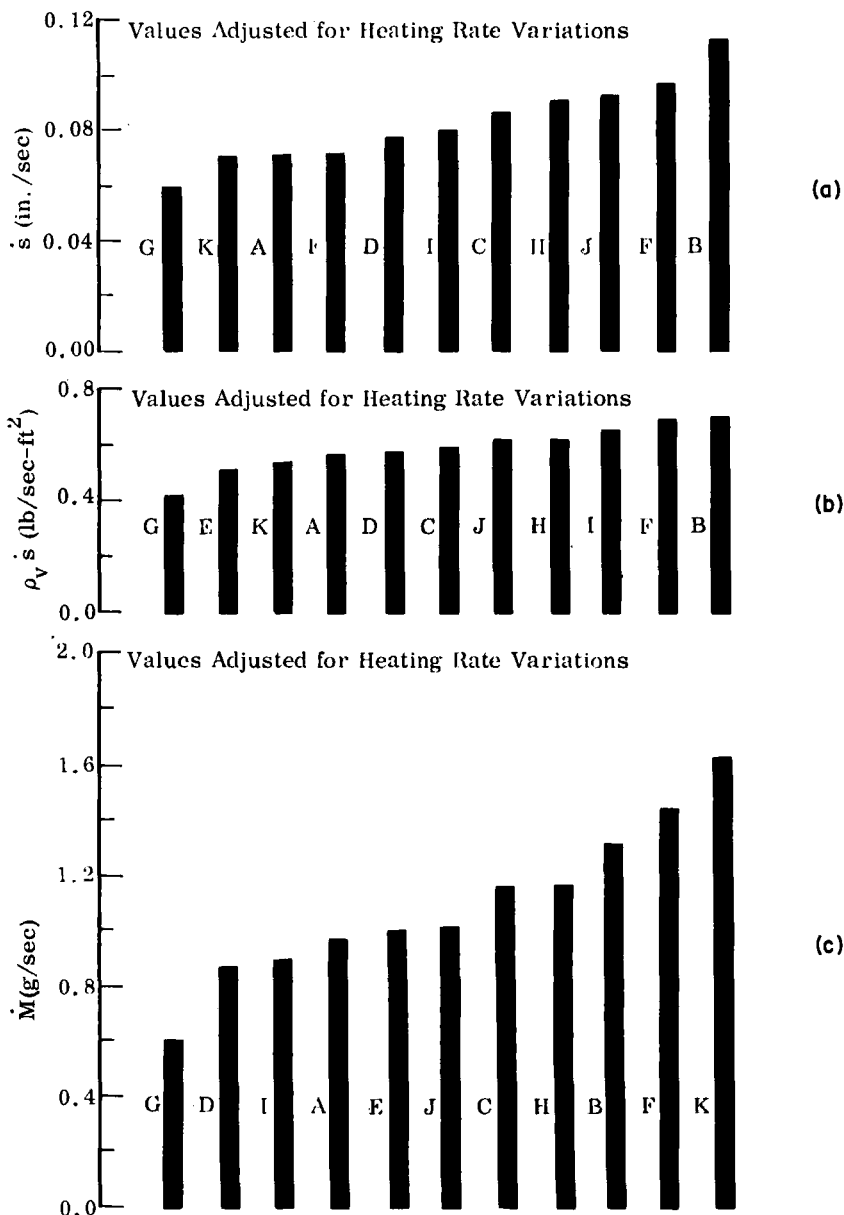


Fig. 6. Ablation results, resin composites.

A—phenol-formaldehyde

B—2,7-naphthalenediol-phenol-formaldehyde

C—o,o'-biphenol-formaldehyde

D—p-phenylphenol-phenol-formaldehyde

E—2,7-naphthalenediol-o,o'-biphenol-formaldehyde

F—polyimide

G—polybenzimidazole

H—polyphenylene oxide copolymer

I—polybenzothiazole

J—polyphenylene (branched)

K—polyamide-imide

Table 2. Qualitative Ranking Summary ^c

	Ablation test data				Mechanical data		TGA data	
	Maximum erosion rate, \dot{S} , in./sec	Mass rate $\rho_v \dot{S}$, lb/ft ² -sec	Total mass loss rate, \dot{M} , g/sec	Char form rate	Four-point flexural	10% Loss	1000°C weight loss	
Resin a + Fabric b								
A. Phenol formaldehyde (SC-1008)	3	4	4	5	1	9	8	
B. 2,7-Naphthalenediol-phenol-formaldehyde	11	11	9	7	10	11	7	
C. o, o'-Biphenol-formaldehyde	7	6	7	4	3	10	3	
D. p-Phenylphenol-phenol-formaldehyde	5	5	2	2	2	7	9	
E. 2,7-Naphthalenediol-o, o'-biphenol-formaldehyde	4	2	5	8	5	6	6	
F. Polyimide (PI-4701)	10	10	10	11	8	3	10	
G. Polybenzimidazole (Imidite 2801)	1	1	1	6	4	1	2	
H. Polyphenylene oxide copolymer	8	8	8	3	9	8	11	
I. Polybenzothiazole	6	9	3	9	7	2	5	
J. Polyphenylene (branched) (Abchar 412)	9	7	6	10	11	4	1	
K. Polyamide-imide (AI-11)	2	3	11	1	6	5	4	

^a Resin content 39-44% of laminate.

^b Fabric used in each case was Pluton B-1 (3M Company).

^c Rankings: 1, best; 11, worst.

resin, its place in a relative ranking of attributes is not completely established.

Polybenzimidazole again appears in the upper group of resins in terms of mechanical property ranking and, except for a somewhat lower ranking in char-forming ability, shows the greatest overall correlation of ablation performance criteria. The lack of a similarly good correlation of thermal and mechanical performance with ablation performance for the other resins may have resulted from many additional factors which were not emphasized in this study. Thus, decomposition kinetics may contribute to differences between TGA and ablation results and char microstructure; integrity and strength may influence linking of composite mechanical properties to ablation as much as the virgin material composite data reported here. Fortunately, polybenzimidazole achieves good correlation in most characteristics studied.

Another interesting resin is the polyamide-imide, which has excellent erosion resistance at the point of greatest heat but a poor overall total mass loss over the entire surface. Its good char-forming rate and moderately good mechanical property and TGA rankings make it an interesting candidate for further processing improvement and continued evaluation.

A qualitative ranking of all the evaluated resins is summarized in Table 2. Individual rankings for each resin that falls within the upper group of four resins are indicated by the outlined areas. Thus, the best performance characteristics of each can be easily identified and the correlation of test results readily seen.

An interesting point to note is that polybenzimidazole resin, following the manufacturer's recommended cure to 850°F, gave results much inferior in ablation to those reported in this paper. However, by increasing the cure temperature to 950°F, the currently reported ablation test results were obtained [2]. The explanation for this effect with the polybenzimidazole lay in the fact that the resin was still thermoplastic at 850°F. This was shown by the ability of the resin to fill the voids in the laminate due to sufficient thermoplasticity under 500 psi pressure and heating between 850 and 950°F. At the upper temperature the polybenzimidazole is reported to become thermoset [2].

Of the resins surveyed in this paper, the phenolic types are known to be thermoset. The polyamide-imide, polybenzimidazole, and polyimide resins may not be thermoset at their postcure temperatures. The remaining resins are considered to be cross-linked or thermoset. To ensure thermosetting and better ablative characteristics, these aromatic resins should be cured to about 950°F where possible and under an inert atmosphere. It has been reported in polyimide systems that under these conditions cross-linking occurs [3]. A free radical degradative mechanism is operative in

this cross-linking. The chemical structure of the aromatic polymer will dictate the temperature or conditions under which this type of cross-linking can occur.

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