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Ablative Polymers in Aerospace Technology

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SUMMARY

Ablative polymers and polymeric composites serve an important function in aerospace technology. They protect aerodynamic surfaces, propulsion structures, and ground equipment from degradative effects of very high temperatures or incident heating rates. This protective function is accomplished by a self-regulating heat and mass transfer process known as ablation. By this relatively new process, thermal energy is expended via sacrificial loss of material. The amount of energy absorbed, dissipated, and blocked depends critically upon both materials and environmental variables, including the properties of the polymeric material, the thermal-chemical-mechanical aspects of the environment, and the complex interaction of the ablator with its hyperenvironment. Important thermochemical and thermophysical parameters of the ablation process are discussed. In addition, a state-of-the-art of polymeric ablators is presented, with emphasis on the advantages, limitations, and current problems associated with ablative plastics. The need for charring, noncharring, inorganic, low-modulus, cryogenic, processible, and low-cost polymers is discussed in considerable detail. Lastly, the service uses developed for ablative polymers during the past decade are reported to illustrate the importance of this new class of engineering materials.

INTRODUCTION

The aerospacecraft has made manned and unmanned hypersonic flight a reality. Its propulsion system assures a successful exit from the earth's surface, and its re-entry vehicle provides for a safe return through the atmosphere [1].

The aerospacecraft operates in an atmosphere and space environment, which is characterized by numerical extremes. Ultrahigh or cryogenic temperatures, intense heating, corrosive gases, and high applied mechanical forces are some of the aerothermodynamic elements which must be coped with. Other environmental extremes may also be present, as shown in Table 1. It is thus apparent that an aerospacecraft must be protected from natural and induced environments to assure a successful flight and completion of its mission.

Table 1. Hyperenvironments, Present and Future

Temperatures	-300°F	to over	50,000°F
Heating rates (peak)	20	to over	50,000 Btu/ft^2-sec
Total heating	10,000	to over	150,000 Btu/ft^2
Heating times	1	to over	3600 sec
Pressures (stagnation)	0.01	to over	400 atm
Loading	1	to over	300 g
Shear stresses	1	to over	1500 lb/ft^2
Composition	Air, planetary atmospheres, propellant combustion gases, entrained particles, and energetic species		

The aerodynamic surfaces and structures of an aerospacecraft are isolated from the hyperenvironment by means of a thermal protection system. The design usually consists of a composite panel made up of a heat shield and a substructure. The heat shield is the energy-absorbing or -reflecting material, and the substructure is the load-carrying member. In some cases, it is possible to combine these functions into a single integrated unit. A variety of thermal protection systems have been developed, which include radiative cooling, heat sinks, transpiration and film cooling, ablation, and combinations thereof [2-4]. Each protective scheme is applicable to a particular environmental regime, with reduced efficiency or no utility at significantly different conditions.

Contrary to expectation, polymers and polymeric composites perform with relative ease a unique heat-protective function. This feature is due to their phenomenal ability to absorb, dissipate, and block heat, which often amounts to thousands of Btu's per pound of material sacrificed. This process is known as "ablation." It provides the aerospace engineer with the means for accommodating the "thermal barrier" of hypersonic atmospheric flight and the internal heating problems of chemical propulsion systems.

The purpose of this paper is to introduce scientists and technologists to the protective functions of ablative polymers in aerospace technology.

ABLATION

Ablation is a geological term at least 120 years old. It is derived from the suppletive past participle of the Latin "au ferre," which means to remove or carry away. Louis Agassiz, the eminent naturalist, first used the term to describe the combined processes by which a glacier wastes. The dominant process was ascribed to thermal effects, a meaning which is still maintained in the aerospace usage of the word.

While the process of ablation is rather complex, many of its important physicochemical aspects have been identified [5-11]. At the onset of heating, energy is absorbed by the polymer and then conducted internally. The rate of heat penetration is dependent upon the surface temperature, but in all cases, thermal diffusion is slow because of the low conductivity of the polymer. Maintaining the heat in the surface region causes its temperature to rise rapidly until material vaporization takes place. The initial volatiles are generally water, residual diluents, or polymers of low molecular weight. At still higher temperatures, thermal agitation becomes severe enough to split pendant and side groups from the polymer backbone. Eventually the chemical bonds in the backbone are also ruptured. The polymer is thus undergoing competitive reactions involving reversible depolymerization and/or irreversible pyrolysis. The rate of decomposition follows an nth-order Arrhenius-type reaction rate law and varies with the temperature and amount of undecomposed material present [12]. If elimination of groups along the polymer chain predominates over chain cleavage, much of the original chain structure will remain as carbon, and a char will develop. Gaseous products formed during pyrolysis will vary greatly in composition and molecular weight. For example, they may be composed of water-gas constituents like hydrogen, carbon monoxide, carbon dioxide, and water vapor, saturated hydrocarbons like methane and ethane, and unsaturated hydrocarbons such as ethylene and acetylene. Those pyrolytic species are injected into the boundary layer, lower the enthalpy of this layer, and undergo further thermochemical reactions.

Organic materials frequently ablate with the formation of a surface char layer which serves to isolate the thermally unstable polymer from the high-temperature environment. This surface layer plays a predominant role in the absorption of heat by endothermic processes involved in its formation, heat capacity due to the high temperature assumed, and endothermic secondary reactions with the newly formed hydrocarbon gases or residual reinforcing agent. The high temperature of the char also reduces the hot-wall heating rate to the material surface, and coupled with a high surface emittance, dissipates a large fraction of the incident heat through surface radiant emission. Under most ablative conditions, the newly formed char layer will remain attached to the virgin substrate for at least a short period of time. A zone of degradation is then formed beneath the char layer wherein virgin material undergoes initial pyrolysis. Gases formed in the degradation zone percolate outward under pressure and through the maturing charred surface region. Interaction of the gases with the hot char material promotes further thermochemical reactions, such as oxidation or decomposition to pyrolytic carbon.

If the polymer melts or the polymeric composite contains a meltable component, additional heat is absorbed at the melting point (latent heat of fusion). Subsequent fusion occurs with the formation of a liquid layer. When the molten material is of low viscosity, all but a very thin layer of the liquid may be removed immediately by gas-dynamic shear forces acting at the gas-liquid interface. On the other extreme, a highly viscous melt tends to remain on the surface until sufficient heat is absorbed to vaporize it. In this case, an additional amount of heat is absorbed by the latent heat of vaporization, and the surface temperature corresponds to the liquidus vaporization temperature. Most cases of melting ablation, however, involve partial flow and vaporization of the liquid layer [13]. The extent of each competing reaction depends upon the environmental parameters (shear, heat flux, etc.) and the temperature-dependent viscosity of the melted material.

The presence of fibers or fillers in charring polymeric composites alters the ablation process. Nylon fibers, for example, undergo melting and vaporization in the substrate degradation zone. Voids are thus created in the region originally occupied by the fibers. A highly porous char is formed, which is relatively susceptible to mechanical erosion [14]. Pyrolyzed species are reduced to lower molecular weight products in passing through the reactive char layer. Like the vapors arising from the organic resin, they also deposit carbon in the char zone. If the ablating surface is essentially carbon, its temperature will be dictated essentially by the incident heating rate and may assume values in excess of 5800°F. With respect to melting oxide fibers like silica, the mechanism of ablation is quite different. The organic resin or its residual char is removed by the environment at a faster rate than the fibers, thus leaving them exposed and unsupported. The vitreous fiber then melts, and the molten material covers the surface as liquid droplets, irregular globules, or a thin film. On the other hand, carbon fibers provide exceptional dimensional stability to charring composites. They remain in the char layer during pyrolysis, provide high strength to the char zone, and firmly attach it to the substrate. Unlike the nylon and silica fibers, the carbon fibers are little affected by high temperatures. Fiber removal occurs primarily by thermochemical reactions such as oxidation.

From a thermophysical point of view, ablation is an orderly heat and mass transfer process in which a large amount of thermal energy is expended by sacrificial loss of surface region material. The heat input from the environment is absorbed, blocked, dissipated, and generated by numerous mechanisms. These mechanisms are illustrated in Fig. 1 for an ablating glass fiber-reinforced phenolic resin composite. They involve (a) heat conduction into the material substrate and storage by its effective heat capacity, (b) materials phase changes such as melting, vaporization, and sublimation, (c) heat absorption by gases in the substrate as they percolate to the surface, (d) convection of heat in a liquid layer, if one exists, (e) transpiration of gases from the ablating surface into the boundary layer with attendant heat absorption, (f) surface and bulk radiation, (g) endothermic and exothermic chemical reactions, and (h) possible yet unrecognized reactions. Such energy absorptive processes take place automatically, simultaneously control the surface temperature, and greatly restrict the inward flow of heat.

ABLATIVE POLYMERIC MATERIALS

Various classes of polymeric materials have been utilized for ablative thermal protection. These include homogeneous plastics (e.g., polytetrafluorethylene), filled plastics (e.g., silica powder containing epoxy-polyamide resin), precharred plastics (pyrolyzed carbon fabric-reinforced phenolic), motor case insulation (boric acid powder-filled polybutadiene-acrylonitrile),

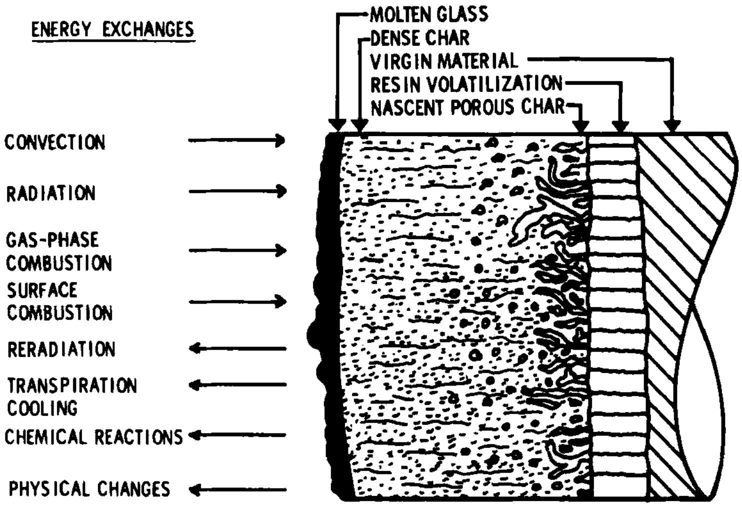


Fig. 1. Energy dissipation of an ablating phenolic-glass composite.

resin-impregnated ceramics (phenolic-infiltrated porous silica), low-density coatings (phenolic microsphere-filled epoxy-novolac), and others [15]. Within each class of material, a wide range of properties can be achieved through variations in the ratio of components, exact type of components used, component (fiber) orientation, processing variables, and fabrication parameters. Room temperature properties for typical high- and low-density ablative polymeric composites are given in Tables 2 and 3.

Polymeric composites are manufactured by a variety of processes. In general, the size and configuration of a heat shield predefines the manufacturing process. The most feasible process also involves a consideration of the required materials properties and the economic constraints. The most common fabrication process employed today involves tape wrapping. Cylindrical and conical sections are made with the aid of large lathes which have been modified for placing and compacting, at a preselected angle, resin-impregnated woven fibrous tapes. The tape is continuously laid down on a rotating mandrel under compaction pressure. It is then cured to a solid state under heat and pressure, which are produced by means of an autoclave, hydroclave, or heat-shrinkable nylon overwrap. Compression molding processes are used to compact and cure resin-impregnated chopped fiber or macerated fabric pieces at extremely high pressures (over 5000 psi). The process enables high-volume fabrication at relatively low costs. Isostatic

Table 2. Properties of High-Density Ablators

Material composition	Phenolic-35%, asbestos mat-65%	Phenolic-35%, silica fabric-65%	Phenolic-50%, nylon fabric-50%	Phenolic-33%, carbon fabric-67%
Density, lb/ft^3	108	102	72	84
Tensile strength, psi	59,000	9225	6100	21,600
Tensile elastic modulus, million psi	5.06	2.71	1.00	3.50
Tensile elongation at failure, %	–	0.52	2.00	1.08
Shear strength, psi	2210	4410	–	4000
Compressive strength, psi	26,900	31,000	15,800	35,000
Compressive elastic modulus, million psi	5.33	2.4	0.4	1.57
Flexural strength, psi	52,700	23,000	13,100	30,000
Flexural elastic modulus, million psi	5.43	2.9	0.44	2.4
Specific heat, Btu/lb-°F	0.19	0.25	0.47	0.24
Thermal conductivity, Btu/hr/ft^2-°F/ft	0.10	0.36	0.10	0.82
Thermal expansion coefficient, 10^{-6} in/in/°F	2.0	7.0	36.0	3.8

Room temperature properties are parallel to the fiber/fabric/mat warp.

Table 3. Properties of Low-Density Ablators

Material composition	Phenolic-25%, phenolic microspheres-25%, nylon powder-50%	Epoxy-novolac-38%, phenolic microspheres-44%, silica fibers-9%, glass fibers-9%	Silicone-66%, microspheres: phenolic-16%, glass-10%, quartz fibers-7%, silica powder-1%
Density, lb/ft^3	37	24	42
Tensile strength, psi	1000	640	167
Tensile elongation at failure, psi	0.9	2.9	5.0
Tensile elastic modulus, million psi	0.125	0.040	0.005
Specific heat, Btu/lb-°F	0.38	0.46	0.37
Thermal conductivity, Btu/hr/ft^2/°F/ft	0.07	0.04	0.07
Thermal expansion coefficient, 10^{-6} in/in/°F	30.5	17.1	44.0

compressive molding followed by oven sintering is another method which involves powdered resins such as polytetrafluoroethylene. Low-denisty composites are generally formed by gunning, casting, trowelling, or spraying. A typical example involves hand-gunning a dry resinous mixture into a plastic honeycomb and then curing the composite under heat and pressure.

Nose tips are fabricated with prepregged woven fabric reinforcements, and the fabric orientation is controlled so as to minimize erosion. The tip is composed of individual layers of resin-impregnated fabric, precut and shaped into a cone by the use of a preform. The cones are stacked on top of each other and molded by compression. Composites may also be produced with one edge of a ply intersecting both the outer and inner surfaces. Precut layers of resin-impregnated fabric are applied to either a female cure fixture or a male mandrel in a generally axial direction and at varying angles to the surface of the fixture or mandrel. The part is then cured by hydroclave molding. Integrated composites, unlike the previously mentioned fabric composites, contain reinforcement in a third direction and hence alleviate the interlaminar shear problem of two-dimensional fabric-reinforced composites. The process involves the interlaying or interlocking of continuous filaments in a woven preform, which is then followed by liquid resin impregnation and curing.

PROPERTIES OF IMPORTANCE

The ablative performance of a polymeric material is influenced significantly by both materials and environmental parameters [16,17]. Important materials variables and characteristics are given in Table 4. More specifically, the composition and structure of the polymeric matrix can alter the ablative and insulative values by a factor of 2 and often more. This effect is shown in Tables 5 and 6, which provide performance features on a variety of silica and carbon fabric-reinforced resins.

Polymers found useful in high-temperature air environments may have limited use in another hyperthermal environment like hot combustion gases. This principle is evident by comparing the data given in Tables 5 and 6 with those reported in Table 7. The latter table provides erosion and insulative indices for a variety of reference and polymeric composites in high-temperature combustion products from oxyacetylene propellants [18, 19].

Table 4. Materials Properties and Characteristics Which Influence Ablative Performance

Polymer	
Elemental composition	Glass transition temperature
Structure	Temperature of thermal decomposition
Molecular weight	Heat of decomposition
Degree of cross-linking	Thermophysical and thermodynamic properties
Curing agent or catalyst	
Elemental composition	Percentage retained in polymer
Reinforcing agent and fillers	
Elemental composition	Thermal decomposition temperature
Physical form	Heats of phase changes
Orientation in composite	Thermophysical and thermodynamic properties
Formulation and compounding	
Ratio of material components	Temperature, time, and pressure
Composite	
Uniformity of material distribution	Presence of defects, voids, extraneous matter
Ablative products	
Solid residue	Gaseous products
Percentage formed	Percentage formed
Elemental composition	Elemental composition
Mechanical properties	Thermal diffusion coefficient
Porosity and pore distribution	Specific heat
Thermal conductivity	Residence time in residue

Table 5. Ablative Characteristics of Carbon Fabric Polymeric Composites[a]

Polymer	Density, lb/ft^3	True surface temp, °F	Cold-wall heat of ablation, Btu/lb	Time to reach 275°F backwall temp, sec
Polyphenylene phenolic	87	5910	89,800	29.6
Polyphenylene	86	6120	76,760	25.3
Polyimide	82	6210	52,000	31.4
Chromium phenolic	83	5960	42,300	–
Napthalene phenol formaldehyde	90	6090	41,200	26.6
Polyphenyl phenol formaldehyde	87	6250	39,300	25.5
Epoxy-silicone	82	6180	37,000	30.0
Polybenzimidazole	84	–	34,800	31.8
Polyamide-imide	73	6200	31,700	19.0
Phenol formaldehyde	89	6250	29,500	20.0
Polyphenylene sulfide	85	6310	28,800	23.2
Epoxy-novolac	86	6160	27,000	19.0
Diphenyl oxide	76	6170	23,400	22.6
Phosphonitrilic chloride	84	6400	16,700	14.3

[a] Nominal 35% resin, fabric perpendicular to the gas stream, 3/4-in. thickness. Environment: 1000 Btu/ft^2-sec, 30 sec, 9300 Btu/lb air, 1.1 stag. pres.

Table 6. Ablative Characteristics of Silica Fabric Polymeric Composites[a]

Polymer	Density lb/ft^3	True surface temp, °F	Cold-wall heat of ablation, Btu/lb	Time to reach 275°F backwall temp, sec
Polyimide	100	4510	13,800	37.5
Polybenzimidazole	103	4570	13,100	38.6
Polyphenylene	97	4830	11,600	65.5
Phenol formaldehyde	99	4950	11,400	35.9
Polyester, carborane-modified	103	4290	11,400	–
Napthalene phenol formaldehyde	100	4670	10,800	35.2
Polyphenylene sulfide	104	5350	10,400	13.0
Phosphonitrilic chloride	111	4460	10,400	53.0
Diphenyl oxide	96	4820	10,200	40.2
Epoxy-novolac	110	4600	9,800	47.7
Polyamide-imide	91	4600	9,600	43.9
Epoxy-silicone	99	4440	7,700	29.1

[a] Nominal 34% resin, fabric reinforcement perpendicular to the gas stream, 3/4-in. thickness. Environment: 1000 Btu/ft^2-sec, 30 sec, 9300 Btu/lb air.

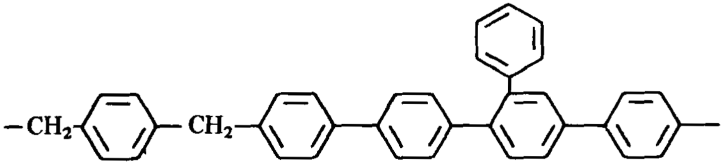
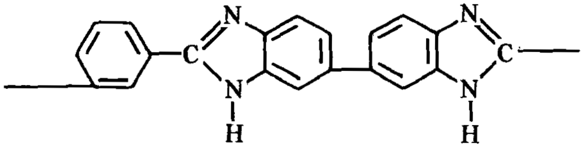
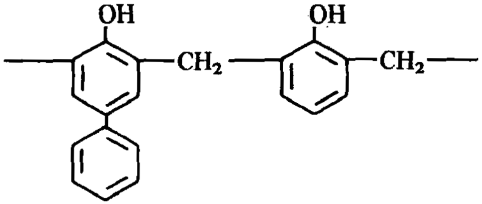
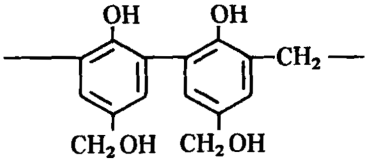
Table 7. Ablative Polymers in an Oxyacetylene Flame[a]

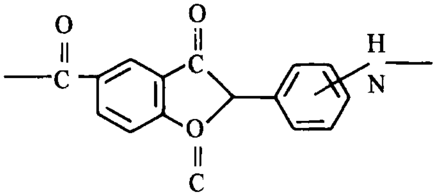
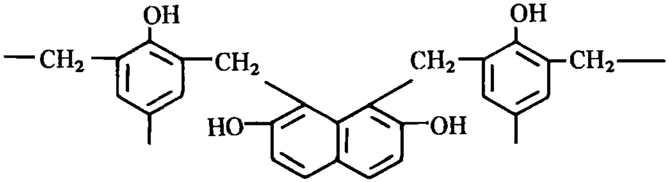
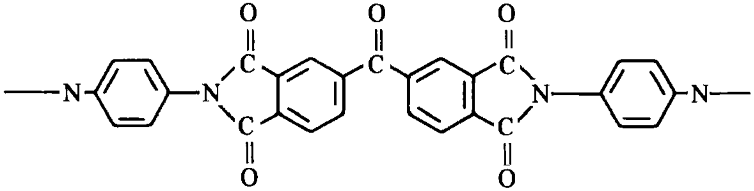
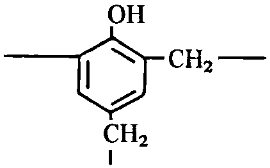
Polymer	Ablation rate, mil/sec	Insulation index, sec[b]
Polymers		
Polyhexamethylene, adipamide	14.4	–
Methyl methacrylate (acrylic)	17.6	11.6
Polyoxymethylene (acetal)	19.1	11.1
Polycarbonate	19.2	8.4
Ethyl cellulose	20.5	10.8
Polystyrene	20.5	10.8
Polytetrafluoroethylene	20.6	11.8
Polypropylene	23.5	9.1
Polytrifluorochloroethylene	24.2	10.1
Polyethylene	26.5	9.4
Resin impregnated composites		
Phenolic-100	4.4	39.6
Phenolic-40, zirconia-60	5.1	38.8
Phenolic-40, alumina-60	5.3	28.3
Fiber-reinforced composites		
Phenolic-40, graphite fabric-60	1.0	24.1
Phenolic-amide copolymer-40, asbestor mat-60	2.5	90.5
Phenolic, silica fabric	2.7	59.0
Phenolic-furfural-40, asbestos mat-60	3.1	80.4
Phenolic-40, asbestos mat-60	3.6	57.3
Phenolic, quartz fiber	5.7	22.0
Phenolic-40, glass fabric-60	7.6	21.8
Phenolic, nylon fabric	15.6	58.0

[a] Specimen 4 in. X 4 in. X 0.25 in. in a chemically neutral flame having a temperature of 5500°F, with a surface heating rate of 550 Btu/ft^2-sec.

[b] Time to achieve 200°C backwall temperature.

Table 8. Char Yields of Ablative Resins

Polymer	Structure	Resin density, lb/ft^3	Char yield, %
m-Polyphenylene (xylyene glycol-cured)		79	77.0
Polybenzimidazole		82	73.9
p-Phenylphenol phenol-formaldehyde		76	70.0
Biphenol-formaldehyde		74	65.1

Polyamide-imide		82	65.0
Napthalenediol phenol-formaldehyde		80	63.4
Polyimide		92	63.0
Phenol-formaldehyde		79	60.0

MATERIALS PROBLEMS

Many problems are being encountered in the development of advanced ablative thermal protection materials. Some of the more critical problem areas are reviewed below.

Charring Polymers

Charred polymeric surfaces are removed during ablation by chemical corrosion and mechanical erosion effects. Chemical consumption of the char may take place by oxidation and sublimation. Mechanical degradation [20, 21] of the char may result from surface erosion involving particle abrasion, gas-dynamic shear, external gas-pressure loads, and acoustical loads. Char spallation may involve internal gas-pressure loads, thermal stresses, and dynamic structural loads. Mechanical erosive effects are the most difficult to cope with. When such processes dominate during ablation, the effects are discernible by a rapidly fluctuating surface temperature and an erratic surface recession. Any induced char defects may grow in size during heating, due to local disturbances of the flow field. A second effect is to reduce material ablation efficiency, which is sometimes only a small fraction of the efficiency obtained in low mass flow environments. The trend toward increasing erosion rates with gas-dynamic shear and pressure is being minimized, however, by the synthesis of improved char-yielding resins and composites.

Erosion-resistant polymers form tough carbonaceous residues during ablation and remain strongly bonded to the underlying material. A variety of organic resins possessing these features are now being developed [22]. They exhibit char yields superior to the state-of-the-art phenol formaldehyde resins. Several of these resins are shown in Table 8, along with the resultant char yield after 1000°C exposure in an inert gaseous environment. It is noted that all of the promising resins have one feature in common—rings in the polymer chain. Both aromatic carbocyclics (containing only carbon atoms) and heterocyclics (containing nitrogen, oxygen, or sulfur in the ring) form a high percentage of char during pyrolysis and hence warrant further attention as potential erosion-resistant ablators. The highly phenylated phenolic resins, on the other hand, are of current technical interest because of their lower costs, ease of processing, and greater availability.

Polymers capable of forming improved structural chars should be further researched, particularly those possessing a high degree of oxidative stability. Of several approaches being pursued, one includes the combining of aromatic-hetrocyclic features with fused rings (stepladder polymers) and with fully fused ring structures (ladder polymers involving two connected parallel chains). A second approach includes the synthesis of those types of polymers which contain a minor amount of oxide-forming elements. The element silicon is a likely choice for incorporation into the polymer structure, since it is capable of forming the oxidative-resistant silica and may react endothermically with polymer carbon to form the refractory silicon carbide.

Noncharring Polymers

Polymers that ablate without the formation of a surface carbonaceous residue are of great interest for low-heating environments, high gas enthalpy environments, and specialized dielectric applications. During ablation, the materials tend to depolymerize rather than cross-link and char. Typical examples are polytetrafluoroethylene, polyformaldehyde, acetal copolymers, and linear epoxies.

Antenna windows on aerospacecraft and missiles represent a critical use for noncharring and very low-charring resins [23, 24]. In this type of application, electromagnetic signals are transmitted through the window for the purposes of communication, data transfer, guidance, and in-flight destruction. To serve these varied purposes, it is necessary for the polymer to exhibit electromagnetic transparency over a wide frequency and temperature range, high thermal efficiency, minimum linear ablation, toughness, nonchar-forming characteristic, low dielectric constant, and adequate strength to withstand natural and induced mechanical forces, and it must be fabricable. Since the antenna window is generally flush-mounted with the primary heat shield and constitutes a portion of the aerodynamic surfaces, it should ablate uniformly and at a rate matching the adjacent heat shield. Invariably, the antennae window ablates at a very high rate because it is denied the use of a highly emissive char layer. Consequently, the incident heating must be expended by other means, such as resin pyrolysis.

The synthesis and development of low-carbon, noncharring polymers thus represent a particularly difficult task. Polymers containing low carbon contents are generally difficult to prepare and process into composites. New polymer synthetic approaches and a better understanding of carbon formation during ablation are thus required to provide a solution to this important materials problem.

Inorganic Polymers

In spite of the great emphasis on ablative carbon-based polymers, inorganic polymers [25] merit attention because of certain attributes. These features include high thermal stability, flame retardency, electrical resistance, oxidative-resistant residues, and low carbon contents. Their uses have been restricted thus far, however, by relatively low mechanical properties (polymer tends to cyclize rather than form long linear chains), moderate thermal stability due to the formation of small ring compounds and low molecular weight polymers during heating, hydrolytic instability, costs, and limited availability.

The silicone or siloxane resins are the most widely used inorganic (semiorganic) materials. They are generally combined with low-denisty fillers to obtain better insulative values (lower thermal conductivity) and with short fibers or plastic honeycomb to improve their structural properties. During ablation, the silicone polymers soften, degrade to a molten material and pyrolytic gases, and tend to swell or bloat excessively [11, 26]. This tendency has been countered significantly by altering the polymer structure, improving the carbon:silicon ratio, increasing the cross-link density, and enhancing the yield of residue.

Other classes of inorganic polymers are also being developed, which offer some potential as ablative matrices. These include the phosphonitrilic polymers which have a backbone of entirely phosphorus-to-nitrogen bonds, the polyborphanes based on boron and phosphorus bonding, the carborane-modified polymers which contain boron-to-carbon bonding, polymetal phosphinates containing metal (chromium, beryllium, zinc, etc.) coordination centers connected by oxygen-phosphorus-oxygen bridging groups, and polymetal phenoxyaldehyde with metal coordination centers linked to the organic ring structure. Only limited ablative screening has been performed on these polymers, but their unique properties justify additional investigations. Continued progress in developing easier-to-process resins, fabrication of void-free composites, and specialized ablative characterization should aid substantially in finding new thermal protective uses for the inorganic polymers.

Low-Modulus Polymers

Most of the ablative polymeric materials used in present re-entry heat shields and rocket propulsion systems are somewhat rigid, low in elongation at fracture, and of relatively high modulus. Problems are occasionally encountered with these materials because of premature cracking, failure to transmit the applied load into the structure, and the accumulation of thermal and mechanical stresses. The cracking of a motor case liner during initial pressurization is an example of this type of material limitation [27]. In an effort to overcome these problems of cross-linked thermosetting resins, a number of different technical approaches have evolved. These include the addition of plasticizers to homopolymers, extending the length of the polymer chain to increase the distance between cross-links, introducing bulky or flexible-chain groups into or onto the polymer backbone, and copolymerizing the resin with other elastomeric polymers. This research has produced a number of flexible phenolics, urethanes, epoxies, and melamines; and of these, the elastomer-modified phenolics have found the widest usage.

Cryogenic Polymers

Hypersonic lifting vehicles and deep space probes spend a considerable amount of flight time in the cold environment of space. Temperatures may be as low as -300°F during cold-soak, followed by very high temperatures and thermal gradients during re-entry [28-30]. Ablative polymers must therefore meet a set of demanding requirements, including thermal and mechanical stability over a wide temperature range and compatibility with a variety of insulative and reinforcing agents, and must form an oxidative-resistant residue during atmospheric heating. In addition, the composite employing the polymeric matrix should be low in thermal conductivity, should be gas-dynamic shear-resistant, should ablate uniformly, and should have a low percentage of interconnected pores and an expansion coefficient close to that of the substructure. Silicone elastomers and epoxy-novolac resins, while not meeting all of these requirements, have provided the best overall performance to date.

New ablative matrices are being synthesized and developed, which exceed the capabilities of state-of-the-art epoxy-novolac and silicone polymers. Glassy resins and polyimides have shown the most promise to date. In low-density composite form, they have exhibited thermal efficiencies equal to or exceeding available materials. In addition, they generate mechanically stable char layers which are relatively uniform in composition and free of gross defects.

Pyropolymers

Ablation is generally viewed as a destructive process, but in a sense, it is a constructive pyrolysis process which results in the formation of a refractory residual product. The properties of this pyrolyzed product can be predetermined by carrying out the reaction in the laboratory under controlled conditions. Heating organic polymers in the absence of oxygen generally results in the formation of a structural char. Heating inorganic polymers in the presence of oxygen yields an oxide residue. Both of these products are pyropolymers which can serve as useful matrices in fiber-reinforced composites. For example, the constructive pyrolysis of a graphite fiber-reinforced phenolic composite results in a fiber-reinforced carbon. The newly formed prechar may then be increased in density or tailored to a specific application by repeated reimpregnation and recharring. The resultant material is light in weight, strong, and insensitive to brittle fracture but ablates at a slightly higher rate as compared with bulk graphite materials [31].

Carbon and graphite fibers represent one of the more important physical forms of pyropolymers. Fibrous polymers like rayon and polyacrylonitrile have been carbonized and graphitized to obtain crystalline and turbostratic forms of carbon, which may possess extraordinary properties [32-35]. Filaments have been obtained with tensile strengths ranging from about 21,000 to over 530,000 psi, and elastic moduli from about 1.5 million to about 90 million psi.

Some of the precursory organic fibers being used to obtain new carbonaceous and graphitic fibers [36] are shown in Table 9. It is apparent that the composition, structure, and processing of the polymer greatly influenced the type of fiber obtained. The relationship between the precursory polymer, nature of the char formed, and the mechanical properties of the pyrolyzed filament is less apparent. By subjecting carbonaceous filaments to graphitization temperatures (2500-2900°C), substantial increases in fiber mechanical properties have been realized. Moreover, further improvements in fiber mechanical properties have been obtained by stressing during graphitization to align the carbon crystallites.

Requirements for improved pyropolymeric fibers are centered on reducing basic materials costs, improving mechanical properties, enhancing abrasion resistance, and obtaining some degree of oxidative resistance. The fibers should be made available as continuous monofilament or multifilament yarns, which are convertible to woven, knit, or wound structural forms.

Table 9. Pyropolymeric Fibers

Virgin polymer	Char yield,[a] %	Diameter, in.	Tensile strength, psi	Tensile elastic modulus, million psi
Viscose rayon				
Carbonized	22	0.00045	180,000	5.4
Graphitized	–	0.00033	40,000	5.0
Stress graphitized	–	0.00026	430,000	74.0
Polybenzimidazole	75	0.00086	44,000	1.6
Polyacrylonitrile (preoxidized)	66	0.00056	81,000	3.8
Acrylic (preoxidized)	42	0.00146	58,000	5.7
Polyacrylonitrile	38	0.00056	51,000	7.5
Polyvinyl alcohol (preoxidized)	35	—	48,000	3.5
Polyphenylene thiadiazole	26	0.00060	25,000	4.7

[a] Heated 8°C/min to 900°C in helium.

Polymer-Fiber Bonding

The use of chemical finishes for promoting strong bonding between resins and oxide fibers is well known in the plastics industry. Amine and silane finishes provide strong interfacial bonding with oxide-type fibers, but they are worthless for accomplishing the same function with carbonaceous or graphitic fibers. The latter fibers, however, are presently of intense interest for both ablative and structural composites [37]. When combining carbonaceous fibers with conventional thermosetting resins, it has been found that the fibers are difficult to wet, contain moisture which inhibits bonding, are contaminated with pyrolysis products and alkali salts, and have variable surface areas [38]. As a consequence, the mechanical and especially the interlaminar shear strengths of composites have been low (in relation to those reinforced with oxide fibers). The interlaminar shear strength of a carbon fabric-reinforced phenolic resin, for example, is a real structural "Achilles heel" in that it is only about 2500 psi.

One approach to promoting the association of resinous matrices and pyropolymeric fibers is to surface-clean the fiber and preserve the nascent surface by means of a polymeric coating [39]. It has been found that the surfaces of graphite fibers are essentially chemically neutral and possess low surface area. Oxidation of the fibers under controlled conditions, such as a 24-hr boil in 60% nitric acid, increased the chemical functionality (concentration of acidic groups) and surface area of the fiber. The altered fiber surfaces were then protected by the addition of various polymeric coatings, like polyvinyl alcohol, polyvinyl acetate, polyacrylonitrile, and polyurethane. The oxidized graphite fibers had increased fiber-to-resin interaction, as indicated by composite shear strengths up to three times those of the nonoxidized control fibers. Further investigation revealed that the increased strength was due to higher chemical activity of the fiber and not to increased surface area. Apparently, the oxidatively induced pores were too small to be occupied by large resin molecules.

Significant progress has been demonstrated in surface treatments for carbonaceous/graphitic fibers, but additional research is necessary to obtain an easier means for preserving the original fiber properties and increasing their structural efficiency in plastic composites. Techniques for physically interlocking the fibers to resinous matrices should also be investigated, such as growing whiskers on difficult-to-bond fibers. Silicon carbide whiskers, for example, have been grown on high-modulus graphite filaments and fabrics and yielded epoxy composites with substantially higher interlaminar shear strengths.

Three-Dimensional Reinforced Composites

Fabric-reinforced composites have served as the work horse of ablative materials, but they possess certain limitations which are difficult to cope with. They have relatively low interlaminar shear strengths parallel to the fabric [40], as previously noted, high thermal expansion perpendicular to the fabric, low tensile strength perpendicular to the composite surface (except for 90° fabric layups), and relatively low resistance to impulsive loading.

New physical forms of fibrous reinforcements are thus being developed, which offer promise for minimizing some of the previously described composite limitations. These reinforcements are of a woven [41] or interlaced construction [42], and are commonly called three-dimensional because fibers are oriented in at least three principal directions. Some basic types of three-dimensional reinforcements include orthogonal non-interlocking, angle interlock, vertical pile, layer-to-layer interlock, four-hardness vertical in-depth interlock, braids, and vertical needle-punched fabric. The volume percentage of fiber in these constructions usually ranges from 30 to 40.

Three-dimensional reinforced composites are prepared by several different techniques. The first method involves hand-weaving the yarn prepreg and then compacting the article under heat and pressure. A second technique is based on hand- or machine-weaving the fibrous construction and then pressure- or vacuum-impregnating with liquid resin and curing by conventional procedure. Several major problems have been encountered, however, which are greatly restricting progress. Condensation, high char-yielding resins are frequently used, but release of volatiles during curing and the resultant porosity result in less than optimum densities. The use of a high pressure during resin-curing buckles the fibers, thus distorting the intended fiber orientation. Another problem is that fiber percentages in present three-dimensional constructions tend to be relatively low, especially for carbon and graphite fibers. Low tensile strengths of the fibers restrict the amount of tension utilized during weaving. Secondly, their low abrasion resistance necessitates the use of a protective surface treatment. The latter problem has been solved at least in part with polymeric coatings like polyvinyl alcohol and paraffin/elastomer mixtures. The surface coatings are applied prior to weaving and then chemically or thermally removed after fabrication of the fibrous three-dimensional construction.

New resins are desired for three-dimensional constructions that are high char-yielding, addition-type, low-viscosity, and compatible with typical fibrous materials.

Processing and Fabrication

Candidate aromatic, heterocyclic, and ladder polymers are being developed for potential uses in ablative composites. While these rigid-chain polymers have the structure and composition desired for future applications, high efficiency will not be realized unless suitable processing and manufacturing conditions are established. Many of these polymers are infusible and insoluble, thus making the preparation of fiber prepreg material and void-free composite impossible or very difficult. The polymers are generally only slightly soluble in hot aromatic solvents, and they must be cured at very high pressures and temperatures.

Processing and fabrication of ring structure polymers are solvable problems, as progress during the past several years has demonstrated [43]. Great strides have been made in synthesizing fusible aromatic and heterocyclic resins containing reactive chemical groups, identifying suitable solvents for the polymers, developing improved processing techniques (like hot melt impregnating fabrics), controlling the curing process by identifying the mechanisms involved, and synthesizing new curing agents to obtain higher molecular weight and structurally sound resins. Polyphenylene resins, for example, have been prepared by the cationic oxidative polymerization of m-terphenyl or related precursors. Fusible polymer fractions were then isolated by extraction with hot aromatic solvents. Polymers having molecular weights up to about 3000 and melting points between 300 and 400°C were prepared and combined with curing agents like xylylene glycol or trifunctional sulfonic acids. The resin lacquers were then deposited onto various reinforcing agents and fabricated into dense composites [44].

Many ablative composites are made by hand layup procedures, such as that employed in preparing elastomeric insulation for large, solid-propellant motor cases. In this application, milled sheets of rubber are adhesively bonded together and then vulcanized in place. The many bonded joints in this type of composite pose potential problems of reliability, quality control, and lower ablative performance, although the composite does permit greater design flexibility and lower costs. The development of trowellable, castable, sprayable, or other easily cured polymeric insulations would offer considerable fabrication advantages.

Low-Cost Polymers and Composites

Most of the polymeric materials utilized in present ablative thermal protection systems were originally developed for other purposes. Because of the broad uses for such materials, their costs have been relatively low, i.e., several dollars per pound. The more demanding requirements of future ablative systems, however, has necessitated the development of special-purpose polymers having a predetermined balance of properties. Such polymers tend to be high priced. Branched polyphenylene resin, for example, was originally sold for $2300/lb. The use of lower-cost precursory materials, improved pilot plant production, and increasing uses for the cross-linkable polymer have reduced the price to about $100/lb within a 3-year period, with indications of even further reductions in the near future. Additional possibilities for lower-cost polymers include the copolymerization of high-priced polymers with lower-cost natural products (aromatic tars) or inexpensive polymers, the use of low-cost fillers (paper, canvas, carbon powder, etc.) to reduce the amount of polymer required in a composite, and easier to use (castable, trowellable, sprayable, etc.) polymers.

Fibrous pyropolymers, like the present carbon and graphite materials, also also tend to be high priced. They cost from about $20/lb for carbon fibers derived from viscose rayon to about $600/lb for high-strength, high-modulus graphite filaments. With respect to carbon fibers, significant price reductions have been effected by using low-cost materials in the precursory organic fiber or low-cost physical forms of reinforcements like nonwoven tapes. For example, inorganic oxides (like sodium silicate) have been molecularly dispersed in viscose rayon dope and then formed into fiber by the conventional process. Subsequent pyrolysis of the bicompositional fiber produced a carbon-silica product having some of the desirable attributes of each component. Price of the fiber is substantially less than that of available carbon fiber [45]. Other cost-reducing methods being exploited include the use of lower-cost precursory fibers, improved pyrolysis methods, and large-scale production.

To ensure satisfactory performance and high reliability, it is common practice to employ the highest-performance materials available. But high-performance materials tend to be high-priced and involve high-cost manufacturing processes. Designing with these materials is justified when the systems requirements are critical, available ablators are only marginally satisfactory, weight is of utmost importance, and/or the part is reasonably small. For other cases, such as first-stage rocket motors, weight is not one of the critical parameters. Emphasis is then given to the relationship between costs of materials and fabrication, performance, and reliability. The savings that can be derived from such a program are illustrated in Table 10. Various ablative propulsion materials and fabrication techniques were investigated and compared with state-of-the-art technology [46]. The first

Table 10. Cost Effectiveness of Solid-Propellant Nozzle Materials[a]

Nozzle component	Material	Basic material costs, \$/lb	Component fabrication costs, \$/in.^{3}	Protective material required,[b] in.^{3}	Cost performance index,[c] \$
Throat approach	Acrylonitrile/ butadiene, silica powder	2.75	2.81	237	738
	phenolic, Kraft paper	2.00	1.75	174	174
Entrance cap	Phenolic-graphite fabric,	18.00	5.31	121	1036
	Phenolic carbon-silica fabric	12.45	5.25	74	559
Throat inlet	Phenolic Chopped carbon fabric	24.65	5.27	102	936
	Phenolic carbon fabric (low conductivity)	25.80	5.27	74	690
Throat	Phenolic carbon fabric	24.65	3.45	134	869
	Phenolic carbon fabric	20.74	3.45	140	826
Throat extension	Phenolic Chopped carbon fabric	24.65	1.68	153	572
	Phenolic carbon-silica fabric	12.45	1.63	153	429
Expansion cone	Phenolic (modif.) silica fabric,	6.00	1.14	264	464
	phenolic asbes.	2.00	1.14	238	321

[a] Motor firing-flame temperature over 5000°F, 60-sec exposure, average chamber pressure of 410 psia.
[b] Volume physically removed and thermally degraded.
[c] Costs of component materials and fabrication times of protective material required.

material is the conventional ablator, and the low-cost ablator follows. It is noted that significant savings can be effected in parts exposed to the least severe environment, i.e., the throat approach and entrance cap. The most critical parts of the motor, such as the nozzle throat, offer few possibilities because of the limited number of materials that will actually provide satisfactory performance.

APPLICATIONS

Ablative polymeric materials are widely used in very-high-temperature aircraft, aerospace, propulsion, and ground-based applications [47,48]. The number and type of hyperthermal uses increase yearly because of (a) a critical need for weight economy, (b) a frequent inability of engineering materials other than plastics to satisfy all of the design requirements, (c) an opportunity for plastics and elastomers to compete with other classes of materials in the initial design stage of an application, rather than being considered later as a substitute material, and (d) a growing awareness of the capabilities of polymeric materials as modern engineering materials. To date, polymeric composites have successfully provided environmental protection for hypersonic flight vehicles such as missile nose cones and decoys, orbital entry data capsules, nonlifting manned vehicles, winged spacecraft, and planetary atmospheric probes. Similarly, thermally protective polymeric composites have been used successfully in chemical propulsion systems for the construction of motor case insulation, rocket nozzles and exit cones, liquid propellant thrust chambers, blast deflectors, motor jetavators, and other important uses.

The optimum design of a polymeric heat shield for a given system depends upon the particular mission for which it is intended. No single heat shield can possibly satisfy simultaneously all of the associated environmental conditions. Moreover, a single ablative material will not satisfy a wide range of operational systems requirements in a highly efficient manner. The selection of heat shield materials for a given application is thus rather involved. Consideration must be given to the detailed thermal, chemical, and mechanical aspects of the time-dependent environment, as well as the physical, chemical, mechanical, permanence, and economic characteristics of the materials. It is often found that the mission imposes conflicting requirements on materials. Trade-off studies on candidate materials must therefore be performed in order to select a material with the best combination of properties and characteristics for the intended use.

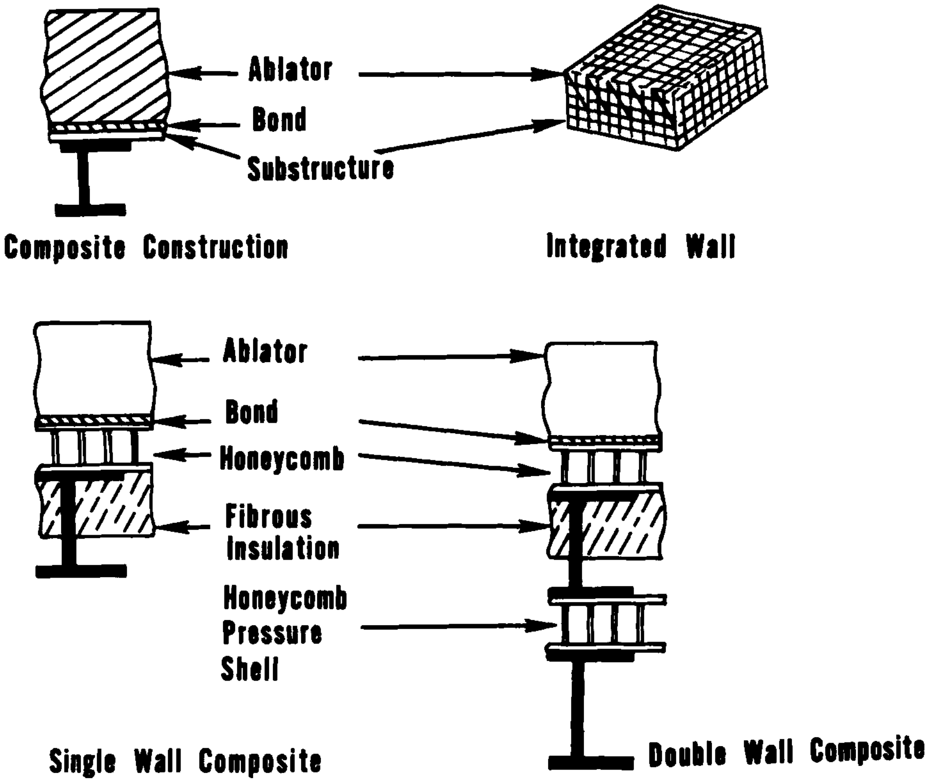


Fig. 2. Ablative heat shield constructions.

The environmental protective shields for aerospace and propulsion systems are generally constructed of various composite materials. Four types of construction are shown in Fig. 2. Ablative heat shields intended for unmanned vehicles or for propulsion systems have tended to be relatively simple. Their construction generally involves a polymeric composite varying in thickness, which has been adhesively bonded to an underlying structural element of aluminum or filament-wound plastic. More sophisticated designs are used for manned vehicles, wherein high reliability is of utmost importance. These structures are of a single- or double-wall pressure vessel design. For the future, the integrated wall construction is an outstanding candidate. It is a lightweight structure in that the heat shield and load-bearing substrate are combined into a single unit and without the use of an adhesive bond to join the units together.

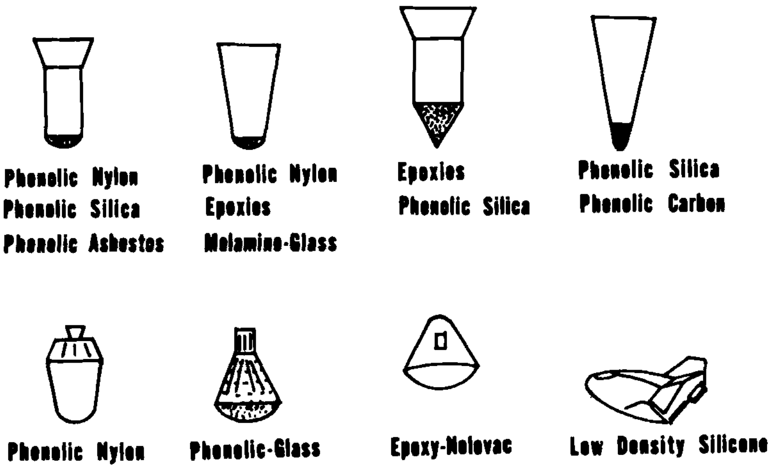


Fig. 3. Hypersonic flight vehicles and materials of construction.

Hypersonic Flight Vehicles

Increasing uses of ablative polymeric materials for thermal protection of high-speed vehicles have greatly extended the flight corridor in terms of higher velocities and higher speeds at lower altitudes. Because of the varying missions of the vehicles, their geometric shape and the type of heat-protective materials vary considerably. Representative vehicle configurations and applicable thermal protection materials are shown in Fig. 3. The compositions of the polymeric materials are given only in general terms because of proprietary considerations and security reasons [49,50]. It is apparent, nevertheless, that the first-generation ballistic entry nose tips were relatively blunt, and hemispheric or ogival in shape to minimize the incident heating rate. Such tips were usually made from molded and/or tape-wrapped nylon, asbestos, glass, or silica fiber-reinforced resins. As the ballistic entry vehicles became more slender to achieve higher entry velocities, serious materials problems were encountered in accommodating the more severe thermal and mechanical environments. The trend then shifted to to the carbon/graphite fiber-reinforced phenolics because of their higher heats of ablation and better retention of configuration during atmospheric heating. Body heat shields for the manned lifting and nonlifting vehicles have experienced different materials trends. For these vehicles, the material acts primarily as an insulator and only secondarily as an ablator. Low-density materials thus exhibit the best performance, provided they can

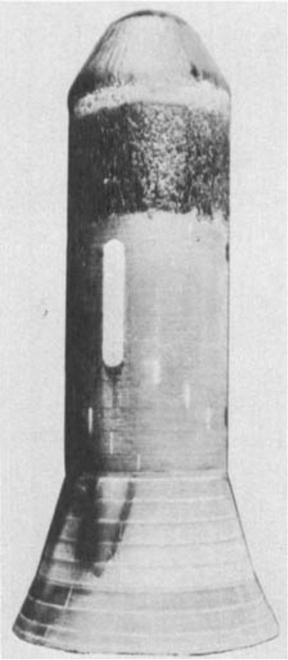


Fig. 4. Ablated nose cone after re-entry heating.

withstand the mechanical aspects of the entry environment. Dense composites utilized on the first manned vehicles (phenolic-glass, 110 lb/ft^3) have yielded to less dense composite syntactic foams of epoxy-novolac or silicone contained in a plastic honeycomb (30-40 lb/ft^3). Even lower-density ablative polymeric composites are possible and are being developed at this time.

In July 1958, the utility of ablative polymeric materials was first demonstrated for re-entry thermal protection. A 600-lb Thor-Able biconic-sphere vehicle was launched over 5000 miles and successfully withstood searing heat during atmospheric entry. Next in the series of experimental re-entry/recovery vehicles was the 700-lb RVX-1 sphere-cone-cylinder-flare vehicle. In April 1959, it travelled over 6325 earth miles and then was recovered [51]. A photograph of this ablated vehicle is shown in Fig. 4. The first man-made object to be recovered from a satellite was the 300-lb Discoverer XIII capsule. After 17 orbits during August 1960, it was ejected from a space orbit and successfully returned to earth with the aid of an ablative phenolic-nylon fabric heat shield. New space information was thus obtained on radiation intensity, biological reactions, environmental measurements, and other data [52]. Deep space probes have also been ablatively protected during earth re-entry. In September 1960, a nuclear emulsion recovery vehicle (NERV) was boosted 1250 miles into space and recovered. The ablative polymeric composite heat shield worked perfectly, thus enabling valuable space environmental information to be recorded and brought safely back to earth [53]. Polymeric materials have also played a vital role in the US manned space program. A phenolic-glass fabric heat shield was used on the suborbital flight of the Mercury capsule [54] in September 1959, and again in September 1961 for an orbital flight. The ablative plastic shields functioned perfectly, losing only 6 lb during re-entry heating of 8910 Btu/ft^2 and a maximum thermal flux of 60 Btu/ft^2-sec. Longer-duration manned space flights were later accomplished with the Gemini spacecraft [55,56]. During April 1964, a composite heat shield of silicone elastomer filled with microspheres and fibers protected an unmanned Gemini capsule. Re-entry heating was 25000 Btu/ft^2, with peak heating rates of 120 Btu/ft^2-sec. One additional unmanned and nine manned flights were also successfully performed. The Apollo spacecraft [57-59] is the next type of vehicle to be flown in the manned space program. Surface heating will be at such an intense level that all of its external surfaces are protected with a low-density ablative composite of epoxy-novolac resin, hollow microspheres, and fibrous reinforcements. A suborbital flight test in February 1966 demonstrated the suitable thermal protective capability of this material. Two additional flight tests of the heat shield have also been accomplished to date. Manned hypersonic flights are also being carried out with winged lifting vehicles. The X-15-2A, for example, has been redesigned to fly at speeds of 8000 ft/sec. Increased heating necessitated covering the vehicle skin with an ablative polymeric composite [60]. All flights with the ablatively protected aircraft have been successful. Other winged vehicles are also being designed, which are capable of higher entry velocities, greater maneuverability, longer range, and other performance features inherent in such aerospacecraft. The PRIME vehicle [61] is a good illustration of this type of flight vehicle. It is ablatively protected over all external surfaces. It contains a phenolic-carbon fabric nose cape, a low-density silicone composite afterbody shield, and polytetrafluoroethylene antenna windows.

Ablative materials are also used on the external surfaces of rocket motors, engines, and boosters to protect them from aerodynamic heating and exhaust radiative heating. Solid-propellant motors, for example, accelerate to high velocities within the atmosphere and thus require substantial thermal protection.

Chemical Propulsion Systems

Propulsion systems provide thrust for the movement of high-performance vehicles, such as missiles, rockets, aircraft, and other high-speed devices. Vehicle thrust is produced by the combustion of either liquid, solid, or hybrid propellants. The combustion process is carried out in a thrust chamber or a motor case, and the reaction products are momentarily contained therein. Because these reaction products are generally chemically corrosive, thermally reactive, and mechanically erosive, they are difficult to contain and control [62].

Ablative polymeric materials have been widely used for the thermal protection of chemical propulsion systems. With respect to their use in liquid-propellant engines, they are most attractive when throttling, restarting, multiple pulses, or low propellant flow rates are involved. If the engine is partially or entirely recessed into the vehicle's interior, ablative cooling becomes essential.

Propulsion involving very high-thrust liquid-propellant engines seldom employs ablative plastics, primarily because of their need for frequent proof testing (present ablators are generally not reusable), the availability of cryogenic propellants for cooling, and high rates of material loss due to combined long firing durations and high mass flow rates. Nevertheless, one very important application has been found for large plastic expansion cones, which are mated onto the end of a regeneratively cooled engine [63].

Greater uses are found for ablative polymers in secondary propulsion systems where engine thrust levels are 20,000 lb or less [64,65]. Thrust chambers or integral combustion chambers and nozzles have been constructed of ablative polymeric composites. The former type of engine is shown in Fig. 5. A metallic injector at the end of the engine introduces liquid fuel and oxidizer into the ablative plastic chamber. Combustion takes place at about 5200°F and 100 psi chamber pressure. After 300 sec of firing time, the plastic chamber was fully operational but only partially charred, as shown.

Ablative composites have scored more impressive gains in the thermal protection of solid-propellant motors [6]. The ablative components make up between 20 and 40% of the inert weight of a solid-propellant motor. The types of ablators employed and their motor positions are illustrated in Fig. 6. Virtually the entire motor [66,67] contains polymers in one form or another, including the propellant case, head-end insulator, entrance cone, nozzle, exit cone, external insulative coating, propellant grain supports, igniter basket, and jet vanes. Even in the most performance-critical part of

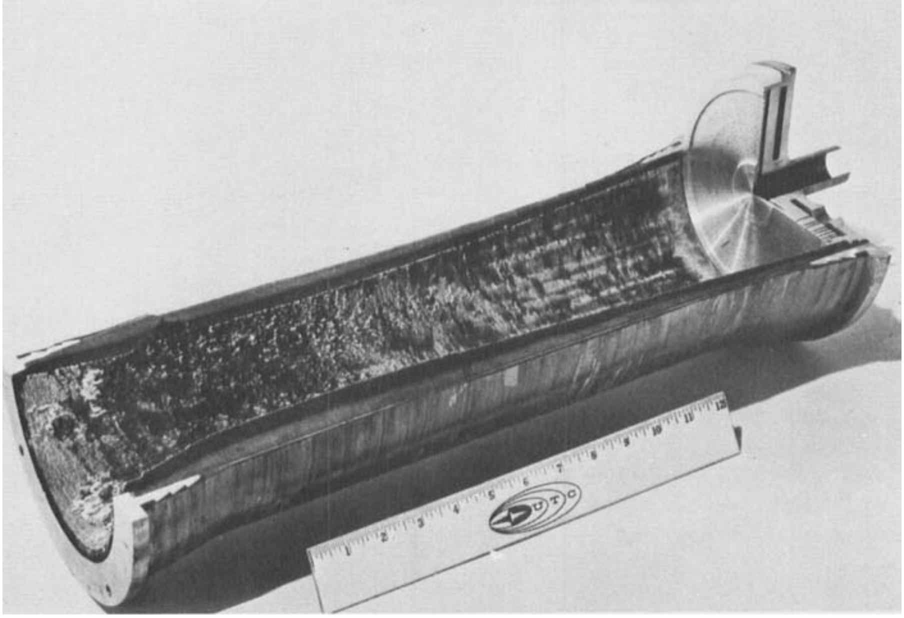
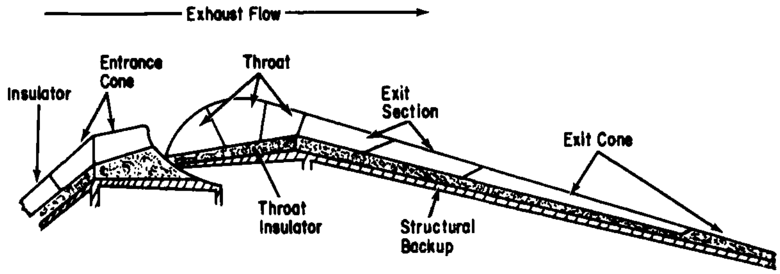


Fig. 5. Ablated plastic thrust chamber after engine firing.

a rocket nozzle, i.e., the throat, ablative plastic composites have been used with consistent success. All of the large-diameter solid-propellant motors (100-260 in.), for example, have employed carbon/graphite fabric-reinforced phenolics [68] without failure.

The role of ablative polymeric composites for thermal protection of hybrid-propellant engines is less apparent [69]. The technology of this type of engine is not well developed, but from the work accomplished, ablative polymers have demonstrated adequate performance.

Specialty purpose ablators are also required in the launching areas of propulsion systems. During motor ignition and take-off, the launch site and equipment are immersed in the exhaust plume for up to five or more seconds. Severe damage by heat and blast may result unless suitable thermal protection is afforded. A number of ablative plastic and elastomeric coatings have been developed, which exhibit a high degree of transient thermal protection, good adhesive properties, permanence characteristics, and ease of application. Millions of dollars worth of cables, hoses, umbilical cords, piping, electronic equipment, etc. have been saved from destruction by these replaceable coatings during a single missile launch.



	Insulator	Entrance Cone	Throat	Throat Insulator	Aft Nozzle	Structure
	Filled NBR Elastomer	Phenolic-Graphite Phenolic-Silica	Graphite Tungsten-Silver Tungsten Phenolic-Graphite	Phenolic-Silica Phenolic-Asbestos Phenolic-Glass	Phenolic-Graphite Phenolic-Carbon Phenolic-Silica Phenolic-Glass	Aluminum, Steel, Filament Wound Plastic
Environment	6,300°F	6,200°F	6,100°F		2,100°F	
GAS TEMPERATURE	800 psia	760-570 psia	450 psia		230-15 psia	
GAS PRESSURE	Low	Subsonic	Sonic		Supersonic	
GAS VELOCITY	Moderate	High	Very High		Moderate	
SURFACE HEATING	High	High	Very High		Moderate	
SURFACE SHEAR						

Fig. 6. Solid-propellant nozzle and materials of construction.

SYNOPSIS

Sufficient technology is now in hand to design, develop, fabricate, proof test, and use ablative thermal protection systems for hypersonic atmospheric flight vehicles, propulsion systems, and other very high-temperature applications. These heat-protective systems have been constructed of a variety of polymeric materials, which differed greatly in composition, construction, and properties. The particular polymer selected for a given application depends critically upon the mission of the system and its associated environment. A material exhibiting high performance in one application may not be suitable for use in a dissimilar aerothermodynamic environment.

Future aerospace missions will bring forth new environmental protective requirements. New and improved ablative polymeric materials must therefore be developed for these applications, because of the need for greater weight efficiency and the property imbalances which exist in present-day ablators. To achieve this goal, it will be necessary to obtain a more comprehensive understanding of the ablation process and synthesize new materials having unique or a different set of properties. Solution of these problems will require a variety of efforts by the materials scientists and technologists as well as assoicated interdisciplinary efforts. For example, the polymer chemist should continue to create new "building block" polymers which will serve as a basis for future ablative resins. The laboratory technician must devise new techniques for processing and handling new resins. The manufacturing specialist should develop methods for increasing polymer availability and at lower costs. The evaluation engineer should measure all of the important design properties of polymeric composites and establish techniques for predicting their performance in service environments. The developmental engineer should utilize the desirable properties inherent in polymeric material and properly apply these materials to new systems hardware. These activities serve to illustrate the many facets of polymer and composite research and development.

While materials considerations have always had some influence in shaping the mission and design configuration of thermally protected vehicles and structures, it is increasingly clear that future decisions will hinge on the feasibility and availability of new and improved ablative materials. Materials scientists and engineers thus have an unparalleled opportunity to make distinctive contributions to future aerospace technology. The successes that can be achieved will depend upon the ingenuity, imagination, and a closer association of those involved. The problems and challenges are many. Their solutions will open new vistas in hypervelocity atmospheric and space flight, rocket propulsion, and other applied areas of high-temperature technology.

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