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Tailoring Polymers for Entry into the Atmospheres of Mars and Venus†

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SUMMARY

Exploring the other planets of our solar system with atmospheric probes and landers places new requirements on polymeric systems. Because of a preoccupation with weight, designers of capsule components are switching over to plastics with increasing frequency. Ablative heat shields, aeroshell structures, antennas, insulators, electronics packaging, parachutes, and many specialty items could be made from plastics which are tailored to the specific environmental needs. In spite of generally poor practices which limit the reproducibility of commercial products, much is being done to delineate the problems set forth by these environments. This paper outlines the specific environments expected for Mars and Venus capsules and discusses some of the efforts in process, or prospective, within or for the National Aeronautics and Space Administration (NASA), to provide the understanding necessary to tailor new composites for these specific environments. Although much of the work is oriented toward ablative heat shield development, the application is generally similar for all of the other capsule components. Based on this work, an idealized polymer would be a reproducible high-temperature plastic with low volatile content, low-temperature flexibility, and a low number of reactive sites after cure. Though we are some distance from this ideal, progress is being made toward this objective.

†This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

INTRODUCTION

In spite of ups and downs, the urge to send man off the earth to the other planets of our solar system, and perhaps beyond, is with us and will remain so for many years to come. Through the Ranger, Mariner, and Surveyor programs we have landed on the moon and have observed Mars and Venus from reasonably close fly-bys. The next generation of missions appears to use capsules which will enter into the atmospheres of Mars and Venus as did the Russian Venus probe last year. The accomplishment of these missions necessitates solutions of new kinds of problems and requires new kinds of materials and technology. This paper outlines some of the improvements in plastics technology which are necessary to cope with the environments expected in probe missions to Mars and Venus. Our capability to explore the planets of our solar system is limited by a materials technology which lags behind the chemical, mechanical, thermal, and electrical performance requirements of the expanding sciences. Plastics are the least understood of capsule materials but have perhaps the highest potential with which to fill the greatest range of needs.

GENERAL CONSTRAINTS

Inherent in every mission to probe the atmosphere of Mars or Venus are certain basic ground rules which are usually scientifically (or politically) derived. Some of the most important relate to planetary quarantines, science objectives, cost, weight minimization, flight opportunity, and reliability. The general applicability of polymeric material must be judged in these contexts.

Planetary quarantine requires that the probability of contamination of the extraterrestrial planets with a viable earth organism be held to less than 1 in 10,000. Because of this, all components entering the planetary atmosphere must be completely sterilized before launch, either chemically or by heat. All of these life forms which are to be sterilized are structurally similar to most of the polymeric materials used as components in the entry vehicle. As the life is destroyed, so are many of the plastics.

The instrumentation necessary to satisfy science objectives essentially dictates the capsule configuration and the mission, within the limits of the other major ground rules. This instrumentation varies in complexity from passive-descent experiments, such as accelerometers, radiometers, and temperature and pressure devices to active-descent experiments, such as gas

chromatographs, mass spectrometers, and chemical gas analyzers which actually sample the atmospheres; from landed payloads which may vary from a simple beeper, which proves impact or touchdown survival, to fully mobile ground units. Plastics are required for all of the possible configurations, but the specific needs vary widely, depending on the individual measurement desired. A brief outline of a typical composite configuration is given later.

The use of plastics to solve any particular material problem is often closely tied to the cost factor. Although the raw material cost is relatively low, the costs entailed in methods of application to achieve a desired result vary widely. Cost is often interrelated with reliability in that the first cost question to be answered is how much reliability can be given up for cost. In addition to the cost consideration, reliability also includes the problems of factor of safety and redundancy.

Weight minimization requirements affect all capsule designs. Launch vehicles have specific maximum delivery capabilities. To get the most out of any mission, it is important to fly as many experiments as are practicable, reliable, and within cost limitations. Since many of the proposed experiments involve only a pound, an ounce saved from each of 16 different subsystems can mean a substantial increase in scientific output.

The expression "flight opportunity" refers to the location of a particular planet relative to earth during a particular conjunction, combined with the launch capability of a particular launch vehicle. Thus, it is more feasible to go to Venus in 1967 and 1975 than in the intervening years. Mars opportunities are best in 1969 and 1971 but require a higher-energy launch for a given delivered payload in later opportunities.

ANTICIPATED ENVIRONMENTS

A more detailed discussion of the environmental exposures a capsule undergoes for a Martian mission is given elsewhere [1]. The important environments include chemical sterilization, dry heat sterilization, launch vibrations and pumpdown, high vacuum, interplanetary radiation, micro-meteoroid impact, guidance engine vibration, entry heating and pressure loads, descent, impact, and landed operation (Fig. 1). Venus missions are essentially the same except for increased solar radiation and more severe entry and descent conditions.

An ethylene oxide-Freon 12 mixture is used as a chemical sterilant at 50°C to provide surface decontamination during assembly so that the

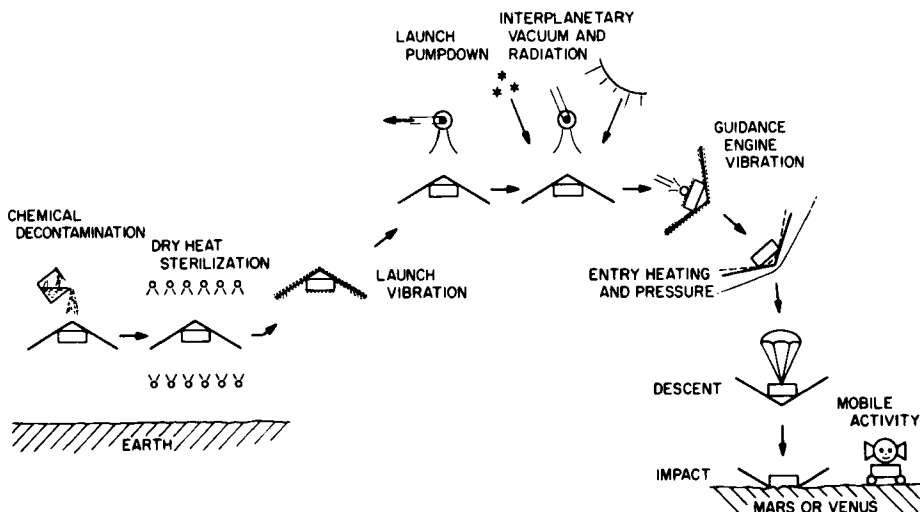


Fig. 1. Transit and entry environments.

number of viable organisms still alive at the beginning of dry heat sterilization will be minimized. Dry heat sterilization is used as a terminal sterilization process. The entire capsule is exposed to 125°C in a sterilization canister for 24–60 hr just before it is moved into the launch operation. The capsule and sterilization canister are launched together and separated only in the reasonably sterile conditions of space. Launch vibration or shock due to engine noise and booster staging operations also have deleterious effects on materials and components because of structural excitation and acoustical coupling. Since booster vibration information is not generally available, the launch environment is approximated by shaped spectra of gaussian noise, random noise spectrum, static accelerations, and low- and high-frequency sinusoidal vibrations (1–2000 cps).

Rapid pumpdown during launch (approximately 1 order of magnitude decrease in pressure per min for 8 min) causes differential pressures in honeycomb sandwiches and foams due to the inability of trapped gases to diffuse from material rapidly. Once the capsule is in space, exposure to vacuum and interplanetary radiation causes two kinds of problems: (1) gradual change in the properties of certain materials because of vaporization or chemical deterioration and (2) migration of recondensable absorbed volatiles from hotter to colder (sunny to shady) surfaces or to surfaces with

greater polar attraction. These recondensable materials change the effectiveness of lenses and temperature control surfaces.

Micrometeoroid impingement is considered a minor problem for most capsule missions. During midcourse corrections and orbital insertion, acoustic vibrations could cause failures in cold components or materials. These failures may not have been observed during the comparatively warm launch.

Entry into planetary atmospheres severely constrains the design. The need to minimize weight forces consideration of lower factors of safety for load-carrying components which are already at the state-of-the-art in fabrication technology. Peak loads, at present, vary up to 200 g during Mars entry and up to 500 g for Venus entry, depending on the mission. Entry heating is complicated by the presence of large percentages of CO₂ in the atmospheres of Mars and Venus which effectively increase both the average radiance of the shock layer gases and the convective heat input. Combustion processes also vary and change the method of handling heat shield performance. Mars heating rates are well within our present experience. Venus entry depends on the mission being considered. Some missions are compatible with present heat shield knowledge; but most of the scientifically more desirable missions contact much higher heating rates and pressures than those encountered through ballistic missile experience. The increased importance of radiation heating because of the entry-vehicle bluntness necessary for high-altitude deceleration complicates matters.

Martian descent is difficult primarily because the atmosphere is so tenuous. Venus descent is complicated by high surface pressures (4–20 atm) and temperatures (536°C) which exceed the upper working limits of most electronic systems. Impact criteria vary from about 2500 g at 100 ft/sec for a hard lander, to 10 g at very low ft/sec for a soft lander. The hard-lander concept necessitates quite a bit of new design. Landed operation provides difficult problems in temperature control because of the hostile surface environment. It also provides a multitude of other problems associated with mobility and sample acquisition or with making meaningful measurements and sending the information back to earth.

TYPICAL COMPOSITE CAPSULE CONFIGURATION

A typical Mars or Venus capsule is a sphere-cone with a cone half-angle, γ , of 40–60° and a nose radius from one-tenth to one-quarter of the base body diameter, D . A generalized configuration is shown in Fig. 2. Numerous alternatives are not delineated. Instead, emphasis was placed on

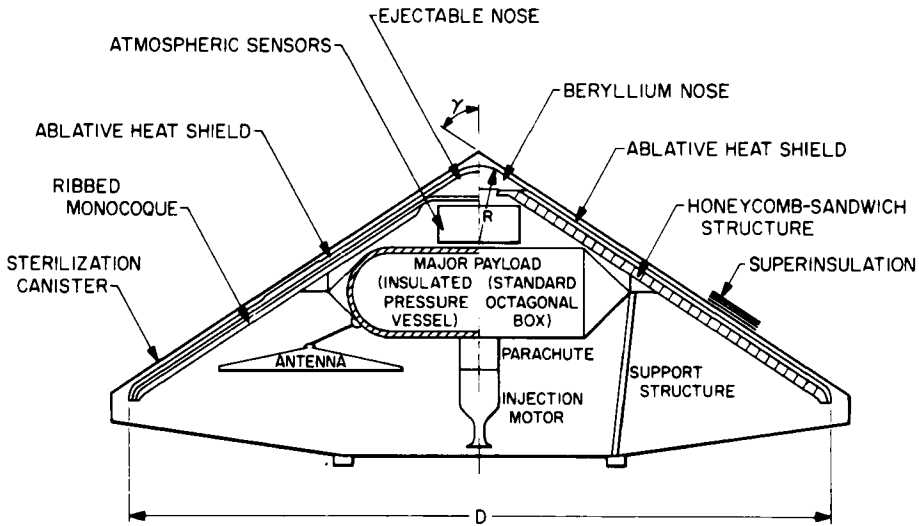


Fig. 2. Generalized configuration for an extraterrestrial atmospheric entry probe.

alternatives which provide the greatest use of plastics. The ablative heat shield can be roller-coated, molded, or gun-filled honeycomb, depending on the severity of the entry environment. The basic structure and the antenna can be a monocoque or a honeycomb in either metal or fiberglass, or a combination of the two. Plastics are required for the superinsulation used to keep out the interplanetary cold as well as for the insulation used for the pressure vessel. The pressure vessel is a possible means of protecting the payload from hostile environments during terminal descent to Venus. The parachute, if needed, and much of the injection motor, will also be polymeric. Myriad plastics are used throughout the electronic system for circuit boards, potting compounds, conformal coatings, cabling, insulation, and others. Many more find use [2, 3] as minor structural parts, bearings, tubing, diaphragms, seals, and such.

EFFECTS OF INDIVIDUAL ENVIRONMENTS ON POLYMERIC MATERIALS

Some general comments on polymer fabrication and definition are

perhaps apropos before a discussion of individual interactions with the environment. Generally lax controls on processing and raw materials in the plastics formulation industry make it difficult, if not impossible, to obtain reproducible polymeric-based composites. A first area of concern is that, for the most part, commercial designations are unreliable. Changes are made in the so-called proprietary additives such as curing agents, processing aids, fillers, diluents, plasticizers, antioxidants, accelerators, vulcanizing agents, etc., without changing the commercial designation. In the past, these changes have cost NASA and others millions of dollars in redesigning and retesting because an ounce or a pound, or whatever, of some designated plastic was no longer the same as it was when qualified for use. Because of this, there is a trend by NASA toward formulating its own polymer systems and completely bypassing the plastics industry [4]. This kind of work will continue to grow as long as industry refuses to make a reproducible, fully characterized set of spacecraft-grade polymers. NASA cannot afford to have a nonfunctioning capsule on Mars or a dead astronaut because a pound of polymer was changed somewhere between its qualification and its use. Present government specifications are not a solution to this problem. Military specifications, for example, are normally too general and allow too wide a range of formulations.

A second general area of concern is the characterization of polymers and polymer composites. Table 1 provides a partial list of the data required to completely analyze ablative composites. Table 2 shows the range of conditions for which these properties must be measured. The thermodynamic, mechanical, and miscellaneous properties are all part of normal heatshield design requirements. The electrical properties are usually needed only when radio frequency transparency or diagnostic instrumentation are built into the ablative system. Except for some chemical compatibility studies and minor modifications in fixtures or specimen size, Table 1 covers most of the material property needs for all plastic components. For the most part, little or none of this data is available for any particular plastic or plastic composite. Of the data that are available, few are meaningful. Only a few investigators have bothered to find out how the dial indicator reading on their instrument or the ink line on their strip chart actually relates to the physical quantity that is supposedly being measured. For planetary missions where the factor of safety needs to be kept as low as possible, the

Table 1. Material Properties to Define Ablative Composites**Thermodynamic Properties****Thermal**

Specific volume
 Expansion coefficients:
 linear and bulk
 Specific heat:
 solid and evolved gases
 Conductance

Optical

Emittance
 Absorptance and absorption coefficient
 Transmittance

Degradation kinetics

Heats of degradation, phase change, and combustion
 Internal gas evolution rate:
 frequency, order, activation energy
 Reaction-rate-limited oxidation rate:
 frequency, order, activation energy
 Diffusion-rate-limited oxidation rate:
 frequency, order, and activation energy, or other
 Sublimation rate:
 frequency, order, and activation energy
 Evolved gas species identification
 Cracking and redeposition of transpiring gases

Mechanical Properties**Standard tests**

Tensile yield and ultimate strength
 Compressive yield and ultimate strength
 Flexure strength
 Shear strength
 Young's modulus:
 tensile and flexure
 Poisson's ratio
 Brittle-transition temperature

Special tests

- Thermal shock resistance
- Impact sensitivity
- Abrasion resistance
- Peel strength of ablator: structure bond
- Popping, shear, or crush strength of char

Electrical Properties**Standard tests**

- Dielectric constant
- Power factor
- Loss tangent
- Volume resistivity
- Surface resistivity

Miscellaneous Properties**Special tests**

- Elemental analysis
- Porosity
- Permeability
- Volatile condensable material content
- Radiation resistance
- Vacuum degradation resistance
- Sterilization resistance:
 - dry heat and chemical decontamination

difference between a 10 and 20% error in measurement on a particular property can be as important to the scientific mission as an order of magnitude error in normal industrial applications. One interesting example of a commonly ignored measurement error is contained in the Chromel-copper and Alumel-copper junctions on the side of common thermocouple amplifiers. In some amplifiers, because of tube placement, these two junctions are not at the same temperature. Biases of up to 55°C have been recorded from this factor alone.

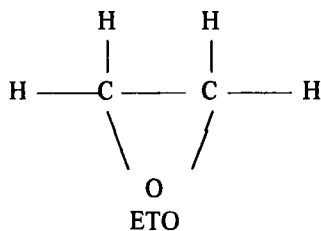
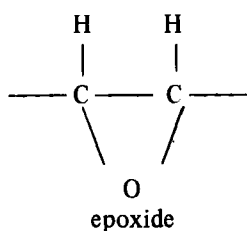
Table 2. Parametric Limits of Property Measurements

Temperature, -200° to 6000°F
Time at temperature
Static pressure, 10 ⁻¹⁶ Torr to 10 atm
Strain rate
Wavelength
Direction, angle of incidence
Before, during, and after ablation
Molecular weight of gases
Fabrication parameters

Ethylene Oxide Surface Decontamination

The effects of ethylene oxide (ETO) on commercial polymeric materials have been studied for the Jet Propulsion Laboratory (California Institute of Technology), at Hughes Aircraft Company [5] and the Autonetics Division of North American Aviation, Inc. [6]. Electrical piece-parts and materials are qualified by the severest of the recommended chemical decontamination procedures [7]. Samples were exposed to a mixture of 12% by weight ETO and 88% dichlorodifluoroethane (Freon 12 or Genetron 12) with an ETO concentration of 450–650 mg/liter of gaseous atmosphere for six 28-hr cycles at 50°C with a relative humidity of 35–55%. All of the basic resins for heat shield formulations were tested in this program, as well as the standard potting compounds, adhesives, tapes, and such. Studies of specific heat shield materials are given elsewhere [8, 9].

Ethylene oxide is used as a decontaminant because of its ability to form free radicals, especially in the presence of water vapor (hence, the percentage of relative humidity first given). As a free radical, it can act as a cross-linking agent or a molecular weight increaser to produce additional brittleness or stiffness in a polymer system, or it can act as a chain breaker or swelling agent to decrease mechanical properties. In a micro sense, it reacts somewhat like an epoxide unit, which it resembles.



In general, most of the high-temperature versions of polymeric systems which are usable at temperatures above 150°–200°C are not affected by ETO. Therefore, aromatic thermoplastics of the polyimide, polycarbonate, polysulfone, or polyethylene terephthalate types were unaffected unless they were weakened by copolymers, plasticizers, etc. A molded form might be all right, but the same material diluted to allow the making of thin films may be severely degraded [5]. The fluorocarbons provide a somewhat amusing problem. Although nearly all of them are unaffected by ETO, they are (except Teflon) softened or degraded to some extent by the supposedly inert carrier gas, Freon 12, which happens to be a good solvent for fluorocarbons. Thermosetting plastics such as epoxies, phenolics, polybenzimidazoles, diallyl phthalates, etc., are unaffected in most high-temperature cures, but tend to be severely degraded or embrittled when cured at room temperature. The additives, not the base polymer, again appear to be the main problem. A problem of secondary importance in ETO surface decontamination is the absorption of ETO molecules during decontamination. If these molecules remain absorbed in the polymer, they may cause degradation during dry heat sterilization. Reactivity at 135°C should be more severe than at 50°C. This problem has been investigated to a limited extent [6, 10].

Ethylene oxide surface decontamination thus requires a clean, high-temperature resin system. What additives are allowed must be completely characterized by structure, quantity, and function so that final compatibility may be determined.

Dry Heat Sterilization

Again, clean, high-temperature polymers are the most resistant to dry heat sterilization. As a first cut, suitable polymers may be chosen from the plethora of thermogravimetric data in the literature. Madorsky's work forms a base for much of this [11]. There is too much activity in this

thermogravimetric measurement area to dwell on it here. Two major problems are found in trying to apply this work to real use situations. First, during sterilization or ablation, the degradation control parameters (sample geometry, gaseous atmosphere, temperature history, etc.) seldom resemble the laboratory thermogravimetric controls. Second, the materials themselves are significantly different in that commercial designations allow a fairly wide range of purity in the base monomer, variation in the state of cure or homogeneity, and only partial limits on the presence or absence of processing aids, mold releases, fillers, diluents, plasticizers, antioxidants, and vulcanizing agents. Because of this, each commercial product must be tested individually before it may be allowed on a spacecraft or capsule as an ablative heat shield or as any other component. It must then be re-tested each time a new batch is received from the manufacturer.

Programs of this kind have already been carried out [12, 13]. In these programs electrical piece-parts and materials were exposed to six 92-hr cycles in dry, clean nitrogen at 135°C [7]. More recent work [10] emphasizes the interactions between ETO and dry heat and some studies of mechanisms in particular problem areas such as tape recorder tapes and battery cases (in process). In general, this more practically oriented work agrees with that of the thermogravimetric people as long as processing variables are known, understood, and controlled. Therefore, common high-temperature silicone elastomers, epoxies, phenolics, polyurethanes, butyl rubbers, fluorocarbons, fluorosilicones, polyimides, etc., could be either suitable or unsuitable, depending on the additives. Studies of actual ablation material composites [8, 9] showed nothing different. Dry heat sterilization degraded few of the materials tested since partial screening from thermogravimetric or other data had already taken place. Most materials were either further postcured, which provides a stronger but more brittle structure, or had their low-molecular-weight constituents vaporized, which provides a lighter composite which may or may not be a weaker (negative) or a better (positive) insulator. Ablators generally show improved performance after sterilization. Coatings and films with low-viscosity processing forms tend to degrade severely during sterilization.

Dry heat sterilization thus also requires a clean, high-temperature resin system with regulated additives. In general, present selection criteria are rigid, so that a specified percentage of change in some property eliminates the material. This practice is frequently much too rigid, though, for slight changes in formulation, or some pretreatment, could eliminate the problem.

Launch Vibration

Most of the booster configurations under consideration for future probe missions to Mars or Venus do not yet have data available on their launch vibration profile. Preboost ground-test vibration specifications [14] are normally extrapolated from similar, but not equivalent, data and tend to be conservative, i.e., more severe than the actual. These tests consist of shaped spectra of gaussian noise, sinusoidal vibrations, static acceleration, and shock. Experience shows that normal polymer crack-propagation theory based on local molecular mobility or crystallinity, on polar adsorption of small molecules, or other phenomena, are not particularly applicable. The wide range of the vibration-test energy spectrum makes it difficult to separate the effects. All that can be said is that if a crack is initiated, it will normally propagate. Avoidance of crack initiation is a matter of fabrication technique and usually entails some trial-and-error process. Since most of the polymeric materials in use are composites or modified pure polymers, the cracking process tends to be more complicated than present theory, which is based on comparatively pure materials, can handle. This is further complicated by any earlier embrittlement caused by improper cure or by ETO surface decontamination and dry heat sterilization.

Clean, high-temperature polymers are also among the best materials for vibration. Although often more brittle than their more diluted counterparts, they lend themselves to analysis by not being susceptible to unexpected local anomalies. All that is required is a fairly low-temperature brittle-transition. For an actual flight, it is important to insulate the structure from the low-temperature liquid fuels used in most of the major boosters.

Launch Pumpdown

Launch pumpdown causes two kinds of problems with heat shields, insulators, structures, or sterilization canisters. Porous ablators, payload containers, or honeycomb-sandwich structures must be strong enough to withstand a sudden atmosphere differential pressure or must be vented sufficiently to allow for the 8-min drop in external pressure from 1 atm to 10^{-6} Torr, a drop which is common during boost into orbit. A rather costly example of this phenomenon was the Mariner 3 shroud which blew apart during launch, terminating the mission [15]. The second problem is related to the first, in that foams and other forms of porous insulators and ablators

are often coated with some form of temperature control substance to allow a reasonable radiation balance between subsystems. It is important that these coatings remain intact during pumpdown. Preliminary studies have shown severe bubbling and general surface disruption [16]. Studies at Jet Propulsion Laboratory (JPL) have shown a good lowering of emittance from vapor-depositing techniques, but thermal performance during entry is severely affected by densification of the surface region because of a passage of the vapor through the surface pores, and deposition in depth.

The container problem can be solved by designing stronger containers, but the temperature control problem for ablators is fairly new and has not yet been fully undertaken.

Interplanetary Vacuum

Interplanetary vacuum causes two problems in polymeric materials for planetary probes: (1) The vacuum pressure and local temperature may be sufficient to volatilize portions of the polymeric materials on the vehicle, changing the mechanical, thermal, or electrical performance; (2) the volatile materials may be recondensable on cooler or more polar areas elsewhere on the vehicle and thus change the optical properties of temperature control surfaces, TV lenses, radiometers, etc. These problems have been important constraints on all of the JPL lunar and planetary missions. Boundy [17] has described the apparatus developed at JPL to qualify materials. This work was extended and modified at Stanford Research Institute (SRI) under contract to JPL [18]. Schematics of the micro- and macro- VCM (volatile condensable materials) tests used at SRI are shown in Fig. 3. The micro- VCM test is used as a basic screening test to qualify polymeric systems. The macro- VCM test provides diffusion dependence so that a more meaningful relation to actual use can be determined. Micro- VCM may also be used in conjunction with salt flats so that infrared spectrophotometric "fingerprints" of the recondensable portions of polymeric products may be determined. Reference [18] has a catalog of these fingerprints which may be used to check conformity of new batches of material or to identify contamination sources in space chamber checkouts.

The present criteria used to qualify materials for use in spacecraft or atmospheric probes are that the polymer system must lose less than 1% of its total weight in a vacuum at 125°C (an upper limit for possible local temperatures during flight) and must have less than 0.1% of its original weight recondensable on a polished aluminum plate at 25°C. The volatile materials

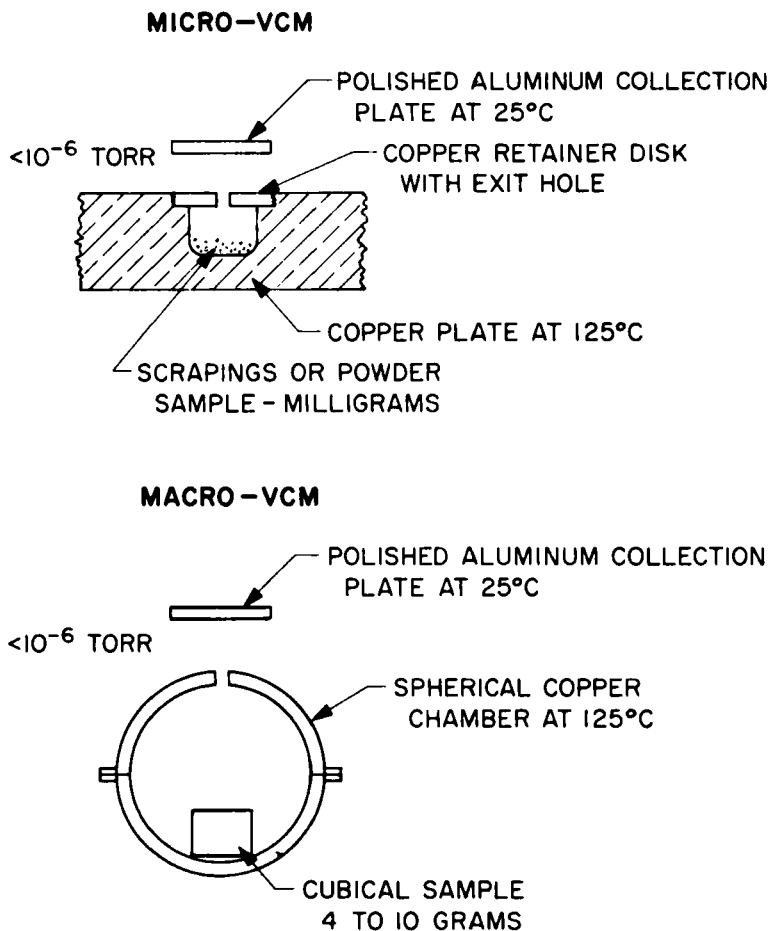


Fig. 3. Micro- and macro-VCM test schematic.

come from four main sources—degradation products, unreacted monomer or fragments of low-molecular-weight polymer from the polymerization or curing process, unreacted or unreactive additives, and absorbed gases or liquids. All of the polymeric products used in spacecraft or atmospheric probes are selected for high-temperature properties and should not show significant degradation products at 125°C unless some additive has reduced their temperature resistance. Absorbed gases or liquids are seldom permanently recondensable on other materials unless a chemical reaction is possible. Ethylene oxide absorption may be in this category. Some materials require

quantities of these absorbed gases in order to perform properly. Nylon cannot be used mechanically in a vacuum because its resilience depends on the absorption of water. Without extremely small quantities of absorbed water, nylon is brittle. For this reason, phenolic nylon heat shields are not at present being considered for extraterrestrial planetary missions. Although nylon is a reasonably efficient ablator, shattering under deceleration loads because of insufficient water vapor in an extraterrestrial planet upper atmosphere is not desirable. On the other hand, there are no data confirming that this will happen since composite strength does not depend on the nylon alone.

Loss of low-molecular-weight unreacted or unreactive additives may change the physical properties of the starting materials significantly (e.g., loss of plasticizer embrittles neoprene seals). In general, ablative heat shields (except those of phenolic nylon) are not adversely affected by vacuum exposure. In fact, tests have shown either no change at all or an increase in mechanical properties and a lowering of thermal conductance because of sterilization or vacuum exposure. The decrease in conductance improves thermal performance during entry. High-temperature epoxies, phenolics, silicone elastomers, polybenzimidazoles, and other efficient ablaters generally do not have significant unreacted curing agents after post-cures. Other additives are generally not needed unless some diluent is used for spray application or similar fabrication needs. A few years ago an enthusiastic program to improve ablation performance by the addition of low-temperature organic or inorganic fillers was stopped when it was discovered that they would gradually disappear during interplanetary transits. Not enough work has been done in the other polymer areas on spacecraft to completely delineate additive problems, and each use is still treated as a special problem.

All thermoplastics polymerize in some distribution of molecular weights. Teflon, one of the more efficient thermoplastic ablaters, leaves only a very small amount of monomer or low-molecular-weight products after polymerization. Polyethylene, generally a poor ablator, often has quite a bit, so that polyethylene splatters during ablation as the low-molecular-weight constituents vaporize under the liquid surface layer. Thermosetting plastics similarly leave small, unreactive fragments although the general polymer may be essentially one large molecule. Probably the worst polymeric system with an identified low-molecular-weight tail is that of the silicone elastomers. Through JPL's contract with SRI [18, 19], the condensable volatiles coming off silicone elastomers were identified as low-molecular-weight silicon-oxygen-based ring structures. Depending upon the polymer

formation, silicone elastomers lose up to 5% by weight with approximately 50% of this loss recondensable on the polished aluminum plate. Microspecimens, but not macrospecimens, could be vacuum thermally treated after cure so that acceptable VCM readings could be registered. In general, these silicone elastomer fragments do not revolatilize with time. Because of this, silicone elastomers have been eliminated or restricted to limited application in all JPL spacecraft. They have also been eliminated as candidates for heat shields for Mars or Venus atmospheric probes, since the large volume of material would completely change any optical systems or temperature control surfaces. Except for this deficiency, silicone elastomers are one of the most desirable base resins for Mars-entry heat shield composites.

In response to this need for better silicone elastomers, Dow-Corning has come up with a new process by which they eliminate most of the low-molecular-weight "tail" of silicone elastomers before cure. Micro- and macro- VCM results for the first polymer processed in this fashion are shown in Table 3. Both the micro- and the macro- VCM are better for the specially processed elastomer than the best micro- VCM sample of normal elastomers after the extreme (232°C) vacuum postcure. This is also as good as the best from other polymeric systems. The posttreated surface and center-core micro- VCM samples also show the extreme diffusion-dependence of the materials. It is also interesting that for silicone elastomers, vacuums of the order of 10^{-7} to 10^{-8} Torr volatilize considerably more of this "tail" than vacuums of 10^{-5} to 10^{-6} Torr. This condition is consistent with some unpublished vapor pressure curves.

The ideal polymer for the interplanetary vacuum is, thus, a clean, high-temperature polymer which has properties unaffected by low-molecular-weight additives or absorbed gases and which has insignificant monomer or low-molecular-weight polymerization or cure products after cure.

Interplanetary Radiation and Particle Impingement

Interplanetary radiation and particle impingement are not normally a problem with polymeric systems used for atmospheric probes. Since radiation penetration is seldom more than several monolayers, the outer surfaces of the heat shield, structure, and subunit container boxes are not affected at all. Only radiation-resistant materials chosen from extensive literature review are used in these locations. The probability of particle impingement is very low, and even so, preliminary tests of micrometeorite impingement upon some of the more likely heat shield candidates for Mars entry [20]

Table 3. Micro- and Macro- VCM Tests on Specially Treated Silicone Elastomers

Material	Treatment	Micro- VCM [18]			Macro- VCM [19]								
		Sample location			Hours of exposure at 125°C and 10 ⁻⁶ Torr								
		Surface	Center core	24	48	96	330	Wt loss, VCM, %	Wt loss, VCM, %	Wt loss, VCM, %	Wt loss, VCM, %	Wt loss, VCM, %	Wt loss, VCM, %
E691-22E	As received	0.19	0.06	0.18	0.03	0.08	0.01	0.11	0.02	0.10	0.01	0.19	0.03
(Specially processed Sylgard 184)	24 hr/150°C/10 ⁻⁶ Torr	0.19	0.06	0.19	0.06								
	24 hr/232°C/10 ⁻⁶ Torr	0.11	0.03	0.17	0.06								
Sylgard 184	As received	1.30	0.65	1.36	0.68								
	24 hr/150°C/10 ⁻⁶ Torr	0.85	0.39	1.09	0.55	0.36	0.15	0.47	0.18	0.58	0.18	0.97	0.23
	24 hr/232°C/10 ⁻⁶ Torr	0.43	0.24	0.93	0.53								
93-002	As received	2.96	0.52	2.98	0.44								
(High phenyl)	24 hr/150°C/10 ⁻⁶ Torr	0.95	0.14	1.55	0.41	0.84	0.03	0.98	0.20	1.08	0.23	1.22	0.16
	24 hr/232°C/10 ⁻⁶ Torr	0.42	0.06	1.15	0.32								
XR-63492	As received	1.86	0.61	1.95	0.62								
(Experimental low temperature)	24 hr/150°C/10 ⁻⁶ Torr	0.99	0.40	1.47	0.28	0.57	0.16	0.69	0.18	0.90	0.22	1.15	0.27
	24 hr/232°C/10 ⁻⁶ Torr	0.47	0.12	0.51	0.50								

have shown little problem. The presence of a metallic sterilization canister surrounding the probe for most of the transit time reduces the problem even more.

Cold Vibration

During motor burn for midcourse guidance and injection into orbit, an atmospheric probe is subjected to a certain amount of vibration and acoustic load. There are no data on the magnitude of these loads and no ground tests have been devised to account for their existence. The problem of these loads, however, is not their relative magnitude compared with launch vibrations, since they are certainly relatively small. It is, rather, that the entire vehicle is cold, so that local brittle failure under much smaller stresses is possible. The problem is accentuated with atmospheric probes, for the entire heat shield structure may be made from low-conductivity plastics and for the most part will be remote from any electronic heat source. Since the cold vibration environment is not defined, and since no conservative ground tests have yet been devised, polymers with as low a brittle-transition temperature as possible must be used in ways which reduce the possibility of brittle failure. Cold effects are discussed in some detail in the next section.

Entry Loads

During entry into the atmospheres of Mars or Venus, a probe vehicle is subjected to a distributed pressure load from the aerodynamic deceleration. Typical Mars and Venus stagnation pressure pulses are shown in Fig. 4. The heat shield and structure are flexed by these loads. Cracking, delamination, or catastrophic brittle failure of the heat shield, structure, or bond line between the two depends on the relative magnitudes of the actual and design loads, on the compatibility of the local temperature with the design loads, and on the magnitude of the fabrication anomalies. The important problem in this discussion is the effects of the local temperature on brittleness.

In a joint JPL-NASA/Langley Research Center effort, a contract was granted to Southern Research Institute (SoRI) to investigate cold flexure problems in heat shield materials for Mars entry [8]. In this test, the specimens were pretreated progressively, in one chamber, with ETO surface decontamination, dry heat sterilization, and high vacuum exposure at less than 10^{-7} Torr at about 67°C to simulate longer times at lower temperatures;

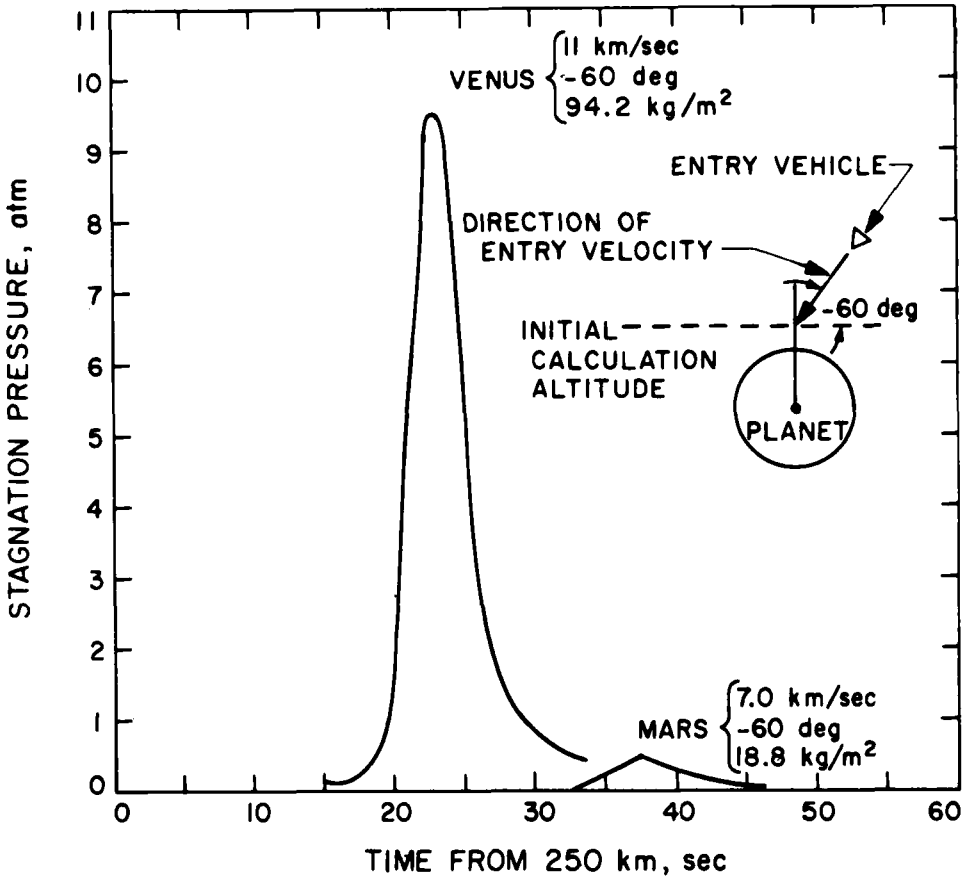


Fig. 4. Typical Mars and Venus stagnation pressure pulses.

then, while still in the vacuum, they were flexed at room temperature, -73 , -101 , and -129°C . Some of the results of this program are shown in Table 4. Each measurement represents about five replicates. The specimens were flexed using the ASTM D797-64 test adapted to a vacuum system.

A number of conclusions can be tentatively drawn from the test data. Because of the VCM criteria mentioned earlier, none of the materials except Teflon can be flown on a Mars mission. The foamed materials of the General Electric Company (GE) appear good here, but actual VCM tests showed them to be more than 1% volatile and more than 0.1% recondensable, and insufficiently improved by a rather severe vacuum-thermal pretreatment.

The silicone elastomers could probably be cleaned up by use of the new "tailless" elastomer mentioned earlier. Investigations are needed to determine the source of the volatiles in the other resin systems and fillers. It may also be concluded that lowering the density tends to decrease brittleness. Consequently, the sterilization and flight environments tend to act beneficially because removing volatiles decreases density, which, in turn, reduces brittleness.

Foamed Teflon has the best low-temperature flexibility. Phenolic nylon, on the other hand, is probably the worst of those tested, for it was the only material to actually fail at -101°C , perhaps because of the brittleness of the nylon in vacuum. The Avco Mod 7 material, which contains a special low-temperature phenyl methyl silane, has better low-temperature flexibility than the Mod 5 material, which uses a dimethyl silane base resin. The phenyl group apparently prevents or lessens local crystallization when there is only one phenyl group to approximately every 19 methyl groups. At higher phenyl contents, the resin may become even more brittle than the original dimethyl polymer. Gradual replacement of the phenolic microsphere filler with cork, as shown in the progression of Mod 5 to Mod 20 to the 893 material, improves the low-temperature performance but not as much as lowering the density does. Replacing some of the silicone elastomer base resin with epoxy (AMG 6 vs. Mod 5) does not degrade the low-temperature performance, despite the basic brittleness of the epoxy material. In fact, even in a brittle, epoxy-based material, brittleness can be reduced significantly by lowering the density (e.g., the two Avco 5026 materials, Table 4).

The ideal Mars-entry heat shield material, from this kind of information, would seem first to be Teflon, and then a clean, low-density, elastomeric material with irregular side chains. The performance of each of these polymers in an ablation environment is discussed in the next section. This work at SoRI is only a first screening. Further work using this test concept is planned to expand the number of Mars heat shield candidates tested, to define in detail the better materials from the earlier study, and to take a first look at Venus heat shield materials.

The problem of the heat shield can not be fully separated from the basic load-carrying structure. It is the load-carrying structure that limits, for the most part, the flexure which the heat shield must undergo. Also, the adhesive joint between the structure and the heat shield contributes to the problem. Through a contract with Rohr Corporation, JPL is investigating the various alternate structures for a Mars entry mission [21]. Here, because of the weight minimization requirement mentioned earlier, "minimum

Table 4. Flexure Tests on Mars-Entry Heat Shield

Material	Base resin	Form	Density, g/cm ³
GE 1004 AP	Silicone	Foamed	0.50
GE 1004 X		Foamed	0.35
McDonnell B47RF		Syntactic foam (glass)	0.39
McDonnell B45RF		Foam	0.60
Martin SLA-561		Cork-filled	0.19
AVCO Mod 5		Syntactic foam (phenolic)	0.72
AVCO Mod 7		Syntactic foam (phenolic)	0.73
AVCO Mod 20		Cork-filled	0.69
AVCO 893	Silicone	Cork-filled	0.44
AVCO 5026-39	Epoxy	Syntactic foam (phenolic)	0.61
AVCO 5026-99	Epoxy	Syntactic foam (phenolic glass)	0.39
AVCO Teflon 1	Tetrafluoroethylene	Foamed	0.77
AVCO Teflon 2	Tetrafluoroethylene	Foamed	0.55
Boeing Carborazole	Carborazole	Foamed	0.56
NASA AMG 6	Epoxy silicone	Syntactic foam (phenolic)	0.61
NASA phenolic nylon	Phenolic	Syntactic foam (phenolic)	0.59

Materials after Exposure to Transit Environment

Modulus of elasticity, psi $\times 10^3$								
Before exposure				After exposure				Wt loss, %
Room temperature	-73°C	-101°C	-129°C	Room temperature	-73°C	-101°C	-129°C	
<10	<10	28	86	<10	<10	<10	66	0.64
<10	<10	16	77	<10	14	<10	27	0.86
<10	<10	21	106	<10	<10	<10	53	2.26
<10	62	133	343	<10	20	113	246	1.58
<10	<10	<10	22	<10	<10	<10	24	3.03
<10	108	162	328	21	45	110	-	1.92
12	21	47	304	18	23	35	-	2.78
<10	39	74	188	<10	18	51	105	1.78
<10	44	46	89	<10	33	53	-	2.12
-	228	260	291	43	208	173	221	2.14
-	93	100	113	35	70	91	96	3.39
<10	23	40	56	<10	23	32	55	0.01
<10	<10	<10	10	<10	<10	<10	16	0.02
<10	113	132	159	<10	109	119	136	7.21
<10	49	88	198	<10	54	68	82	2.49
-	176	177	194	130	123	145	167	0.73

gauge" becomes important. Minimum gauge is the lightest structure that can be fabricated in any given configuration. Fiberglass and aluminum honeycombs have been compared for minimum gauge fabricability, high- and low-temperature properties, vacuum performance, sterilization effects, and interaction with candidate heat shield materials. This activity has led to the making of more reproducible structures from fiberglass. Phenolics and polyimides have been chosen over polyesters and epoxies because of the latter's short-time performance at 317°C, the design maximum-bond-line temperature for entry thermal performance. Sterilization was shown to improve all design mechanical properties in phenolics; and no decrease in flatwise tension (adhesive-determined) and flexure (laminate-determined) was shown during in situ vacuum tests. As the need increases, for structures that are resistant to higher temperatures, such as those of Venus entry, cleaner, higher-temperature "B" stage laminating resins are needed.

Honeycomb-sandwich adhesives are another area which needs study. Years of using metallic honeycombs have caused the industry to rely heavily on supported film adhesives. For metallic honeycomb sandwich, there is good reason to use supported film adhesives. For fiberglass honeycomb sandwich, the supported film adhesive gives less bond strength (i.e., poorer filing) than does the unsupported film. The support fabric is just excess weight without function. The Rohr activity has shown that 4-mil epoxy adhesives give just as good a bond as thicker versions. Phenolic and polyimide adhesives do not appear to be available in unsupported film in weights actually comparable to the 4-mil epoxy. This use of support fabric, then, gives a weight penalty of about a pound on a 6½-ft fiberglass entry vehicle, to provide the short-time 317°F performance of which the available epoxy is not capable. The Rohr activity [21] answers many questions and defines a sort of state-of-the-art, but it also opens many doors for new polymer requirements.

Once the heat shield and structure are reasonably optimized, some indication of their combined performance, while they are bonded together, is necessary. For Mars entry, a combined test similar to that shown in Fig. 5 is planned at JPL. In such a facility the heat shield structure composite can be sterilized, exposed to a vacuum, flexed under a distributed differential pressure, and heat-loaded with radiant lamps simulating the actual heat to the surface after blocking by the evolved gases. Only under such a combined environment test is bond integrity really ensured.

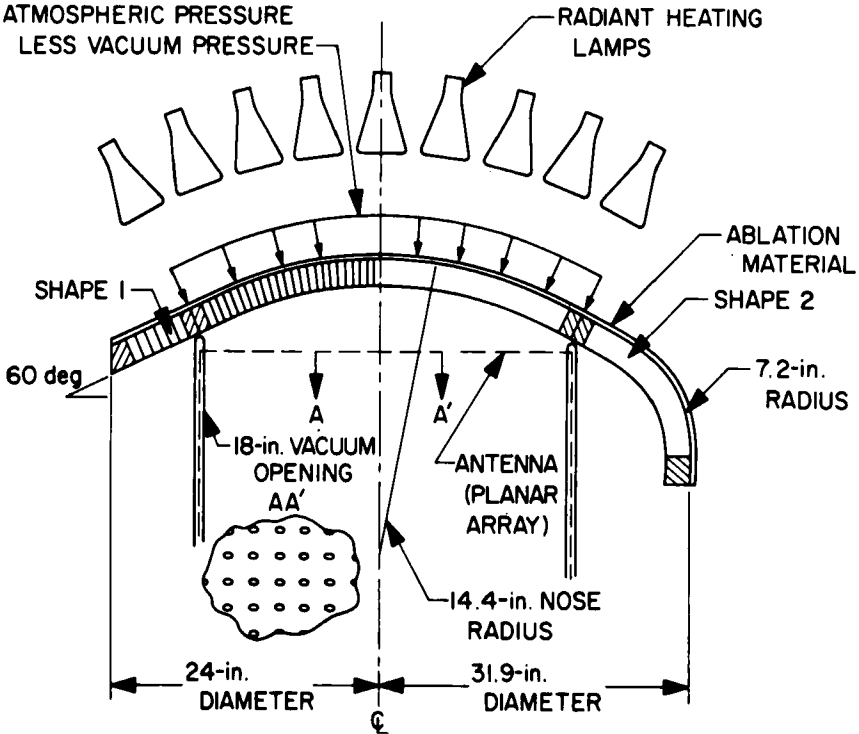


Fig. 5. Tests proposed for small, doubly curved test models of lightweight resin-fiberglass honeycomb-sandwich planetary-entry structures.

Entry Heating

During entry into a planetary atmosphere, velocity is converted into heat near the surface of the entering body. Typical peak heating conditions for entry into Mars and Venus are shown in Table 5. For Mars these heating rates and pressures are very mild, so mild, in fact, that it is possible to simulate the full magnitude and shape of the convective heating pulse, the radiative heating pulse, and the pressure pulse simultaneously with the actual assumed atmospheric composition. Such a pulsing capability is being set up at JPL now [22]. Entry into the Venus atmosphere is not so easy to simulate. The light vehicle case in Table 5 is designed to use Apollo heat shield technology and is well within available data except that convective heating,

Table 5. Typical Peak Conditions for Entry into the Atmospheres of Mars and Venus

Parameter	Symbol	Entry mission			
		Mars, out-of-orbit entry 60° cone	Mars, direct entry 60° cone	Venus, direct entry heavy vehicle 51.5° cone	Venus, direct entry light vehicle 60° cone
Ballistic coefficient, kg/m ²	Δ	31.4	18.8	18.8	18.8
Initial entry velocity, km/sec	VE	4.9	7.0	11.0	11.0
Initial entry angle, deg	γ_E	-16	-60	-60	-60
Inverse scale height, km ⁻¹	β	0.199	0.071	0.142	0.128
Peak stagnation point pressure, atm	P_s	0.1	0.48	0.17	4.50
Peak stagnation point heating, cal/cm ² sec	q _c q _r	11 5	76 34	34 3	923 126
Total stagnation point heating, cal/cm ²	Q _c Q _r	300 407	325 17	456 18	3887 292
Peak edge heating, cal/cm ² sec	q _c q _r	3 1	19 14	8 5	236 367
					169 170
					69 187
					239 239
					1210 194
					1910 239

radiative heating, and pressure have never been simulated at the same time. The so-called heavy Venus vehicle (it is still about a factor of 5 lighter per unit area than the successful Russian probe) is not within the capabilities of our present test facilities except that it is close enough that the available extrapolation techniques are considered adequate. Available earth flight-test data are also inadequate, first because of the difference in combustion heating in the two atmospheres and second because of the differences in thermo-mechanical loading.

Some of the materials being investigated for the four missions shown in Table 5 are described in Table 6. Although the major components of each of these materials can be found by inspection, specific formulation, processing, and fabrication techniques are normally proprietary. Differences in the different manufacturers' products under the same base system may be in the specific resin, the percentage of resin to filler, the relative magnitudes of the different fillers, small amounts of additives, variations in the density, and variations in the specific processing technique. Any or all of these can make drastic differences in the ablation performance for any specific mission.

Ablation is essentially energy absorption through the sacrificial loss of material. The major energy inputs and energy absorption processes in Mars and Venus entry are listed in Table 7. These can be broken down into four major modes of ablation for a charring ablator, as shown schematically in Fig. 6. This figure represents an exaggerated example of the kinds of sudden changes in the mode of ablation which can take place at particular combinations of heating rate and pressure. In the first mode, at low heating rates an ablator degrades internally but with a gradual char buildup and no front-surface recession. In the second mode, oxidative or sublimation removal of the front surface is superimposed upon the internal degradation of the first mode. For some materials, this mode can be broken down into submodes of ablation. As heating rate and pressure increase, actual transitions are measurable as ablation transfers from a reaction-rate-limited combustion process to a diffusion-rate-limited combustion process to a sublimation-rate-limited process. Other materials undergo one or the other, but not all, of these submodes; and still others are complicated by a liquid surface layer caused by glassy fillers and the silica-producing main chain from the silicone elastomer resin. For convenience, they are grouped here as one thermochemical mode of surface ablation, with Arrhenius functions as the single most common method of curve fitting to the available data.

The third mode of ablation involves thermomechanical removal of the char caused by a summation of the various superimposed stress

Table 6. Ablative Composites for Mars and Venus Entry

Resin	Major fillers	Available forms	Typical manufacturers and designations
Tetrafluoroethylene		Foamed	AVCO
Polycarbonate		Foamed	Ames
Nitrile rubber	Glass fibers	Foamed	Boeing Carborazole
Silicone elastomer	Glass fibers	Foamed	GE ESM 1004AP, GE ESM 1004X, McDonnell B45RF
	Glass fibers, glass microballoons	Molded, sprayed	McDonnell B47RF, Martin ESA 220
	Glass fibers, glass microballoons, cork	Molded,	Martin SLA 561, AVCO Mod 20
	Glass fibers, glass microballoons, phenolic microballoons	Molded, sprayed, rolled	AVCO Mod 5, AVCO Mod 7, Langley E4A1
	Glass fibers, glass microballoons, nylon powder	Molded	Langley MV65
	Glass fibers, cork	Molded	AVCO 893
Silicone elastomer	Carbon fibers	Molded	Martin ESA 5500
Phenolic-silicone elastomer	Phenolic microballoons	Molded	Langley E6A7
Epoxy-silicone elastomer	Glass fibers	Foamed	GE ESM 1030
Epoxy	Glass fibers, phenolic microballoons	Molded	AVCO 5026-39
Epoxy	Glass fibers, phenolic microballoons, glass microballoons	Molded	AVCO 5026-99
Phenolic	Nylon	Molded	Hughes, Ames, Langley
	Nylon, phenolic microballoons	Molded	Hughes, Ames, Langley
	Nomex	Molded	Ames
Phenolic	Carbon fibers or cloth	Molded	AVCO 6300, GE CP 109, Martin FM5065
Polyimide	Carbon fibers or cloth	Molded	Narmco
Diphenyl oxide	Carbon fibers	Molded	Ames

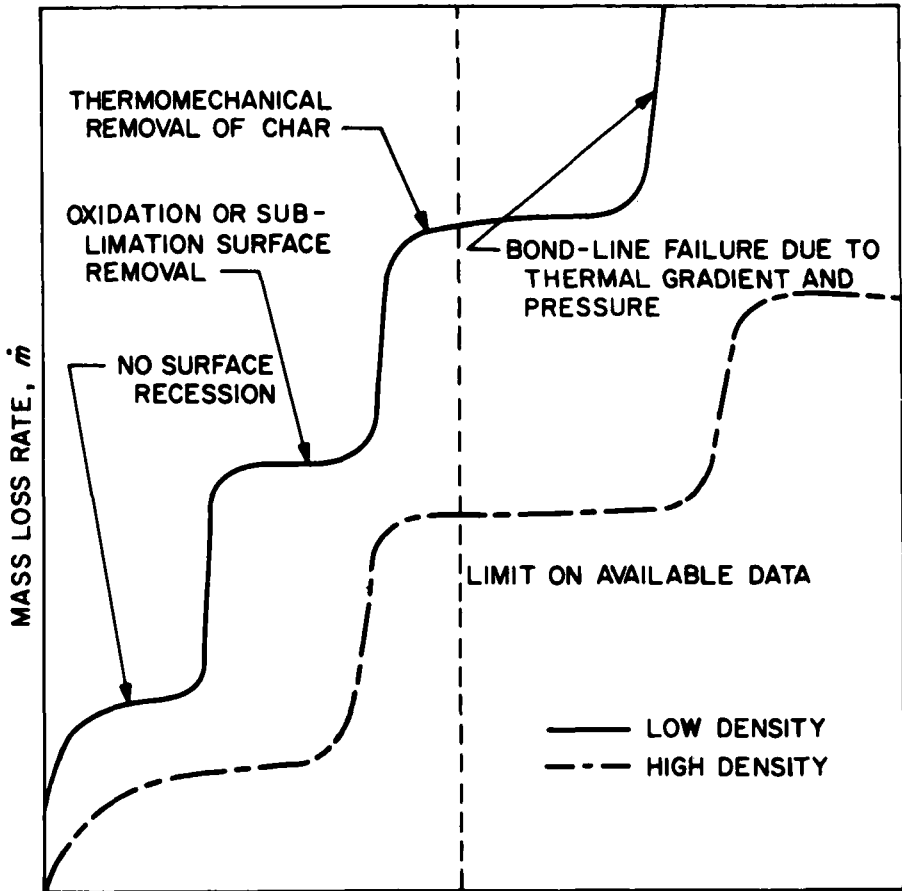
Table 7. Energy Balance for the Ablation Process

Energy inputs	Energy absorption processes
Convective heating	Gaseous blocking
Radiative heating	Surface reradiation
Combustion heating	Endothermic chemical reaction
Pressure forces	Phase change
Exothermic chemical reactions	Specific energy
	Conduction
	Thermomechanical removal
	Mass transfer

environments. These include thermal stresses caused by the temperature gradient across the specimen, internal pressure stresses caused by the confined evolution of gases at the internal degradation boundary or region, externally applied pressure stresses caused by the compressive forces and bending forces from the shock layer pressure, and shear forces caused by the motion of the external gases along the body. Stresses caused by vibration are also possible, but are, at this point, uncalculable. This mode of ablation has been identified in ground tests for some materials [23] so that reasonable limits might be set on the environments for which these materials are considered useful. For higher-density materials there are insufficient data to set realistic limits.

The fourth mode of ablation consists of catastrophic failure of the un-ablated material that comes from internal delamination or bond line failures. In this mode, prestresses during cure, thermal expansion mismatches, ablator thermal gradients, and external pressure and shear combine to locally disintegrate the ablator-structure bond and then peel the ablator off the vehicle.

Entry into Mars from out of orbit is so mild that most of the materials of interest ablate in the first mode only. Thus, insulation rather than ablation becomes the most important function of the heat shield material. The insulation capabilities of several classes of ablation materials of interest for Mars out-of-orbit entry are shown in Fig. 7. These data were taken at Ames Research Center for JPL [24] and were later extended at Langley Research Center [25]. In these tests, back-face temperatures were monitored on specimens exposed to several typical heating rates.



f (HEATING RATES, PRESSURE), $f(\dot{q}_c, \dot{q}_r, p_s)$

Fig. 6. Changes in mode of ablation for a charring ablator.

From Fig. 7, it is fairly clear that low density is desirable to minimize conductance and, therefore, improve insulation efficiency. By extrapolating material densities to lower values than those of the materials tested, an estimation of the maximum insulation capability of a particular class of composites can be made. Teflon foam lines are drawn to provide standards for comparison. Teflon foam seemed to be the most efficient material for its weight, but at the time of these tests it could not be made homogeneously in densities lower than those shown. In these samples, the void structure is

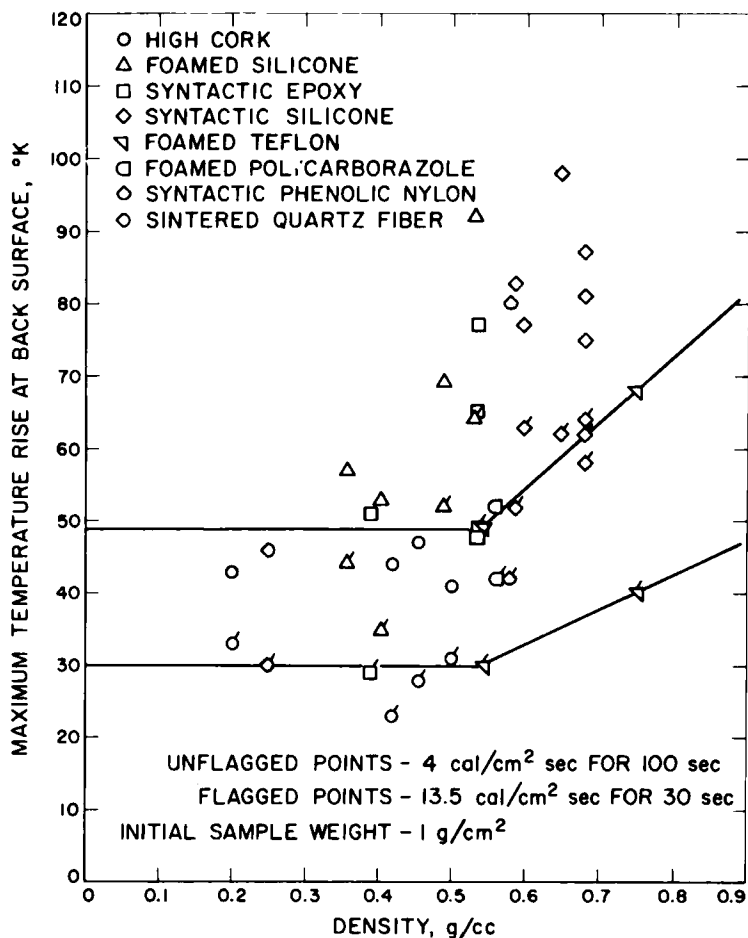


Fig. 7. The effect of density on the insulation capability of various candidate material systems for out-of-orbit entry into Mars.

so fine and even that it can barely be seen with the naked eye. Because of this, effort is being expended to make both a lower-density Teflon and a low-density, high-temperature polycarbonate material with even lower conductivity. Cork-filled materials also appear promising. Cork provides a very low conductance owing to the fact that it consists of essentially unconnected hollow polygons on the microlevel. Foamed silicone elastomers also look promising if lower densities can be achieved. This has been accomplished

by replacing some of the silicone resin with epoxy resin (see Table 6). Several other materials are also competitive, provided that lower densities can be achieved. Langley Research Center tested several of these materials for radio frequency (rf) transparency before and after ablation [25]. Of the materials tested, only Teflon allows sufficient communication through the heat shield for a radar altimeter capability. Several of the other materials look promising, with modifications to reduce retention of carbonaceous char, but the results are inconclusive at this time.

The slightly higher heating rates of direct entry into Mars require materials of somewhat different makeup. Good insulative properties are also very important, but now significant front-surface recession due to CO_2 oxidation can be measured in the lowest-density materials. Thus, compromises must be made between good carbonaceous char-retention characteristics and low density. Teflon-like materials are no longer acceptable. Silicone elastomers perform better with slightly higher densities and phenolic microballoon filler, or with limited replacement by phenolic or epoxy resins, as outlined in Table 6. Langley E4A1, Langley E6A7, AVCO 5026-39, and low-density phenolic nylon (described in Table 6) are being tested at Ames and Langley Research Centers as a first cut at defining the response of typical candidate ablation materials to the anticipated Mars direct-entry environment. The test conditions are shown in Fig. 8.

Exact simulation of the expected direct-entry environment is not possible on one facility, as suggested for out-of-orbit entry. Either heating-rate enthalpy or heating-rate pressure can be simulated, but only for special conditions can both be simulated (see the flagged conditions in Fig. 8). The dotted lines represent high- and low-entry-angle trajectory limits for a specific Mariner Mars mission. The regions marked out by solid lines represent the test capabilities of various Ames and Langley ablation test facilities for the available exit nozzles and specimen configurations. As many tests as possible will be run in various combinations of CO_2 and N_2 to determine the CO_2 combustion response of the four initial materials. From these tests, a more realistic set of evaluation environments will be chosen, and additional materials incorporating lower densities, other forms of char structure, and varying types and amounts of filler will be tested to optimize the overall insulation-ablation balance.

Venus entry provides a different kind of challenge, in that many of the more interesting entry missions skirt the maximum capability of our ground test capability. The major problem in Venus entry is that ablation modes 3 and 4 (from Fig. 6) now come into play. At some combination of heating rate and pressure the mechanical strength of the material or its char is exceeded, and significant increases in ablation rate take place, usually in a

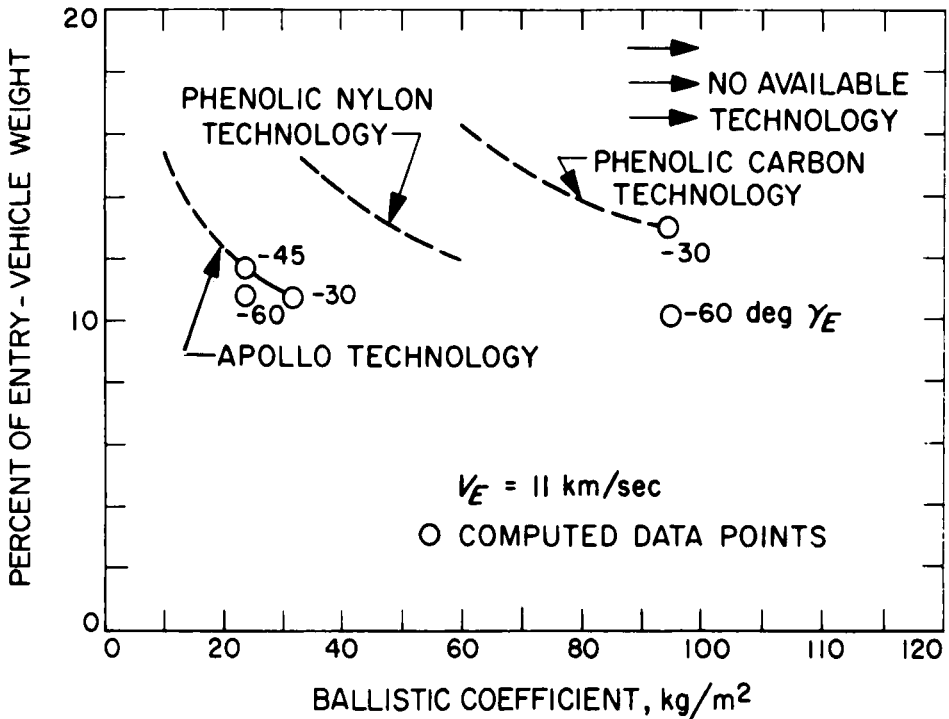


Fig. 8. Test condition for Mars direct-entry simulation.

sawtooth manner. For a Venus mission, there is some combination of entry angle, entry velocity, ballistic coefficient, and atmospheric density gradient at which these pressure and heating-rate limits are exceeded for a particular material system. At this point, either a new material system must be found for the more severe conditions or the mission must be constrained to less severe entry conditions.

An example of the transfer from material system to material system is shown in Fig. 9. For a fixed initial-entry velocity of 11 km/sec, a lowering of the ballistic coefficient increases the per cent of heat shield needed because of an increase in the duration of the entry pulse. This increase in duration effectively increases the total heat to the body despite decreases in the maximum heating rates. For carbon-phenolic there are no available ground-test data to confirm or deny suitability of the material for ballistic coefficients greater than about 95 kg/m^2 , when the initial entry velocity is 11 km/sec and the initial entry angle is greater than -60° . More severe

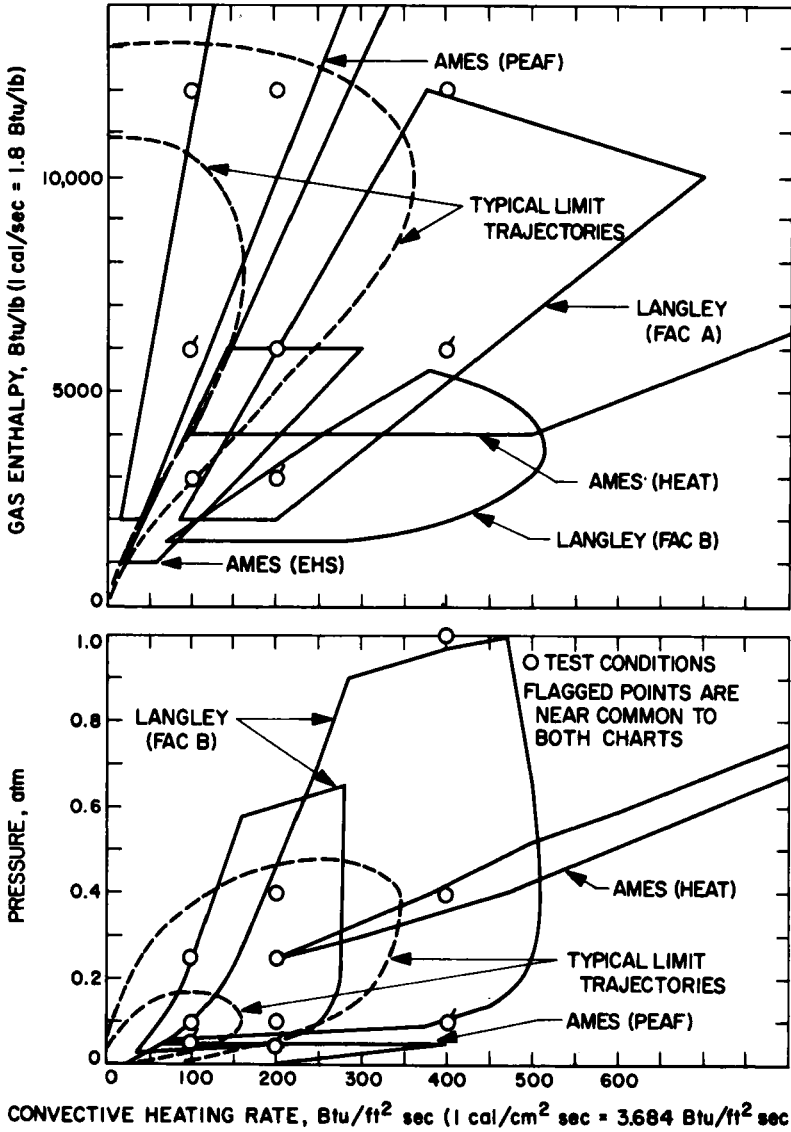


Fig. 9. Effect of ballistic parameter on heat shield weight for a Venus mission.

flight-test data are available but interpretation is difficult. Taking the -60° angle as a technology limit, the heat shield thickness is determined by the lower limit of the entry angle (in this case -30°) owing to the greater total heat to the surface from the wider heat pulse. If ballistic coefficients were decreased, carbon-phenolic requirements would increase as the heat pulse broadens and the total heat to the surface increases. At some combination of heating rate and pressure, phenolic nylon (high density) and Apollo material technology regimes become available, and less material is needed since a reduction in char strength can now be traded off against increased gas evolution per unit original mass and increased insulative efficiency. Similar curves could be drawn to compare the effects of initial-entry velocity and initial-entry angle on the heat shield weight requirements for the nominal heavy vehicle mission listed in Table 4. The phenolic-nylon technology regime is entered at an initial-entry angle of about -20° . The vehicle skips out before the Apollo material becomes apropos. Velocities below about 9.2 km/sec allow phenolic-nylon technology, and below about 8 km/sec, Apollo technology.

For a Venus mission there are two ways to extend the technology limits illustrated in Fig. 9. One method is to generate new ablation data at such severe conditions that the actual limits on existing polymeric-based heat shield composites can be determined. To do this, new test facilities with greater capacity, using new concepts (such as, perhaps, a laser), will have to be developed. Another method entails tailoring new resin systems and composites to the specific problem. Ideally, this would mean a resin which leaves all its carbon behind but evolves reasonable quantities of low-molecular-weight gases. Such a resin would have to be semilinear with a predominantly aromatic ring structure. A step in this direction is the diphenyl oxide system being worked on at Ames.

An idealized ablative material system is a clean, high-temperature, polymeric-based composite with good low-density insulative properties, no char at low heating rates, and a strong char at high heating rates. There are a number of ways of achieving most of these items, or at least the most important ones, for each specific mission, but the major problem is still a lack of polymer reproducibility and control at the producer's level. Much of the data on ablative materials available throughout the country are useless because no one can remake that specific material or even approximate it closely enough to reproduce the original data.

Descent

Descent problems center around three areas: supplementary drag devices, payload insulation from Venusian ambient conditions, and scientific data-taking. The two major supplementary drag devices are retrorocket systems and parachutes. Retrorockets provide several major problems. Not only do polymeric components such as solid propellants, nozzles, liners, antennas, etc., need to resist sterilization treatment and transit conditions, but supplementary radar-altimeter control devices must either look around or through rf-transparent heat shield. As discussed in the last section, rf transparency is not particularly compatible with ablation efficiency. Teflon, some filled silanes, and some as-yet-unmade thermoplastics appear to provide the most promise.

Lightweight parachutes were investigated some years ago [26]. Silk and rayon degrade when sterilized. Nylon becomes brittle in a vacuum and snaps apart during the opening loads. Dacron (polyethylene terephthalate) and Nomex prove adequate solutions, but only Dacron is, so far, manufactured in fine enough fiber sizes to allow the required minimization of weight for a particular design. The same discussion applies to ballutes and balloons.

Insulating the payload during Venus descent is a new problem which has not yet been solved. Surface temperatures of 536°C are difficult for electronic payload survival. One possible solution is an insulated, evacuated chamber—evacuated to reduce convective heat transfer, insulated to reduce conductive heat transfer. The usual ceramic foam or powder is much too heavy, partly because a container is needed to hold the powder in place. Most of the very low-density, low-conductivity polymeric foams such as polystyrene or polyurethane are not compatible with the expected temperature excursions. The foaming concepts are applicable to higher-temperature materials but have not yet been applied in usable quantities.

The taking of scientific data is affected by the polymer used in the heat shield only if there has been migration of recondensables to lenses or if ablation products obscure radiometer readings of shock layer radiation. In all of these descent problems, work has only just begun in understanding the real interaction between the plastic and the environment.

Impact

Impact need be mentioned only briefly. Polymeric materials appear to

make the best impact absorbers. Most of the work up to now has been done with balsa wood [27]. Balsa wood, like nylon, has its properties affected by the presence of water. The problems of humidity control and reproducibility have led to consideration of other solutions. So far, no foams with properties better than those of balsa wood have been developed. Much effort is now being made to develop new kinds of honeycomb-sandwich composites, which appear to be superior to balsa wood if the unidirectional problem can be met [28].

Landed Experiments

Landed experiments provide a whole new class of problems that lie outside the scope of this paper. Not only do they have to survive all the environments from sterilization, to flight, to planet surface, but they carry an entire set of polymer compatibility problems in the biological experiments of interest. Some real examples include (a) a plastic vacuum cleaner with an inlet hose only 1/4 in. in diam but necessarily 100 ft long, to get out of the touchdown area; (b) a New Year's Eve party toy which rolls out flat 100 ft, attracts dust and bacteria by an electrostatic charge between the flat sides, then rolls back to return the bacteria for testing; (c) a new class of lightweight tires, designed to go over jeep terrain, but only one-quarter the weight of normal tires.

SUMMARY

The ideal polymeric material for an interplanetary spacecraft or atmospheric probe is a reproducible, homogeneous, high-temperature plastic with good low-temperature flexibility or strength, low volatile content including low recondensables, and a small number of reactive sites after cure. Numerous basic polymeric structures are capable of meeting these criteria, provided special care is taken in formulating them to minimize unreacted or unreactive additives and to eliminate low-molecular-weight products of the polymerization process. Very few commercial products meet these criteria, primarily because the volume sales are in less exotic fields. The new problems of planetary exploration require either that the polymer science community instigate a new class of truly space-grade materials, or that NASA, in protection of the taxpayers' dollars and the lives of astronauts, do it for them at some loss to the commercial community. The production of

improved methods to obtain the necessary design data on these materials is an adjunct to this problem.

Present data indicate that specially processed, low-density, phenyl methyl silicone elastomers with no low-molecular-weight "tail" provide the best base resin for Mars-entry heat shields. These materials are unaffected or improved by exposure to ETO surface decontamination, dry heat sterilization, and interplanetary vacuum. Their low- and high-temperature strength is adequate for all entry flexure and vibration environments, and the low-density versions provide the best insulation capability for the mild heating conditions of Mars entry. The lack of char buildup also allows for rf transparency during descent into the tenuous atmosphere. Phenolic fiberglass load-carrying structures act as a high strength-to-weight compliment to the ablative shield.

Venus entry is not sufficiently well understood to choose a particular polymeric system except in a general fashion. The same general environmental problems face a Venus probe, except that during the entry process the material must be a very high-efficiency ablator with a strong, thick, char and extremely-high-temperature resistance. Such polymers may be available, but they have not been characterized sufficiently to allow immediate use.

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