

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Ablative Degradation of a Silicone Foam

Thomas McKeon^a

^a Missile and Space Division Re-Entry Systems, Materials Laboratory Operation Valley Forge Space Technology Center, General Electric Company, Philadelphia, Pennsylvania

To cite this Article McKeon, Thomas(1969) 'Ablative Degradation of a Silicone Foam', Journal of Macromolecular Science, Part A, 3: 4, 585 — 612

To link to this Article: DOI: 10.1080/10601326908053831

URL: <http://dx.doi.org/10.1080/10601326908053831>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ablative Degradation of a Silicone Foam

THOMAS McKEON

General Electric Company

Missile and Space Division

Re-Entry Systems, Materials Laboratory Operation

Valley Forge Space Technology Center

Philadelphia, Pennsylvania

SUMMARY

The ablative degradation performance of elastomeric shield materials is interpreted in terms of a hypothesis based upon the study of the ablation residue which is correlated to seven parameters.

INTRODUCTION

A hypothesis has been developed which permits the understanding of the ablative degradation performance of elastomeric shield materials (ESM) under a variety of conditions. This general understanding is basic to the efficient design of thermal shield systems employing ESM and to the accurate prediction of flight performance. ESM's are a generic class of foamed, low-density re-entry thermal protection formulations based on room-temperature condensation curing silicone elastomers and containing iron oxide, silica, and aluminum silicate fillers.

The development of this hypothesis was based upon the study of the ablation residue, which included the following areas: (a) possible chemical reaction paths, (b) theoretical thermodynamic heats of reaction, (c) visual, microscopic, and photographic studies, (d) overall density profiles, (e) compositional change profiles, (f) solid-phase specific-gravity profiles, (g) porosity profiles, (h) internal pressure development.

REACTION PATHS

The possible paths by which the base silicone elastomer in the foam formulation (RTV 560)[†] may degrade are summarized in Fig. 1. The following generalizations may be made: (a) In the absence of oxygen at relatively low temperatures, only the volatile cyclic species will be formed.

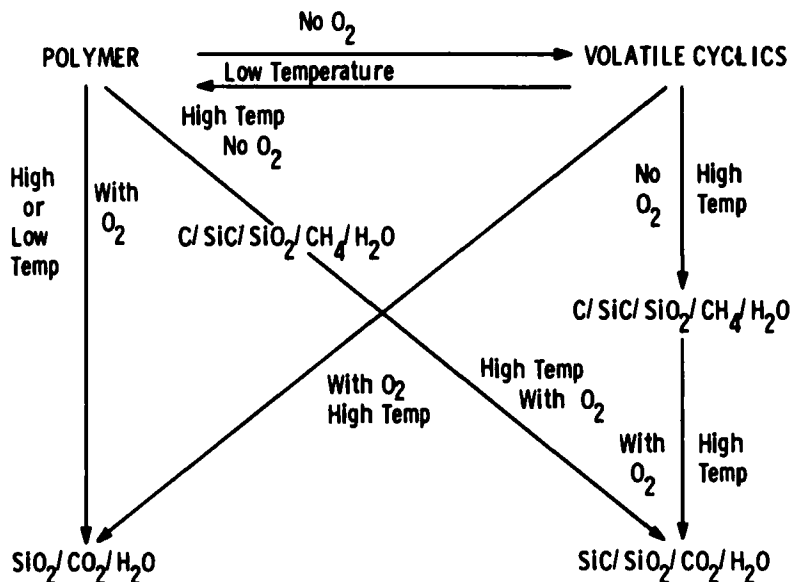


Fig. 1. Silicone polymer degradation.

These cyclic species are reversion or depolymerization products and this process is reversible. (b) In the absence of oxygen but at higher temperatures, there will be some irreversible degradation to the mixture of inorganic residues and hydrocarbon gases as well as some reversion products. (c) In the presence of oxygen at both high and low temperatures only the combustive reactions will be evident. No carbide would be formed, only silicon dioxide, carbon dioxide, and water. (d) The volatile cyclics will behave similarly to the base polymer in the presence of oxygen. (e) The volatile cyclics in the absence of oxygen could theoretically produce carbide and carbon in a manner similar to the base polymer. (f) If the

[†]General Electric Company's RTV 560, a methyl-phenyl polysiloxane condensation polymer.

carbide-carbon-silica mixture once formed is then exposed to oxygen, a partial combustion could take place, leaving the refractory carbide and the already oxidized silica.

The formation of hydrocarbon mixture and hydrogen during the thermal degradation of ESM has been confirmed. The various species have been demonstrated to be present in the off-gases of isothermal decompositions run over the temperature range of 780-2675°F. Amounts and ratios within the series were shown, by use of vapor phase chromatography, to vary with temperature.

The reversible formation of volatile cyclics would be affected by the ambient pressures on the system. Since it is an equilibration, the equilibrium will be shifted by the removal of one of the products, as by volatilization in this case. At the reduced pressures of typical flight conditions, the rate of removal of volatile species would be far greater than for tests run at 1-atm pressure. Consequently, ablation under reduced pressures would favor the removal of the volatiles from a primary degradation zone at such a rate that their secondary reactions would occur much closer to the surface than in the case of the reactions at atmospheric pressure.

Ferric oxide is used as the filler in the base elastomer, RTV 560. Any reactions that it may take part in or influence may play a significant role in the overall ablation process of ESM. Some of the potential reactions of the ferric oxide are illustrated in Fig. 2. The possible reduction of ferric to ferrous oxide can be accomplished by reaction with carbon, hydrogen, or hydrocarbons. The reduction with carbon is typical of what may occur in a blast furnace, starting at temperatures as low as 600°F. Reduction with hydrogen is similarly a known reaction, starting at 300-500°F. The reduction with hydrocarbons, as illustrated by methane, ethane, and propane, has been demonstrated in the laboratory. The reaction takes place at roughly 900-1000°F with an instantaneous change from red to jet black. This change is irreversible and also occurred when the vapors of decomposing silicone elastomer were passed over ferric oxide in the same temperature range. It appears highly probably that the color change associated with the line of demarcation of virgin ESM and the primary degradation zone is directly related to the formation of ferrous oxide.

The formation of ferrous oxide may be of considerable significance to the development of the mechanical integrity of the nonvolatile residue from the ablation process. The principal significance is probably related to the reaction with silica to form ferrous silicate. The ferrous silicate produced has a melting point (2156°F) lower than any other combination predictable from the composition of the foam formulation.

If any oxygen is present in the depth of the ablating foam, it is possible that the subsequent reoxidation of freshly formed ferrous oxide to ferric oxide will have a major detrimental effect on the development of the mechanical structure of the degradation residue.

If the ferrous oxide does have a high affinity for silicon dioxide, then there may exist a related affinity for the oxygen-silicon-oxygen sequence as it exists in the polymer and in the volatile cyclic siloxanes produced in the primary degradation zone. If this is the case, it may be reasonable to postulate that the freshly formed ferrous oxide could be a catalyst, or promoter, for the chemical cracking of these species to form carbide, silica, and hydrocarbons. This latter possibility would be highly desirable since it would support both the development of a mechanically stable residue and the development of a low-molecular-weight off-gas.

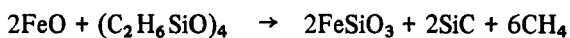
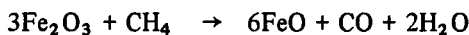
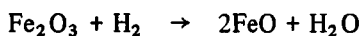
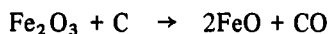
ESM has been evaluated in a differential scanning calorimeter by tests in air and in nitrogen. In the absence of oxygen, only an endothermic process is observed up to the temperature limit of the instrument, 900°F. In the presence of oxygen, there is the apparent onset of an exothermic process at 500°F.

HEATS OF REACTION

The specific degradation path will have a significant effect on the overall thermodynamic balance of the ablation process. This will be affected by the presence of oxygen as well as by the balance between the reversible and irreversible modes of degradation. The reversible reversion process which produces the cyclics is highly undesirable from several standpoints. First, the molecular weight of the volatiles is extremely high, and the volatiles do not provide efficient blocking, or transpiration cooling, action. Second, the formation of the cyclics involves the breaking of silicon-oxygen bonds in the polymer chains and the remaking of silicon-oxygen bonds in the cyclic species. Thermodynamically, this process is essentially neutral. The theoretical heats of reactions are summarized in Fig. 2.

The combustive process is highly exothermic to the extent of liberating 10 times as much heat as the endothermic processes could possibly absorb. It is significant to recognize that the heat of oxidation for even a small portion of the material would completely offset any endothermic reactions taking place. These comparisons hold only for the heats of reaction and do not factor in any effects of blocking action and transpiration cooling.

Possible iron oxide reactions



Theoretical heats of reactions

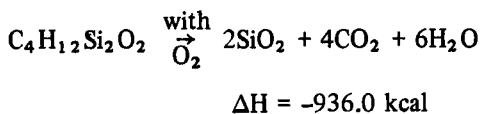
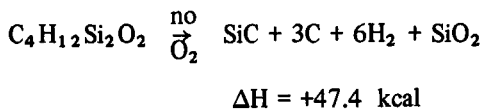
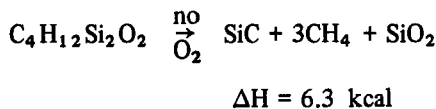
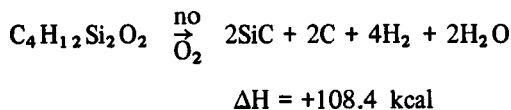
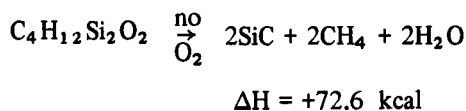


Fig. 2. Iron oxide reactions and theoretical heats of reaction of siloxanes.

VISUAL EXAMINATION

Examination at low magnification (Fig. 3) clearly illustrates the dramatic change in both cell size and orientation from the virgin ESM to the degraded material. The change is both large and abrupt, as is the color change.

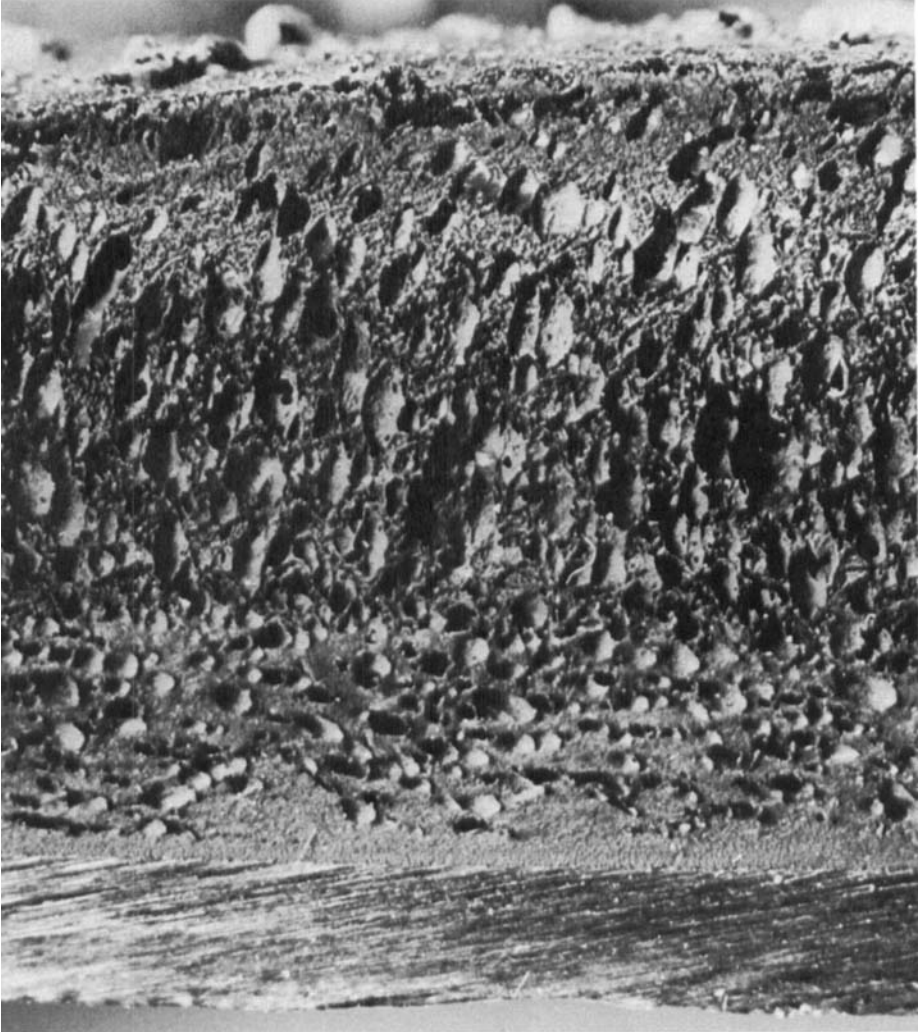


Fig. 3. Cross-sectional view of silicone foam ablative degradation residue (tested at atmospheric pressure at 20-40 Btu/ft²/sec).

Several changes in structure take place through the thickness of the sample: (a) There does not appear to be a structural discontinuity at the interface between virgin material and the primary degradation zone. (b) In the center portion there is an area of very large cell structure and minimum solid phase. (c) Closer to the surface there is the suggestion of densification having occurred. (d) There is the suggestion of a very thin crust of the immediate surface which may have achieved the molten state. (e) Color changes associated with the densification close to the surface suggest the deposition of material, including carbon. (f) Of the original 0.25-in. thickness, 0.125 in. remains undegraded. Therefore, that portion which degraded has expanded over 100% in thickness.

The general appearance of the material in this cross section shows that a ballooning expansion must occur and that it begins at, or very close to, the interface between virgin and degraded material. A very sharp or abrupt color change from red to black or brown-black also occurs at this same line of demarcation.

DENSITY PROFILE

The overall density profile through the thickness of the degradation residue has been determined on a number of ablation samples. These samples include models tested under a variety of conditions. The overall density is an average number accounting for both solid phase and cellular space. In Fig. 4, the structural interface is at the left and the ablating surface is at the right. There is a rapid drop in the overall density in the zone immediately adjacent to the undegraded material. This zone, which is recognizable by color, is considered to be the area where the first degradation reactions are initiated and is defined as the primary degradation zone. The transition from the virgin material to the primary degradation zone is very clearly marked by the abrupt change in color from red of the ferric oxide filler to a very intense black. This primary degradation zone is marked by both the rapid initial drop in overall density and the minimum density that is observed throughout the thickness of the degradation residue. Closer to the ablation surface, the overall density gradually increases until at the immediate surface the density can be in excess of the original density of the ESM.

The model used as the basis of Fig. 4 was tested at atmospheric pressure. The presence of a similar profile but the absence of the expansion in other models (see Fig. 5) tested at reduced pressures strongly suggests

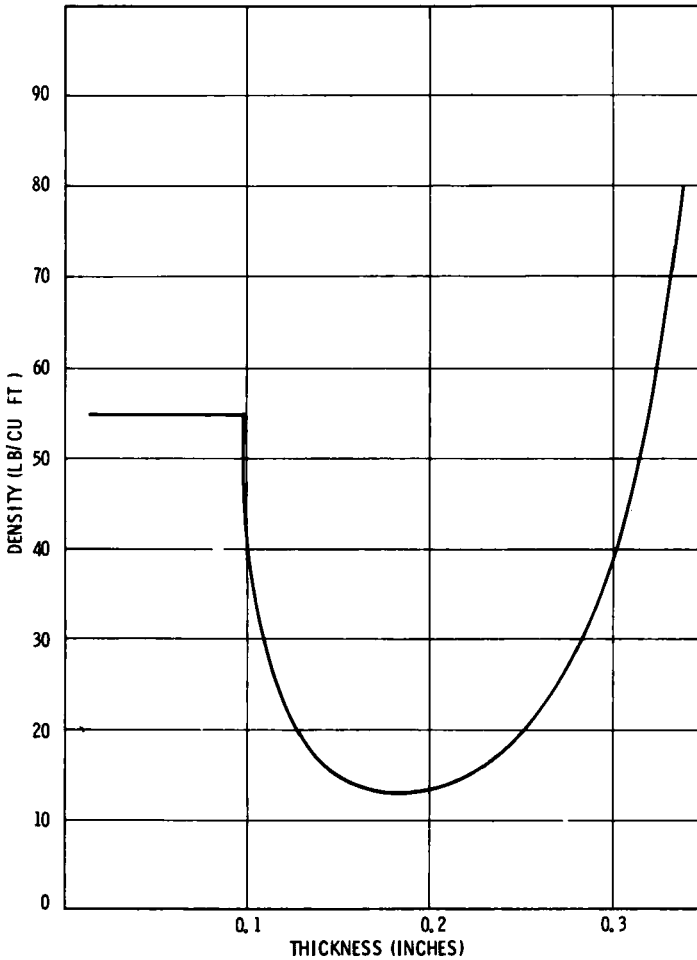


Fig. 4. Overall density profile of 55-lb-density foam tested at atmospheric pressure.

that more than one process is operable, and that the balance between the several processes varies with test conditions.

During very short runs, only the drop in density associated with a primary degradation zone would be observed. As test times increase, the development of the area of minimum density would become discernible. As the times increase even further, the minimum density area, or primary

degradation zone, will gradually migrate to greater depth in the material. Then the layers of higher density, or secondary reactions, will continue to develop further (Fig. 6).

The general shape of the density profiles suggests that either a ballooning expansion or a loss of material by volatilization, or both, occurs in the primary degradation zone. The subsequent densification nearer to the surface suggests the possibility of chemical cracking, of any volatile species produced in the primary degradation zone, to produce nonvolatile solids.

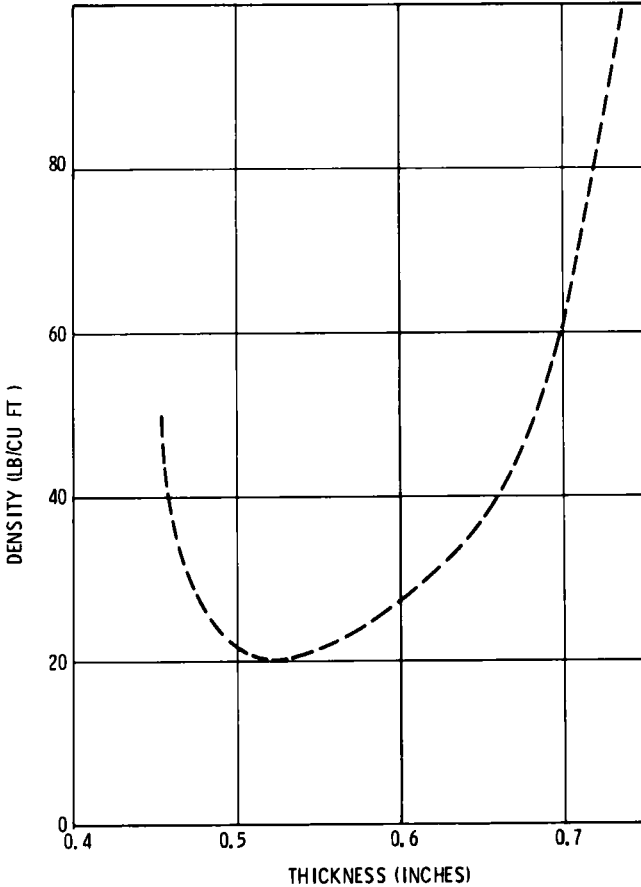


Fig. 5. Overall density profile of 55-lb-density foam tested at reduced pressure.

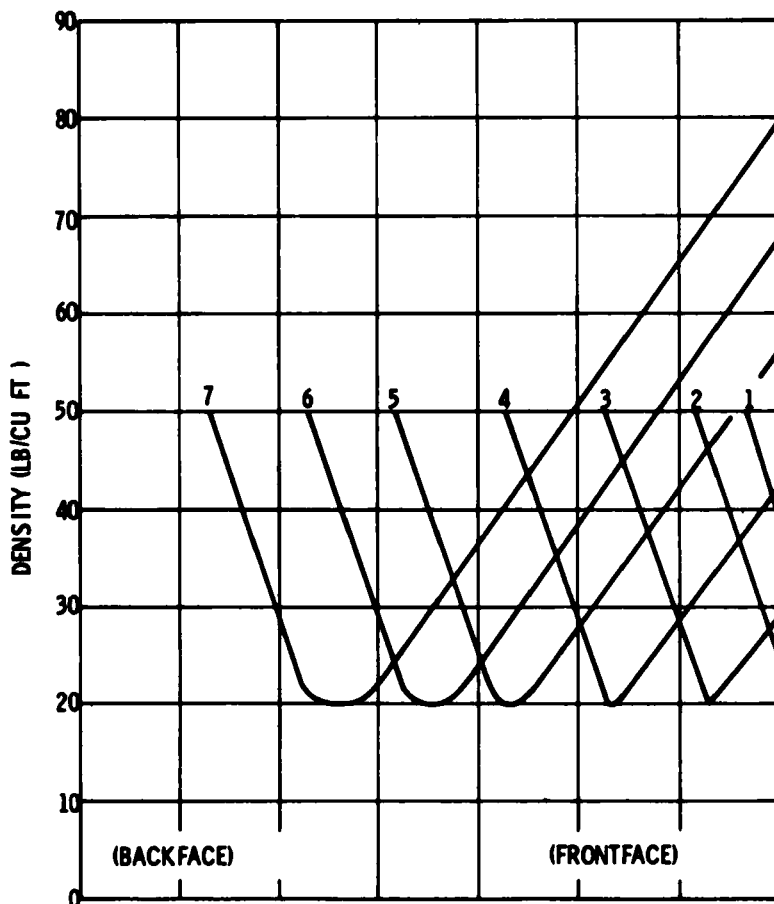


Fig. 6. Overall density profile vs. test time.

COMPOSITIONAL CHANGES

Elemental analyses have been made on sequential thin layers through the degradation residue. The analyses performed included carbon, hydrogen, silicon, iron, and aluminum, as well as identification of carbon as carbide.

The presence of silicon carbide has been confirmed by X-ray analyses. It is found in the depth of material close to the primary degradation zone as well as nearer to the surface. The appearance in depth strongly suggests

that the carbide is formed by a direct decomposition of the silicones and not from a subsequent reaction of carbon and silicon dioxide.

In the ablative degradation of ESM occurring in the depth of the material, the iron contained in the formulation is considered to contribute only to the solid phase of the degradation products and not at all to the volatile phase. Advantage has been taken of this fact to evaluate the changes in atomic ratio through the degradation layers. Theoretically, if all of the species present contributed only to the nonvolatile phase, then the ratio of one element to another would remain constant. This is illustrated by the constancy of the ratio of iron to aluminum as plotted in Fig. 7.

If however, specific elements contribute to both the volatile and non-volatile phases, then the ratios will change as the degradation proceeds. The actual variation in iron content through the degradation layers is presented in Fig. 8.

The very abrupt change in concentration in the area of the primary degradation zone directly reinforces the comments made in the section on solid-phase density profiles. The increase in density is clearly related to the increased amount of iron in the primary degradation zone.

Figure 9 shows a typical plot of the variations in atomic ratio of silicon to iron through the degradation residue. The portion of the silicon used for this calculation is corrected to reflect only that which comes from the polymer and not that which comes from the silicon dioxide filler. As with the previous graphs, the undegraded material is at the left and the ablation surface is at the right.

A pronounced change is observed between the undegraded material and the primary degradation zone. The ratio of silicon to iron drops very rapidly. This drop in ratio strongly suggests that a distillative process occurs in the primary degradation zone.

In all probability this would be illustrated by the reversion processes (Fig. 10) producing the volatile cyclic species. These cyclics, once formed, would rapidly distill and/or diffuse from the primary degradation zone toward the surface (particularly at reduced pressures).

Ratio of silicon to iron increases closer to the surface and this change suggests that the cyclic species that have distilled from the primary degradation zone are now undergoing a chemical cracking, i.e., a further degradation. As it nears the surface, the ratio, in fact, exceeds that of virgin material. This gradual increase when approaching the surface (approaching the higher-temperature regimes) would reflect the chemical cracking to form silicon carbide, more silicon dioxide, and

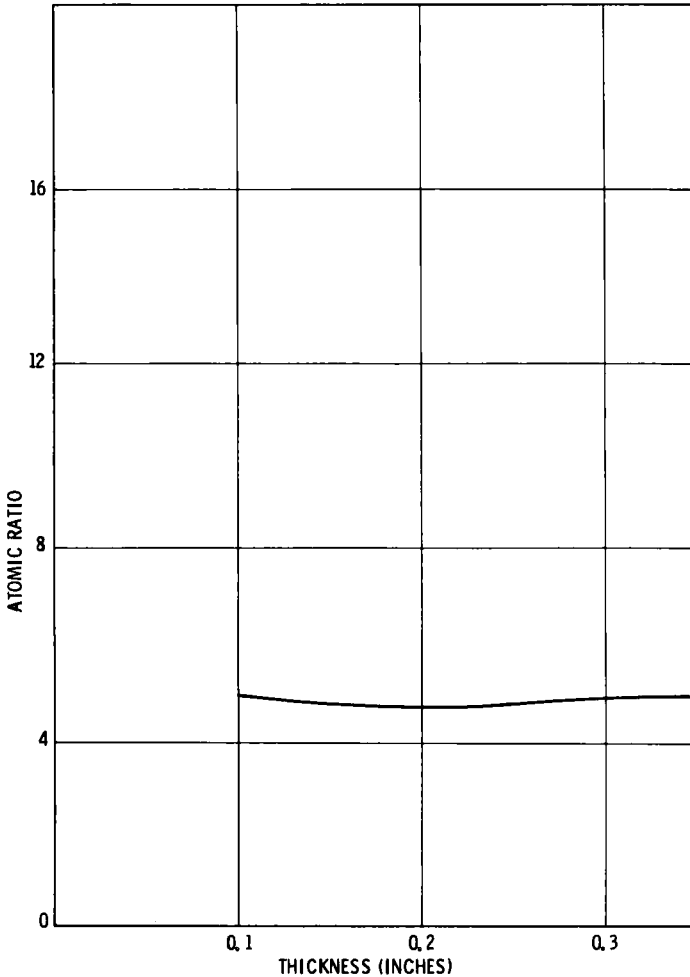


Fig. 7. Iron aluminum ratio vs. thickness.

possibly carbon. Figure 11 illustrates the changing ratio of carbon to silicon through the degradation residue. In this calculation, the carbon represents all carbon present since the polymer is the sole source. The silicon is corrected to show only that coming from polymer. There is a significant change in the ratio in the primary degradation zone. However, compared with the change in the silicon/iron ratio, this change is small. The silicon/iron ratio would reflect the extent of the reversible reversion process to

produce cyclics. The change in carbon/silicon ratio would reflect the extent of the irreversible degradation to produce inorganic residue and hydrocarbons. Up to a point somewhat beyond the primary degradation zone, the carbon/silicon ratio continues to decrease. In the next short distance closer to the surface, however, the ratio increases appreciably. From this point on, it continually decreases toward the surface. The relationship of the data points suggests the possibility that they represent a combination of two reactions or mechanisms rather than one. The early portion of the curve (in the primary degradation zone) would reflect any direct decomposition of the polymer by the irreversible process to produce only the inorganic residue and hydrocarbon gases. The second portion of the curve would reflect the subsequent chemical cracking of these hydrocarbon gases and of any cyclic siloxanes to produce a mixture of carbon, silicon carbide, silicon dioxide, hydrogen, and hydrocarbons as the off-gas. A comparison

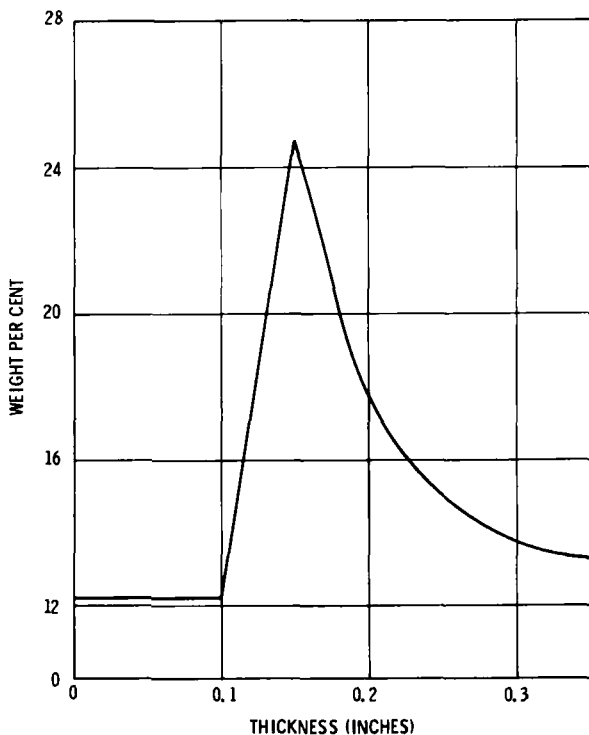


Fig. 8. Per cent iron content vs. thickness.

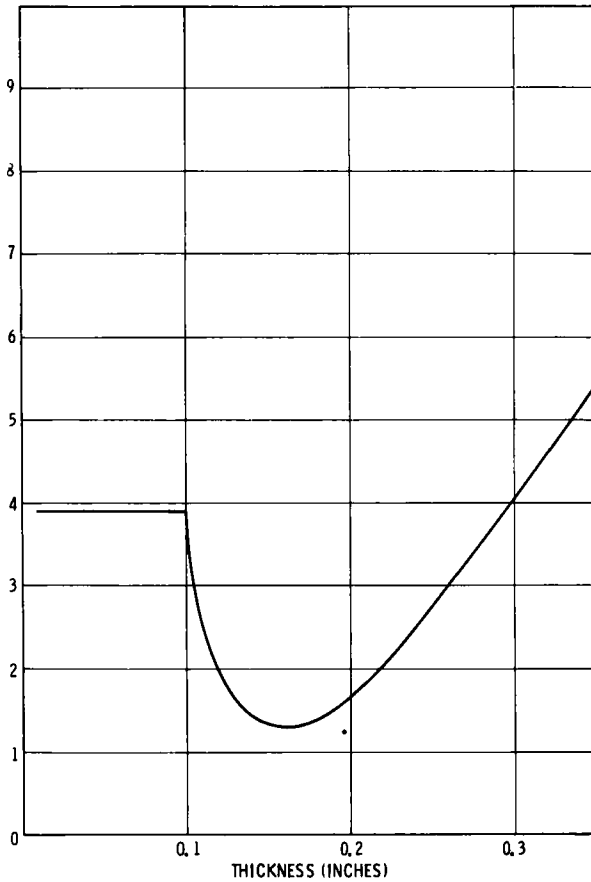


Fig. 9. Silicon (from polymer)/iron ratio vs. thickness.

of the concentrations of species in the primary degradation zone and a consideration of the changes in these two ratios suggest that in the primary degradation zone, approximately 95% of the polymeric degradation proceeds by the reversible reversion process and only 5% proceeds by the irreversible process to furnish inorganic residue.

The variation in actual total carbon content is presented in Fig. 12. The general shape of this curve also suggests the possibility of more than one mechanism being operative. The early portion of the curve would correspond to that portion of the carbon silicon ratio plot (Fig. 11) that may represent the irreversible degradation of siloxane polymer in the

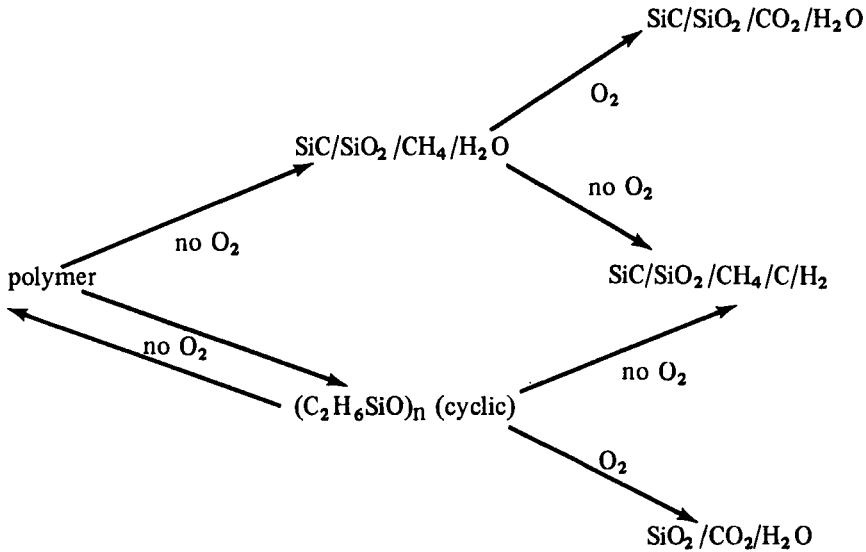


Fig. 10. Competing polymeric degradation paths.

primary degradation zone. The second portion of the curve would correspond to the portion of Fig. 11 that represents the chemical cracking of those species that were volatilized in the primary degradation zone.

Figure 13 illustrates the change in ratio of hydrogen/carbon through the degradation residue. The figures used here represent total hydrogen and total carbon since the base polymer is the sole source of both species. As would be anticipated, this ratio continually decreases toward the ablation surface. This reflects the gradually increasing amount of chemical cracking that occurs as we reach the higher-temperature regimes. In close approximation to the surface, the ratio increases again. It is conceivable that this may be explained on the basis of the base polymer being a copolymer of dimethyl and diphenyl siloxane units. During a reversion process, the non-volatile residue would gradually become enriched in the diphenyl siloxane units, as they are far more thermally stable and less volatile than the dimethyl units. The hydrogen content close to the surface could represent a residual concentration of these diphenyl siloxane units.

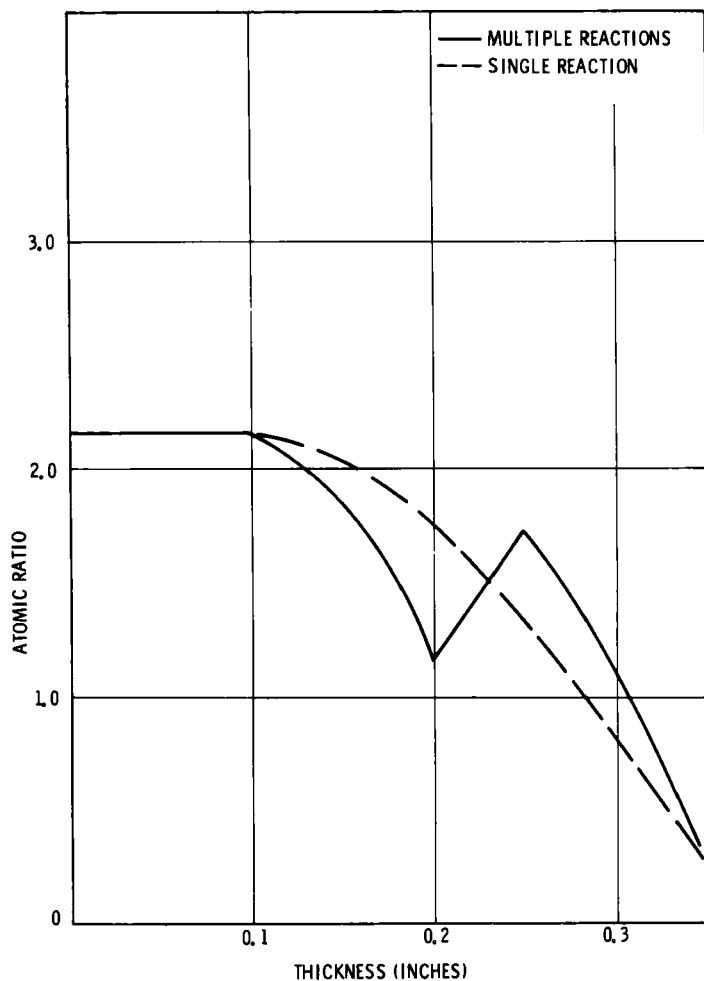


Fig. 11. Carbon (total)/silicon (from polymer) ratio vs. thickness.

SOLID-PHASE SPECIFIC GRAVITY

A typical solid-phase specific gravity profile has been determined. This profile is based on the elemental analyses described earlier. These analyses were used to approximate the molecular compositions, and from these an average specific gravity was calculated for each layer. This calculated profile is shown in Fig. 14.

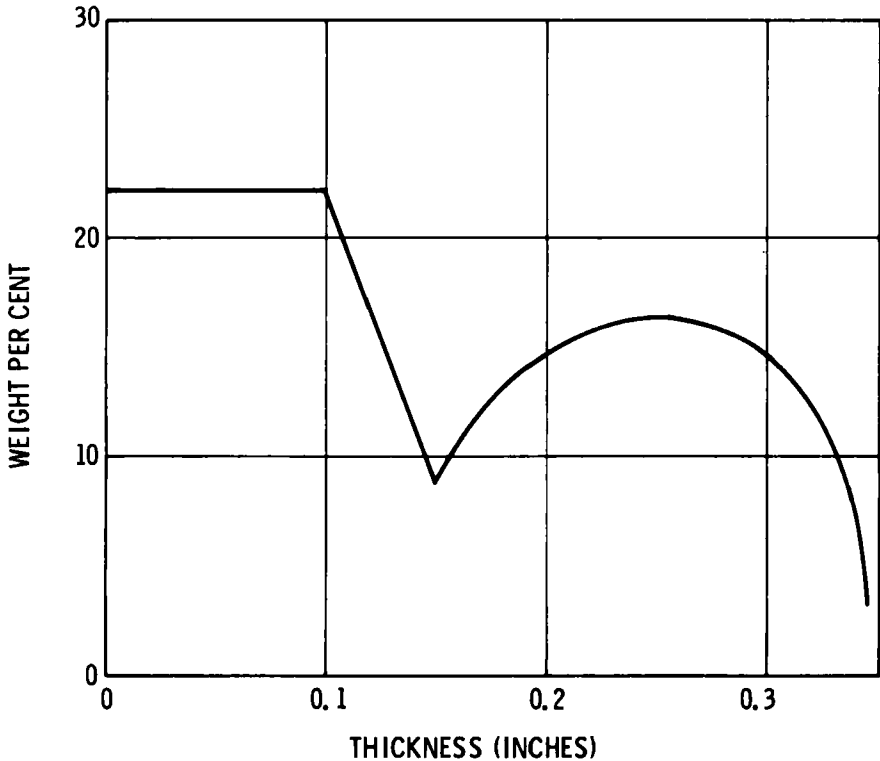


Fig. 12. Per cent carbon content vs. thickness.

The abrupt increase in specific gravity from the virgin material to the primary degradation zone is significant. The observed specific gravity of the solid phase almost doubled in a thickness of less than 50 mils. While this specific gravity is increasing, the overall density is undergoing a marked decrease. As the overall material is expanding, the solid phase is shrinking. These observations agree with the visual changes in cell structure noted previously. After this maximum, the value gradually decreases toward the surface, from 3.7 to approximately 2.9 at the immediate ablation surface. These observations agree with the prior suggestions that a volatilization of the organic species occurs in the primary degradation zone followed by a subsequent chemical cracking of these volatile species as they reach the higher-temperature regimes closer to the ablating surface. The species anticipated as being formed during this secondary cracking would include

silicon dioxide, silicon carbide, and carbon. All of these species have a significantly lower specific gravity than the iron oxides which comprise a large portion of the solid phase in the primary degradation zone.

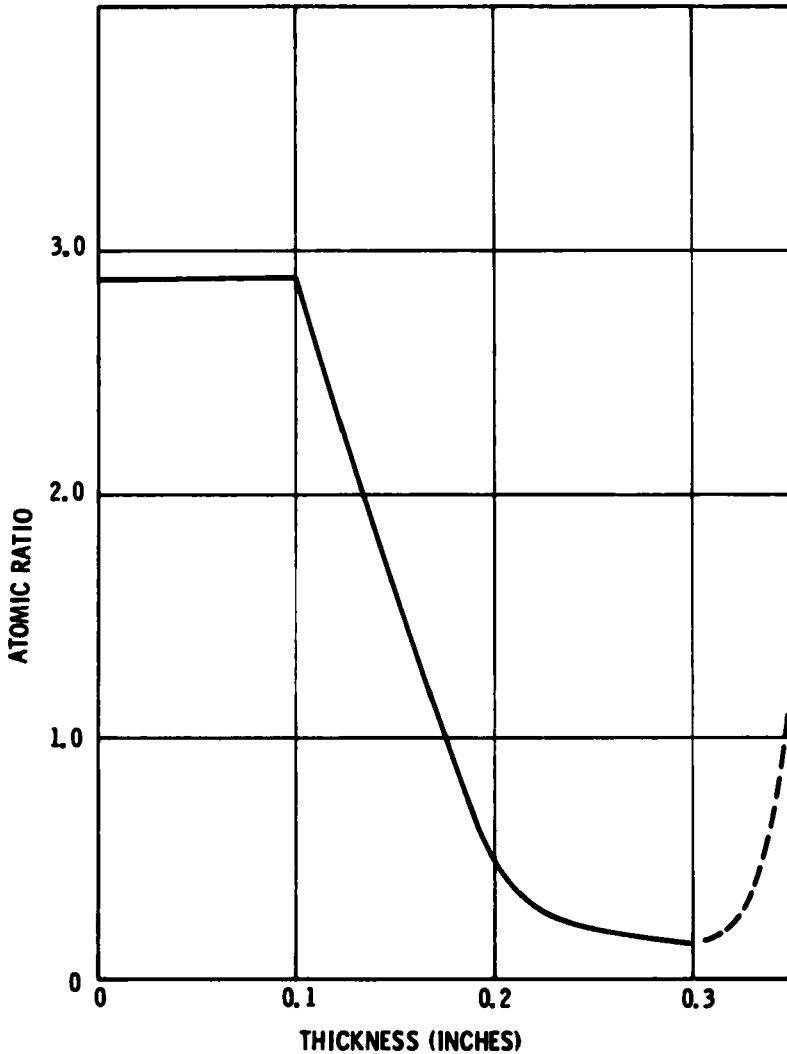


Fig. 13. Hydrogen (total)/carbon (total) ratio vs. thickness.

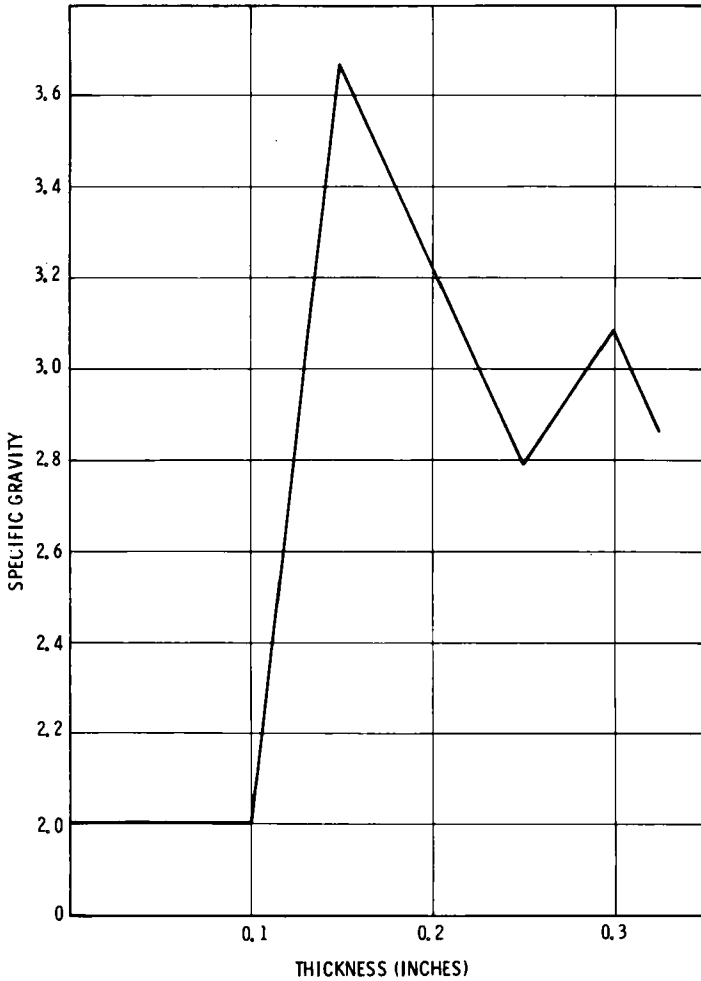


Fig. 14. Typical solid-phase specific gravity profile.

POROSITY

The overall density profile and solid-phase density profile have been combined to produce a porosity profile (Fig. 15). The most abrupt change is associated with the change from the virgin material to the primary degradation zone. At the same depth of material that corresponds to the

minimum observed overall density, the maximum porosity is 95%. Therefore, there is only a 5% solid phase remaining at this depth of material, which must hold the already ablated material and the virgin material together. This maximum porosity-minimum solid phase suggests a plane of weakness which has been, in fact, observed in earlier ESM ablation models. In line with the general observation made earlier on the cross sections, the porosity gradually decreases closer to the ablation surface.

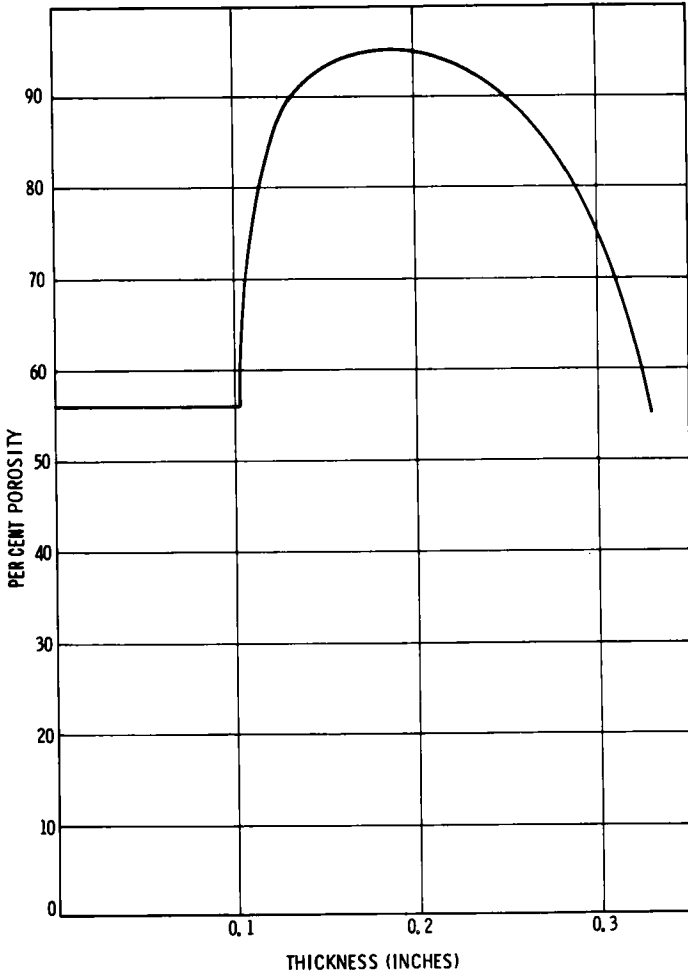


Fig. 15. Typical porosity profile.

DETERMINATION OF THEORETICAL INTERNAL PRESSURES

In an attempt to understand the driving forces involved in the overall ablative degradation of ESM, a preliminary attempt has been made to calculate the theoretical internal pressures that could develop within the cells of the ESM by the degradation process. This calculated pressure would provide an approximation of the forces attempting to cause a ballooning expansion as well as providing a measure of the forces causing diffusion of the produced volatile species. The pressures that were calculated are to be considered only as upper limits. The calculations were based on assumptions of instantaneous decomposition, of a given fraction decomposition, of a final temperature, of specific average molecular weights of gases, of specific densities of ESM, and of zero loss of products by diffusion. Figures 16-18 summarize the calculations that have been made. In Fig. 16, the internal pressure in atmospheres that could be developed during the degradation of ESM at 800°F (1260°R) is plotted against per cent degradation for densities of ESM ranging from 15-65 lb lb/ft³. This graph assumes average gaseous molecular weight of 28. It is clear from data that the initial density of ESM has a very significant effect on the theoretical pressures. It is recognized that the pressures calculated here are only the upper limits; but even if the actual developed pressures are as much as 1-2% of these values, the levels obtained will be significant.

In Fig. 17, the internal pressures are calculated at 800°F for the 55-lb-density ESM assuming molecular weight of hydrogen to be 2; carbon monoxide, 28; and a typical cyclic siloxane reversion product, 223. It is significant that even assuming only the high-molecular-weight species to be produced, the pressures still could reach a level of several atmospheres. This latter case would occur only when all of the degradation occurred by the reversion path. If any degradation occurs to produce inorganic species (irreversible process), the pressures would be greater.

Figure 18 shows the theoretical pressures for the 35-lb-density ESM at various assumed gaseous molecular weights. As previously shown in Fig. 16, the pressures here are lower than for the 55-lb-density material but are still of a significant magnitude.

A simplified calculation has been made comparing the relative pressures that might be developed within the cellular structure of the 35- versus the 55-lb-density ESM in light of the observed expansion of the two degradation residues.

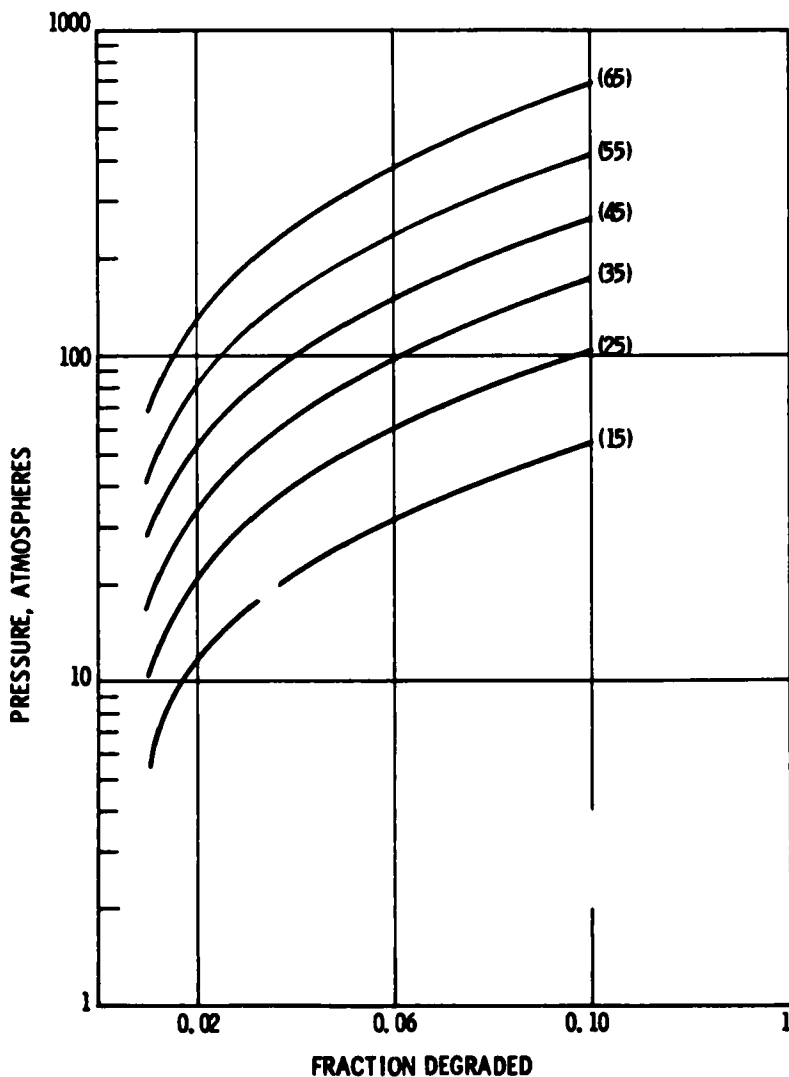


Fig. 16. Theoretical internal pressure development in ESM for degradation at 1260°R. Numbers in parentheses indicate the density of ESM in lb/ft³.

For the 55-lb material, there is: (a) 1.56 times as much polymer to produce gases, (b) 0.64 times as much air space to accept gases, and (c) 1.56 times as much polymer for gases to diffuse through to escape. Therefore:

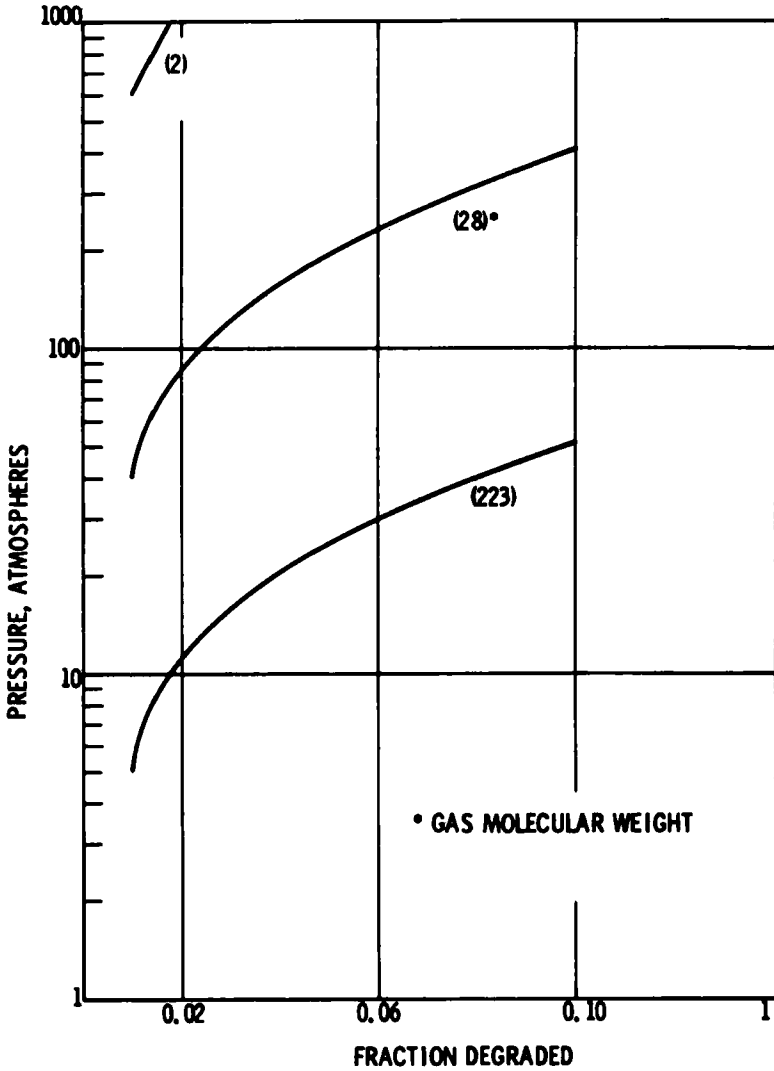


Fig. 17. Theoretical internal pressure development in 55-lb ESM with varying gaseous molecular weight.

(1) (1.56) (1/0.64) (1.56) = $P_2 = 3.8$

3.8 times greater pressure developed in the cells of the 55-lb ESM

From calculation of the expansion of the air space in the actual degradation residues, we obtain a 115% expansion for the 55-lb ESM and 34% for the 35-lb ESM for a ratio of 3.4 against the theoretical 3.8.

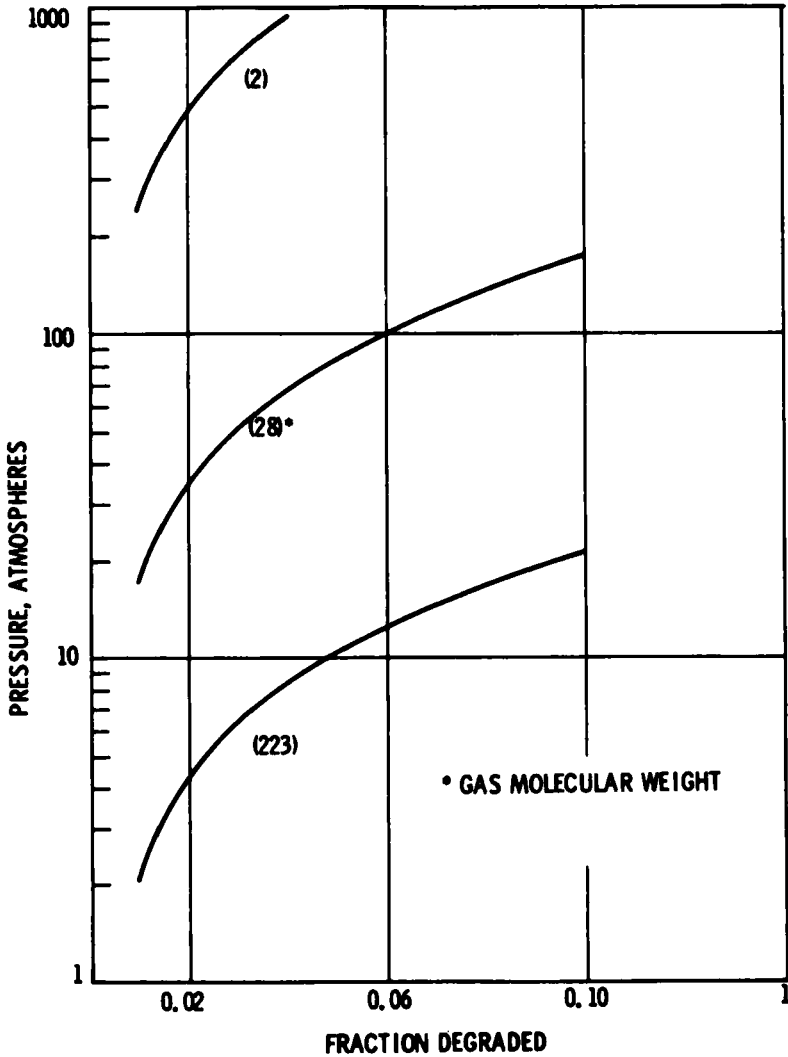


Fig. 18. Theoretical internal pressure development in 35-lb ESM with varying gaseous molecular weight.

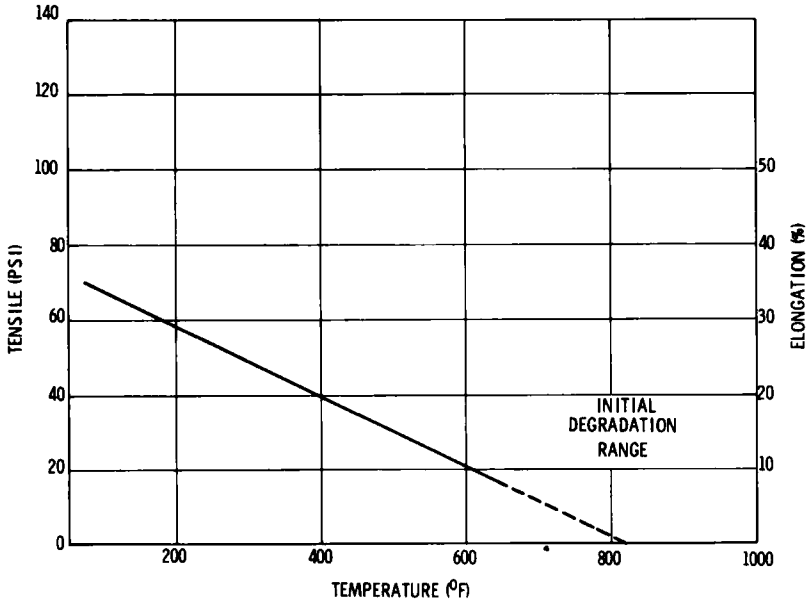


Fig. 19. Silicone foam (ESM) strength vs. temperature.

The potential ballooning expansion is also dependent on the susceptibility of the ESM to expansion. It is estimated that temperatures associated with the primary degradation zone where the expansion occurs are in the order of 800-1000°F. From the plot shown in Fig. 19, it is clear that the ESM would be quite weak and able to expand under even mild internal pressure (assuming no degradation).

HYPOTHESIZED MECHANISM

A generalized hypothesis permitting an understanding of the overall ablative degradation of ESM may be synthesized from the information obtained in this program. The significant factors to be considered are enumerated below, not necessarily in order of importance.

1. For purposes of visualization, the overall process may be likened to an emulsion inversion process. The base elastomer is the continuous phase prior to the degradation, and the additives and fillers are the discontinuous phase. During the degradation, or inversion, the polymer becomes

discontinuous, and the inorganic species, the additives and fillers, must react with each other and/or with products of the degradation to become continuous. The rates of these two reactions must at all times be in balance so that there is a continuity of mechanical structure.

2. There are two competitive degradation reactions of the base silicon elastomer. The first is the reversible depolymerization to produce only a volatile species, the cyclic siloxanes, and no solid phase. The second is the irreversible reaction to produce an inorganic residue containing silicon dioxide, silicon carbide, and possibly some carbon, as well as a gaseous phase containing hydrocarbons, hydrogen, and possibly some water.

3. The primary degradation zone has been defined as that area directly adjacent to the virgin material, clearly recognizable by the abrupt change in color from red to black, where the initial polymeric degradation reactions occur.

4. Most of the polymer in the primary degradation zone degrades by reversible depolymerization to the cyclic siloxanes. This is then followed by a rapid diffusion of the cyclics toward the surface.

5. The balance between the two competitive reactions and the rate of diffusion of the products of the primary degradation reaction from this zone are highly sensitive to the ambient pressure on the system.

6. In a porous material such as ESM, the ambient pressure on the system will have a significant effect on the rates of diffusion of volatiles from the site of their formation, and therefore on the "residence time" of these volatiles diffusing through the degradation residue. This will affect their availability for secondary reactions, as will the relative thickness and density of the residue.

7. Those factors contributing toward a slower rate of diffusion of the volatiles from the primary degradation zone will similarly contribute to the development of higher internal pressures, and therefore greater tendencies toward the ballooning expansion.

8. The cyclic siloxanes may undergo secondary reactions when exposed to the higher temperatures near the surface. These reactions will include a chemical cracking to form silicon dioxide, silicon carbide, and hydrocarbons.

9. Any silicon carbide formed during the ablative degradation is formed by direct degradation of either the base polymer or the cyclic siloxanes and not by the secondary reaction of silicon dioxide and carbon. Temperatures attained in the degradation of ESM are not sufficient to promote this latter reaction.

10. Temperatures attained, particularly in the body of the ESM, are

relatively low. Therefore, the development of a mechanically integral residue must depend on a combination of consolidation, sintering, vapor deposition, and related processes. No fusion as such occurs, except at the immediate surface.

11. The lowest predictable melting point material from the ESM formulation is a ferrous silicate (2156°F).

12. The abrupt change in color from red to black associated with the primary degradation zone is associated with the formation of ferrous oxide by reduction of ferric oxide with either hydrogen, hydrocarbons, or other species formed during the degradation.

13. The freshly formed ferrous oxide would readily react with the silicon dioxide present to form ferrous silicate. The reaction of the ferric oxide during the degradation is probably critical to the formation of a mechanically sound degradation residue.

14. The direct formation of silicon carbide from degradation of the base polymer or from the cyclic siloxanes is an endothermic process and therefore desirable. If oxygen is present, however, the carbide formation will not occur. Instead, a highly exothermic oxidative degradation will take place. The exothermicity of this reaction is sufficient to have a significant effect on the total heat delivered to the test sample.

15. The possible subsequent reactions of the carbide with silica at high temperatures, to form a mixture of volatile monoxides, is also endothermic and highly desirable.

16. At atmospheric pressure the diffusion of volatile species from the primary degradation zone is delayed sufficiently that they will contribute to an internal pressure development adequate to cause a ballooning expansion. At the temperature at which this primary degradation occurs the ESM will have diminished to minimal strength and would therefore be highly susceptible to an expansion caused by internal pressure.

17. Mechanical cracking, which occurs through the degradation residue in some models, is caused by the rapid change in both total volume and specific gravity of the solid phase in the primary degradation zone. The total amount of the solid phase is being reduced by the loss of material through depolymerization. The specific gravity of the solid phase is rapidly increasing as it becomes largely inorganic instead of organic. These changes occur at a critical time, when the phase inversion process is just beginning to develop the mechanical structure of the degradation residue. Unless the "consolidation processes" are well advanced, mechanical cracking cannot be avoided.

18. If ablation is occurring at reduced pressures, mechanical cracking

may be initiated but will be limited in character. If, however, the ablation is occurring at atmospheric pressure where the ballooning expansion occurs, then cracking will be magnified by the expanding shape change.

Accepted by editor December 24, 1968

Received for publication January 3, 1969