THE DEVELOPMENT OF POLYBENZIMIDAZOLE COMPOSITES AS ABLATIVE HEAT SHIELDS

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INTRODUCTION

Low-density (0.3 gm/cm³), char-forming polymeric composites have found application as re-entry heat shields for both orbital and lunar manned spaceflight missions (ref. 1). The low-density materials have a low thermal conductivity (ref. 2) and consequently a low heat transfer rate to the substructure (ref. 3 and 4). The carbonaceous char surfaces formed by these materials have high surface emissivities (ref. 5) and attain high surface temperatures (ref. 6 and 7). These two factors permit the char surface to reradiate large amounts of energy back into space. Thus, both low-density and char-forming capability are necessary properties for effective performance.

Materials formulated from phenolic and related polymers pyrolyze to produce stoichiometric char yields of 23 to 60 percent (ref. 8) as well as vapor species. The char layers form with appreciable volumetric shrinkage (20 to 30 percent for low-density phenolic nylon) which leads to a mechanically weak structure full of fissures and voids (ref. 9). Such chars contain an imperfect carbon lattice which may make them more susceptible than graphite to removal by surface oxidation. In addition, fissures and interconnected porosity provide internal pathways for intrusion of the hot air stream into the char layer with catastrophic effects on heat shield performance. The extent of this mode of failure increases with increasing pressure and decreasing density of a particular composite (ref. 10). Furthermore, the presence of oxygen in the virgin polymer results in oxygen-bearing vapor species being evolved during the pyrolysis process. In transpiring through the char, these vapors may react with the char, thereby removing and weakening it.

In light of the inherent deficiencies of the conventional char-forming materials (phenolic and related polymers), aromatic heterocyclic polymers are considered potentially useful for the development of new heat-shield composite materials. Such materials are attractive because of the high-temperature stability of the virgin polymer as well as the high concentration of multiply bonded aromatic ring structures needed to produce high char yields. In particular, the polybenzimidazoles (PBI) were selected for this investigation for the following reasons: (1) Prepolymer staging of the polymer permits compounding with fillers and fibers and provides a large weight fraction of volatiles (phenol and water) to form during cure. These volatiles provide the internal blowing needed to secure a low density foam structure. (2) The PBI materials have pseudo-conjugated, multiply-bonded aromatic ring structures which are potentially capable of producing high char yields. Moreover, they produce low molecular weight vapor species which are most effective in providing convective blockage by the mass-transfer effect (ref. 11). (3) The PBI materials are capable of producing a highly organized char structure with a minimum of shrinkage, good physical integrity and excellent high temperature mechanical properties. Furthermore, the chars contain interstitial nitrogen atoms which result in substantially lower thermal conductivity than graphite or carbon. (4) The PBI polymers contain no oxygen bearing functional groups to interact with the char and cause internal oxidation.

The purpose of this paper is to briefly describe the formulation of some new PBI composites and to present some preliminary results of arc-jet tests conducted on these materials. We begin with a discussion of the synthesis of the new materials and then describe the char formation process.
in these materials. Next the processing and characterization of the materials is described. Finally, the experimental procedure is described, followed by a presentation and discussion of the test results.

DESCRIPTION OF PBI MATERIALS

Prepolymers were synthesized by thermally condensing 3,3'-diamino-benzidine (I) and diphenylisophthalate (II) to give low molecular weight prepolymer resins (III) as follows:

\[
\begin{align*}
\text{O} & \quad \text{H}_2\text{N} \quad \text{NH}_2 \\
\text{C} & \quad \text{H}_2\text{N} \quad \text{O} \quad \text{NH}_2 \\
\text{O} & \quad \text{H}_2\text{N} \\
\end{align*}
\]

where \( n = 2 \) to 3.

Thermogravimetric pyrolysis of these prepolymers in helium (at a heating rate of 5°C/minute) was employed to characterize their polymerization. It was found that elimination of end groups (through evolution of phenol and water) was not complete until a temperature of at least 400°C was reached, whereupon a stable high molecular weight linear PBI was formed. From this result it was concluded that early studies of the ablation of PBI composites (ref. 12), which were found to give low char yields and high molecular weight imidazole fragments as vapor, were performed on under cured specimens.

In the present study, the PBI prepolymers of the type shown in equation 1 were first cured at a temperature of 400°C and then post cured at 800°C. The first cure cycle resulted in an essentially linear PBI polymer which was free of the easily degraded end groups. Postcuring of these linear polymers, in an inert gas environment at a heating rate of 3°C/minute, gave a tough, black solid in yields of about 85 percent. In the postcure process, the hydrogen atoms are driven off, but the heteroatoms are retained. It was concluded that when the end groups are reacted by adequate post cure, a high-temperature crosslinking reaction can occur if sufficient time, at temperatures in excess of 700°C, is allowed. The result is a thermally crosslinked structure which is similar to the three dimensional hetero network proposed by Bruck (ref. 13) for a similar pyrolysis of aromatic polyimides. The material which results from the post cure is a hydro-polybenzimidazole (pyrobenzimidazole) which has an empirical formula of \([C_{47}H_{14}N_8]_n\). It is very oxidation resistant at high temperatures, compared with the simple linear PBI; and, because of its crosslinked structure, it also resists viscous shear at high temperatures. Thus, it was expected to
perform well in a combined oxidation-shear environment. Note that the thermal crosslinking reaction is very slow, and cure times of as much as 10 hours may be required to complete the reaction. Thus, of course, the materials must be postcured prior to use as an ablative heat shield.

In addition to thermal crosslinking, the feasibility of chemically crosslinking the linear PBI was investigated. A controlled number of crosslinks were introduced into the system by using both triphenyl trimesate as a comonomer and polyfunctional amines derived from low temperature oxidation of 3,3'-diaminobenzidine. The latter crosslink site has not been completely resolved, although the material can be prepared reproducibly by the oxidation of the amine. Several structures have been proposed to account for the point branching functionality of the oxidation product, all of which require coupling of the benzidine and introduction of effective functionalities greater than two. Such structures have a number average molecular weight about double that of the monomer with a 10 percent reduction in primary amine content.

A series of PBI polymers were prepared from diphenylisophthalate and amines which were preoxidized to varying degrees. These complex materials were characterized both by amine assay and by sulfuric acid extractability of the cured polymer. The amine assay varied from 86 to 98 percent, the extent of crosslinking increased with decreasing amine assay and was accompanied by a decrease in the sol content. Both amide and arylene imidazole crosslinks may be present in the polymers (ref. 14). It will be shown that these chemically crosslinked systems perform about as well as the thermally crosslinked system in a coupled oxidation-shear environment.

Finally, a second series of chemically crosslinked PBI's was prepared by replacing part of the diphenylisophthalate with triphenyl trimesate in the polymerization with 3,3'-diaminobenzidine. At comparable crosslink density, these materials do not have the resistance to coupled shear and oxidation exhibited by both the thermally crosslinked materials and those chemically crosslinked by the preoxidized amine. It was concluded that the second type of chemical crosslinking interferes with the formation of a stable crosslink structure at high temperatures.

In summary, four types of low-density PBI composites have been evaluated in an ablation screening test program. These are (1) high molecular weight linear PBI, (2) thermally crosslinked PBI, (3) chemically crosslinked PBI obtained from preoxidized 3,3'-diaminobenzidine, and (4) chemically crosslinked PBI obtained from trimesate derivatives. Before describing the test programs and discussing the test results, the char formation process in PBI's and the chemical processing and characterization of the PBI composites will be described.

THE CHAR FORMATION PROCESS IN POLYBENZIMIDAZOLES

Examination of the thermogravimetric test results indicate that conventional PBI's yield no char when pyrolyzed in air at heating rates of 3 to 10°C/minute. Decomposition begins at 260°C and is complete (with zero char yield) at 700°C. Thus, at first inspection, we might conclude that these systems are not useful as char-forming ablative materials. Note, however, that the rapid oxidation of the linear PBI is not the oxidation of a preformed char but rather the oxidative scission of the imidazole ring at the =NH group. Thus, elimination of the =NH groups by thermal crosslinking reduces the oxidative scission reaction. The result is that the thermally crosslinked PBI's show a stability toward oxidation similar to that of graphite. That is, in thermogravimetric tests they are completely oxidized at a temperature of 1000°C.

Tests of the linear PBI's in arc-heated air streams indicate that they
can be made to form a char without oxidative scission of the polymer. The different behavior of the linear PBI's between the thermogravimetric tests and the arc-jet tests can be explained as follows. In the arc-jet tests, permeation of the oxygen species below the char surface is inhibited by the transpiration of ablation vapors and by consumption in both gas-phase and surface combustion reactions. Thus, in the absence of oxygen below the surface, char formation can occur without oxidative scission. This suggests, then, that thermogravimetric tests in an inert environment are more representative of the char-formation process in the arc-heated air stream tests than are thermogravimetric tests in air. A char yield of 85 percent at 1000°C is obtained in thermogravimetric tests of linear PBI in helium. Note, however, that this conclusion depends upon the material density and interconnected porosity. If, in the low density materials, there is insufficient polymer to provide a low concentration of interconnected porosity, the oxygen species can permeate below the surface with resultant oxidative scission. In addition to the porosity, the permeation of oxygen will also increase with increasing surface pressure.

PROCESSING AND CHARACTERIZATION

Two basic processes for the preparation of low-density PBI composites were investigated. In the first process, mixtures of unadvanced prepolymer (n=2 to 3) with advanced prepolymer (n>3) were molded at atmospheric pressure and temperatures of 260°C for 20 minutes followed by 375°C for 10 minutes. Free standing foams with densities from 0.24 to 0.61 g/cm³, depending upon the concentration of end groups, were obtained. These foams were brittle and contained many large cavities resulting from high local rates of gas evolution. These problems were eliminated in the second process by including in the formulation about 10 to 12 percent of chopped carbon or alumina-silica fibers to control the gas-evolution. This resulted in uniform foams of small cell size and free of defects. In addition to the fibers, about 10 to 15 percent by weight of hollow microspheres were included in the formulation to obtain the degree of density control necessary to fabricate a reproducible material. Both phenolic and silica microspheres were investigated.

A typical high performance PBI composite was formulated from a chemically crosslinked prepolymer (poly 2,2'-(m-phenylene)-5'-bibenzimidazole) from preoxidized amine. It has the following characteristics.

1. Polymer melt temperature: 118 - 125°C
2. Volatiles evolved (650°C): 25 - 27%
3. Particle size: <50 mesh, 90 % with 50 - 200 mesh
4. Amine assay after preoxidation: 96.5%
5. Glass transition temperature (400°C cure): 360°C
6. Solubility in sulfuric acid (hot after 350°C cure): 1 - 5 percent

A molding formulation, with enough of this crosslinked resin to cover the microspheres and fibers and produce an interconnected porosity less than 50 percent, is as follows: (1) PBI prepolymer, 69 percent; (2) HITCO C carbon fibers, 13 percent; and (3) phenolic microspheres, 18 percent. This and other formulations were performed in a Teflon vacuum bag by heating at a controlled rate from 120°C to 315°C. Postcuring was accomplished by heating in argon from 215°C to 455°C.

The resulting composite gave a bulk density of 0.48 ± 0.008 g/cm³, a compressive strength of 8.3 x 10⁶ newtons/m², and an interconnected porosity of less than 40 percent.
The ablation tests were conducted in the Ames Heat Transfer Tunnel. This is an arc-driven wind tunnel in which the air (or other gas) is heated to high temperatures in an electric-arc heater. A Linde Model 24000 heater was used for these tests. The hot air is discharged through a converging-diverging nozzle into an evacuated test chamber as a supersonic free jet. For these tests, a nozzle with a 1.91 cm diameter throat and a 5.08 cm diameter exit was used. Retractable support arms were used to mount the ablation specimens and to insert them into the test stream for the desired time of exposure.

The instrumentation employed in these tests was very simple. The stagnation point heating rate, in the absence of ablation, is measured by a transient-type copper calorimeter of the same size and shape as the ablation models (ref. 7). The sensing element is a 0.792-cm diameter copper slug of known weight which is thermally isolated from other parts of the calorimeter model. A thermocouple embedded in the sensing slug measures the rate of temperature rise. The calorimeter model also has three pressure orifices spaced around the sensing element so that surface pressure can be measured simultaneously with heating rate. An automatic optical pyrometer with a band pass centered at 0.65 microns was used to measure surface brightness temperature of the ablating specimens.

The ablation models were machined from molded billets of the various PBI composites to be tested. The blunt-faced models had a nose-radius of 6.12 cm, a diameter of 3.81 cm, and a thickness of approximately 2.66 cm. All of the materials were tested in air at a nominal stagnation-point cold-wall convective heating rate of 800 watts/cm² and a stagnation point surface pressure of 2.5 atmospheres. The enthalpy of the stream was determined in the manner described in reference 7. For these tests, the nominal stream enthalpy was $9.3 \times 10^6$ J/kg.

The test procedure was identical for all ablation runs. The arc jet was started and brought up to the predetermined running conditions; whereupon, the combined calorimeter and pressure probe was inserted momentarily into the jet to measure the stream conditions. Immediately following this, three ablation models for each material were inserted and retracted one at a time. The three models were exposed to the stream for different lengths of time (usually 5 to 20 seconds). Following the ablation test, the thickness of the ablated specimens were measured and compared with the prerun measurements to determine the amount of surface recession. For each material, the three surface recession measurements were plotted against time. These curves are linear, since the shortest run time was always selected to be longer than the initial transient period. The slope of the linear curve is the surface recession velocity.

The test results for some of the PBI materials are presented in Table 1 along with the results of an identical test on low-density phenolic-nylon for comparison. A descriptive classification of the type of PBI is included along with the virgin material density and the stagnation point surface recession velocity. Since the virgin material density varied somewhat, a direct comparison of the recession velocities is not feasible. Consequently, the product of density and recession velocity is used as a comparison ablation parameter. This product represents the mass rate at which the material ablates. Since there is no surface shear stress at the stagnation point, the mass removal at this point is the result of oxidation alone. At body points away from the stagnation point, the surface shear stress becomes finite and the mass removal may be the combined result of both oxidation and
shear. In order to give a measure of the combined effect, the product of the virgin material density and the surface velocity at a radius equal to 0.8 of the body radius \( r = 0.8 \) is given.

### TABLE 1. ABLATION PERFORMANCE OF PBI MATERIALS

<table>
<thead>
<tr>
<th>Mat'1</th>
<th>Type</th>
<th>( \rho ) (gm/cc)</th>
<th>([\rho V]_r/R=0) (cm/sec)</th>
<th>([\rho V]_r/R=0.8) (gm/sec cm²)</th>
<th>([\rho V]_r/R=0.8) (gm/sec cm²)</th>
<th>Char Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Linear</td>
<td>0.480</td>
<td>0.053</td>
<td>0.025</td>
<td>0.047</td>
<td>Rough surface</td>
</tr>
<tr>
<td>2</td>
<td>Thermally crosslinked</td>
<td>0.550</td>
<td>0.037</td>
<td>0.020</td>
<td>0.026</td>
<td>Rough surface</td>
</tr>
<tr>
<td>3</td>
<td>Chemically crosslinked (oxidation of 3.1'-diamino-benzidine)</td>
<td>0.496</td>
<td>0.053</td>
<td>0.026</td>
<td>0.025</td>
<td>Slightly rough surface with small pits</td>
</tr>
<tr>
<td>4</td>
<td>Chemically crosslinked (triphenyl triameasate)</td>
<td>0.416</td>
<td>0.094</td>
<td>0.039</td>
<td>0.051</td>
<td>Very irregular surface with deep fissures</td>
</tr>
<tr>
<td>5</td>
<td>Chemically crosslinked (oxidation of 3.3'-diamino-benzidine)</td>
<td>0.048</td>
<td>0.041</td>
<td>0.018</td>
<td>0.023</td>
<td>Smooth surface</td>
</tr>
<tr>
<td>6</td>
<td>Phenolic-Nylon</td>
<td>0.545</td>
<td>0.061</td>
<td>0.033</td>
<td>0.060</td>
<td>Slightly rough surface</td>
</tr>
</tbody>
</table>

#### DISCUSSION OF RESULTS

The materials which were tested are listed in Table 1 in the same order they were described in the previous sections. Material 1 is a linear PBI with a composition of 65 percent polymer, 20 percent phenolic microspheres and 15 percent carbon fibers. At the stagnation point the mass removal rate for this material is 0.025 gm/cm²/sec, while at the \( r/R=0.8 \) point the rate is 0.047 gm/cm²/sec. Thus, the mass removal rate in the combined oxidation-shear environment is about 87 percent greater than in the oxidation only environment. It is hypothesized that the reason for this behavior is as follows. Even in the presence of the transpiring ablation vapors, some oxygen permeates below the char surface and attacks the linear polymer chains with resultant chain scission. This effectively reduces the number average molecular weight, and since the shear compliance of the material is proportional to its molecular weight (ref. 15), the material is less elastic and more easily removed by the local shear stress. Even so, the linear PBI has a lower mass removal rate than the low-density phenolic nylon (material 6) in both the oxidation only and the combined oxidation-shear environment.

An example of thermally crosslinked PBI is material 2 which has the same composition as the first material. For material 2 the stagnation point mass removal rate is 0.02 gm/cm²/sec and at the \( r/R=0.8 \) point the rate is 0.026 gm/cm²/sec. Hence we can conclude that the thermally crosslinked
material has considerably better performance than the linear PBI, especially in the combined oxidation-shear environment. This improved performance is attributed to the fact that the material is crosslinked and thus less susceptible to oxidative scission as noted in the section on char formation.

Materials 3 and 4 are examples of chemically crosslinked PBI; they have the same composition as the first two materials. In material 3, the crosslinking is obtained by use of preoxidized amines. In this case, the mass removal rate is essentially the same at the stagnation point and the $r/R=0.8$ point and comparable to that of the thermally crosslinked material at the $r/R=0.8$ point. When chemical crosslinking is obtained by use of triphenyl trimesate as a comonomer, the ablation performance is inferior to both of the other crosslinked materials and even to the linear material. The reason for this is not clear at the present time.

Thus far, all the materials discussed have had the same composition. In order to investigate the effects of small changes in composition, material 5 was formulated. This is a chemically crosslinked PBI similar to material 3 except that the composition is 69 percent polymer, 18 percent microspheres, and 13 percent carbon fibers. The results listed in Table 1 indicate that this small increase in resin content reduced the stagnation point mass removal rate by about 30 percent. This improvement is believed to be the result of better wetting of the filler materials and a consequent reduction in interconnected porosity. Note that at the $r/R=0.8$ point the mass removal rate is comparable to that of material 3. This is a result of the fact that material 5 is not as extensively crosslinked as material 3.

In summary, it must be emphasized that the results and discussion above are for only one test condition, and as such are not necessarily indicative of a material's performance over a wide range of test conditions. The purpose of these initial screening tests was to make a selection of the more promising materials for more extensive testing. Certain conclusions can be drawn, however, regarding the performance of the PBI composites at the selected test condition: (1) the linear PBI composite has a lower mass removal rate than low-density phenolic nylon in both an oxidation only and a combined oxidation-shear environment. (2) The performance of PBI can be improved by crosslinking. This can be done either thermally by postcuring to a higher temperature or chemically by use of polyfunctional preoxidized amines. (3) Chemical crosslinking by use of triphenyl trimesate as a comonomer results in performance which is inferior to that of linear PBI. (4) A small increase in resin content provides better wetting of the filler materials and a reduced mass removal rate.

REFERENCES


