The Development of Polybenzimidazole Composites as Ablative Heat Shields

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SUMMARY

The excellent high-temperature mechanical properties and other desirable characteristics of polybenzimidazole (PBI) polymer systems make these systems attractive candidates for development as ablative heat-shield materials. This paper describes the formulation of several new low-density polybenzimidazole composites. The proposed structure of the basic linear PBI prepolymer and of several highly cross-linked PBI polymers are presented. The cross-linked PBI's were obtained either thermally (by post-curing to a high temperature) or chemically (by the use of either pre-oxidized polyfunctional amines or triphenyl trimeasate as a comonomer in the polymerization).

Both the linear and the cross-linked PBI composite materials were tested in an arc-heated wind tunnel at a stagnation-point heating rate of 800 W/cm^2 and a surface pressure of 2.5 atm. For comparison, a standard phenolic-nylon material of approximately the same density (0.5 g/cm^3) was also tested. The test results show that the linear PBI composite had a lower mass-loss rate than the phenolic-nylon material. The results also indicate that the ablation performance of PBI composites can be substantially improved by cross-linking. The improvement is particularly noticeable in regions of high surface shear.

INTRODUCTION

Low-density (0.5 g/cm^3), char-forming polymeric composites have found application as re-entry heat shields for both orbital and lunar manned spaceflight missions [1]. The low-density materials have a low thermal conductivity [2] and consequently a low heat transfer rate to the substructure [3, 4]. The carbonaceous char surfaces formed by these materials have high surface emissivities [5] and attain high surface temperatures [6, 7]. These two factors permit the char surface to radiate 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 23-60% [8] as well as vapor species. The char layers form with appreciable volumetric shrinkage (20-30% for low-density phenolic nylon) which leads to a mechanically weak structure full of fissures and voids [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 instrusion 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 [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 weakening and removing 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 [11]. In particular, the polybenzimidazoles (PBI) were selected for this investigation for the following reason: (a) 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. (b) 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 [12]. (c) The PBI materials are capable of pro-
ducing a highly organized char structure with a minimum of shrinkage,
good physical integrity, and excellent high-temperature mechanical proper-
ties. Furthermore, the chars contain interstitial nitrogen atoms which re-
sult in substantially lower thermal conductivity than graphite or carbon.
(d) The PBI polymers contain no oxygen-bearing functional groups to in-
teract with the char and cause internal oxidation.

The purpose of this paper is to describe briefly 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 de-
scribed. Finally, the experimental procedure is described, followed by a
presentation and discussion the the test results.

DESCRIPTION OF PBI MATERIALS

Prepolymers were synthesized by thermally condensing 3,3'-diaminoben-
zidine (I) and diphenylisopthalate (II) to give low-molecular-weight pre-
polymer resins (III) as follows:

$$(\text{II}) + (\text{I}) \longrightarrow (\text{III}) + \text{H}_2\text{O} \qquad (1)$$
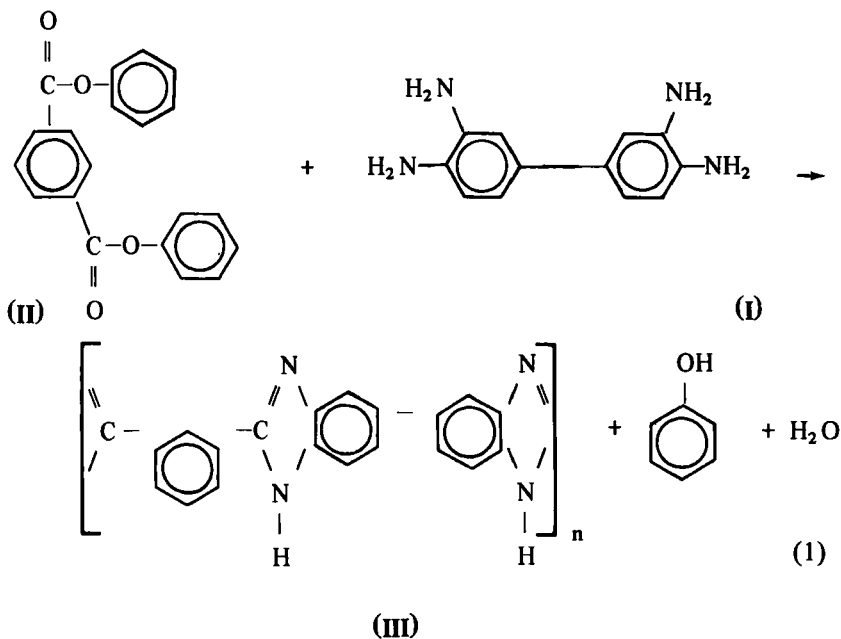
where n = 2-3.

Thermogravimetric pyrolysis of these prepolymers in helium (at a heating rate of 3°C/min) 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 [13], which were found to give low char yields and high-molecular-weight imidazole fragments as vapor, were performed on specimens that were not fully cured.

In the present study, the PBI prepolymers of the type shown in Eq. (1) were first cured at a temperature of 400°C and then postcured 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/min, gave a tough, black solid in yields of about 85%. 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 postcure, a high-temperature cross-linking reaction can occur if sufficient time, at temperatures in excess of 700°C, is allowed. The result is a thermally cross-linked structure which is similar to the three-dimensional heteronetwork proposed by Bruck [14] for a similar pyrolysis of aromatic polyimides. The material which results from the postcure is a dihydropolybenzimidazole (pyro-benzimidazole) 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 cross-linked 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 cross-linking reaction is very slow, and cure times of as much as 10 hr 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 cross-linking, the feasibility of chemically cross-linking the linear PBI was investigated. A controlled number of cross-links were introduced into the system by using both triphenyl trimeasate as a comonomer and polyfunctional amines derived from low-temperature oxidation of 3,3'-diaminobenzidine. The latter cross-link 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 2. Such structures have a number average molecular weight about double that of the monomer with a 10% reduction in primary amine content.

A series of PBI polymers were prepared from diphenylisopthalate 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 86-98%; the extent of cross-linking increased with decreasing amine assay and was accompanied by a decrease in the sol content. Both amide and arylene imidazole cross-links may be present in the polymers [15]. It will be shown that these chemically cross-linked systems perform about as well as the thermally cross-linked system in a coupled oxidation-shear environment.

Finally, a second series of chemically cross-linked PBI's was prepared by replacing part of the diphenylisopthalate with triphenyl trimeasate in the polymerization with 3,3' -diaminobenzidine. At comparable cross-link density, these materials do not have the resistance to coupled shear and oxidation exhibited by both the thermally cross-linked materials and those chemically cross-linked by the preoxidized amine. It was concluded that the second type of chemical cross-linking interferes with the formation of a stable cross-link 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 cross-linked PBI, (3) chemically cross-linked PBI obtained from preoxidized 3,3' -diaminobenzidine, and (4) chemically cross-linked PBI obtained from trimeasate 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 are described.

THE CHAR FORMATION PROCESS IN POLYBENZIMIDAZOLES

Examination of the thermogravimetric test results indicates that conventional PBI's yield no char when pyrolyzed in air at heating rates of 3-10°C/min. 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

cross-linking reduced the oxidative scission reaction. The result is that the thermally cross-linked PBIs show a stability toward oxidation similar to that of graphite. That is, in thermogravimetric tests they are not completely oxidized until a temperature of 1000°C is reached.

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 difference in 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% 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 increasing with porosity, the permeation of oxygen will also increase with 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~2-3) with advanced prepolymer (n>3) were molded at atmospheric pressure and temperatures of 260°C for 20 min followed by 315°C for 10 min. Free-standing foams with densities from 0.24 to 0.61 g/cm^3, 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 10-15% 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 10-20% 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 cross-linked prepolymer (poly 2,2'-(m-phenylene) -5' -bibenzimid-azole) from preoxidized amine. It has the following characteristics: poly-mer melt temperature, 118-125°C; volatiles evolved (650°C), 25-27%; particle size, <50 mesh, 90% with 50-200 mesh; amine assay after pre-oxidation, 96.5%; glass transition temperature (400°C cure), 360°C; solu-bility in sulfuric acid (hot after 350°C cure), 1-5%.

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

The resulting composite gave a bulk density of 0.48 ± 0.008 g/cm^3, a compressive strength of 8.3 X 10^6 N/m^2, and an interconnected porosity of less than 50%.

ARC-JET TESTS AND RESULTS

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 N4000 heater was used for these tests. The hot air is discharged through a converging-diverging nozzle into an evacuated test chamber as a super-sonic free jet. For these tests, a nozzle with a 1.91-cm-diam throat and a 5.08-cm-diam 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 in the ablation models [7]. The sensing element is a 0.792-cm-diam 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 μ was used to measure the 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 2.86 cm.

All of the materials were tested in air at a nominal stagnation-point cold-wall convective heating rate of 800 W/cm^2 and a stagnation-point surface pressure of 2.5 atm. The enthalpy of the stream was determined in the manner described in Ref. [7]. For these tests, the nominal stream enthalpy was 9.3×10^6 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 5-20 sec).

Following the ablation test, the thickness of the ablated specimens was 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 ablation 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 a comparable 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 an ablation parameter for comparative purposes. 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, however, 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/R = 0.8) is also given.

Table 1. Ablation Performance of PBI Materials

Material	Type	ρ, g/cc	$[V_s]_r/R = 0$ cm/sec	$[\rho V_s]_r/R = 0$ g/sec-cm^2	$[\rho V_s]_r/R = 0.8$ g/sec-cm^2	Char appearance
1	Linear	0.480	0.053	0.025	0.047	Rough surface with pits
2	Thermally cross-linked	0.550	0.037	0.020	0.026	Rough surface
3	Chemically cross-linked (oxidation of 3,3'-diamino benzidine)	0.496	0.053	0.026	0.025	Slightly rough surface with small pits
4	Chemically cross-linked (triphenyl trimeasate)	0.416	0.094	0.039	0.051	Very irregular surface with deep fissures
5	Chemically cross-linked (oxidation of 3,3'-diamino benzidine)	0.448	0.041	0.018	0.023	Smooth surface
6	Phenolic-nylon	0.545	0.061	0.033	0.060	Slightly rough surface

DISCUSSION OF RESULTS

The materials which were tested are listed in Table 1 in the same order as they were described in the previous sections. Material 1 is a linear PBI with a composition of 65% polymer, 20% phenolic microspheres, and 15% carbon fibers. At the stagnation point the mass removal rate for this material is 0.025 g/cm^2-sec, while at the r/R = 0.8 point the rate is 0.047 g/cm^2-sec. Thus, the mass removal rate in the combined oxidation-shear environment is about 87% 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 [16], 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 cross-linked 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 g/cm^2-sec, and at the r/R = 0.8 point the rate is 0.026 g/cm^2-sec. Hence we can conclude that the thermally cross-linked 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 cross-linked and thus less susceptible to oxidative scission, as noted in the section on char formation.

Materials 3 and 4 are examples of chemically cross-linked PBI; they have the same composition as the first two materials. In material 3, the cross-linking 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 cross-linked material at the r/R = 0.8 point. When chemical cross-linking is obtained by use of triphenyl trimeasate as a comonomer (material 4), the ablation performance is inferior to that of both the other cross-linked materials and even to that of 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 cross-linked PBI similar

to material 3 except that the composition is 69% polymer, 18% micro-spheres, and 13% 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%. This improvement is believed to be the result of better wetting of the filler materials and a consequent reduction in inter-connected 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 cross-linked 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 in-dicative 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: (a) 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. (b) The performance of PBI can be improved by cross-linking. This can be done either by thermally postcuring to a higher temperature or chemically by use of polyfunctional preoxidized amines. (c) Chemical cross-linking by use of triphenyl trimeasate as a comonomer results in performance which is in-ferior to that of linear PBI. (d) A small increase in resin content provides better wetting of the filler materials and a reduced mass removal rate.

ACKNOWLEDGMENTS

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