LOW DENSITY POLYBENZIMIDAZOLE FOAMS

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For publication in the Proceedings of the Society of Plastics
Engineers 32nd Annual Technical Conference, San Francisco,
Calif., May 13-16, 1974.

BIOGRAPHY

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ABSTRACT

Aromatic polybenzimidazole (PBI) foams in the density range of 24-80 kg/m^3 produced by controlled thermal crosslinking of the prepolymer have been developed and shown to have excellent thermophysical properties, fire resistance and low smoke evolution when exposed to heat or flame; they also retain their mechanical properties up to 473°K without any significant degradation. In addition to superior thermal properties, these foams maintain a high degree of flexibility, a good modulus-to-weight ratio as well as a high strength-to-weight relationship. Consequently, these combinations of excellent thermal and mechanical properties make this foam an attractive candidate for aircraft fire barriers and space shuttle thermal insulation where the combination of low weight and high temperature insulation is critical.

This paper describes the relationship between prepolymer purity, processing parameters and additives to the thermophysical properties of these foams. Studies included the addition of surfactants and fibers and variations in the cure and postcure schedules. It was determined that foam properties were affected by differences in prepolymer purity, curing schedule and the presence of solid additives in the foam. A direct relationship between the amount of fiber additive and resultant foam density was established. High temperature compressive performance was improved by postcuring at 800°K. Surfactant additives were found to improve the uniformity of cell size. Foams were characterized as to their ambient and high temperature compressive strength and modulus, density, porosity, thermal conductivity and efficiency, and other thermal properties.

Studies were conducted to determine the effect of prepolymer purity on foam properties with the aim of utilizing low cost prepolymers to produce these foams. It was concluded that foams made from prepolymer having an ortho-diamine purity of 95% had approximately the same properties as foams made from higher purity and cost prepolymer.

1.0 INTRODUCTION

Polybenzimidazoles as a class of materials possess exceptional high-temperature stability, both from mechanical and thermal points of view. Marks and Rubin (Reference 1) and D'Alelio and Parker (Reference 2) compared and reviewed various high temperature polymers, including phenolics, polyimide, polyphenylene, polyquinoxaline, and polybenzimidazole, in order to determine which had the best high-temperature properties. Table 1 presents a comparison of resins studied with respect to temperature of pyrolysis, primary char yield and indication of the foam fabricability of the polymer. The temperatures of pyrolysis shown in the table and char yield directly measure the stability of the polymer chain. As shown, the combination of thermal stability and ease of foam production makes this material attractive for various high temperature applications. Structural foams produced from these polymers are candidates for such applications as (a) thermal insulation for upper surfaces of the space shuttle vehicle where temperatures of 600°-700°K are encountered and (b) insulation material for use in various aircraft applications where a high temperature fire-resistant and low smoking foam insulation is required. This latter application may include high temperature insulation in jet engine nacelles and insulation for aircraft fuselages, providing burn-through protection in crash fires. The primary objective of this study was to optimize and characterize the thermophysical properties of the PBI foam. Secondary objectives included (a) determination of the prepolymer purity required to achieve adequate foam properties, (b) development of optimized processing techniques including curing and postcuring schedules, (c) determination of the effect of inert additives such as fibers on the thermophysical properties of the foam, and (d) evaluation of the high temperature properties of the foam.

The remainder of the paper presents a discussion of the chemistry and characterization of the prepolymer, the method of fabrication of low density foam billets and a description of the thermophysical properties of the foam.

2.0 TECHNICAL DISCUSSION

2.1 PREPOLYMER PREPARATION AND CHARACTERIZATION.

One method used for synthesizing high-molecular-weight polymers which exhibit desirable thermal stability characteristics is to combine benzene ring structures with other aromatic heterocyclic groups to form a totally aromatic structure. The procedure used for synthesizing the prepolymer is described by Marvel and Vogel (Reference 3), whereby polybenzimidazole-containing recurring aromatic units is produced by condensing aromatic tetramines and the phenyl esters of aromatic dicarboxylic acids. Even though the actual mechanism of reaction is undoubtedly complex, several authors have postulated the reaction steps. Wrasidlo and Levine (Reference 4), in studying the reaction (Figure 1) of diphenyl isophthalate and 3,3' diaminobenzidine (DAB), postulated the reaction mechanism in which the final event in the condensation is phenol evoluation with the formation of the benzimidazole ring.

Three prepolymer groups were selected for study which were prepared from batches of 3,3' diaminobenzidine judged to contain, respectively, 87.5%, 95.0% and 97.6% theoretical ortho-diamine groups. Foams produced from the lower purity (87.5%) group were brittle and had relatively high density. Consequently, this prepolymer group was not utilized for any further evaluations. Foams produced from the other prepolymer groups had good thermophysical properties, with no significant differences being observed in the foams produced from the two different lots. Prepolymers were characterized by analyzing the prepolymer and char for C, H, and N, determining the polymer melt temperature and the volatile content.

Table 2 represents the properties of the prepolymers utilized to prepare the foams. The results of the elemental analysis of the virgin polymer and char residues produced at 970°K have been weight normalized to 100%. The laboratory analysis of the virgin polymer does not correspond to the idealized structure as closely as might be expected. The deviation in nitrogen content is particularly large. The idealized PBI structure can be represented as C_{20}, H_{12}, N_4 (Reference 5), while the normalized laboratory results represented a structure of $C_{18.3}$, $H_{12.2}$, $N_{3.5}$. Calculations are based on a mer unit of polymer represented as $C_{20}H_{12}N_4$. No attempt was made to correlate the results of the elemental analysis and thermogravimetric analysis experiments reported here, since making a mass balance on the reacting PBI system was beyond the scope of this program.

The prepolymer melting temperature was determined by placing a small quantity of the prepolymer in a capillary tube and recording the temperature range between the time the prepolymer began to melt and the time it was in solution. The ranges indicated are within the volatile confines of the prepolymers used. Volatile content was determined by heating the prepolymer sample to 700°K and determining the weight loss.

Thermogravimetric analyses were performed on the prepolymers and polymer to determine the volatile content of the prepolymer at 700°K and the polymer weight retention at 1275°K. Figure 2 represents a thermogravimetric trace of the three prepolymer batches and of a polymer sample previously cured. The reduced weight loss of the prepolymer samples recorded between 300°K and

700°K reflects the volatile content of the prepolymer. These volatile contents have been found to agree very closely (Δ 0-3%) with the volatile content obtained during the curing schedule of the foam samples. Therefore, the thermogravimetric analysis is used as a tool to calculate the amount of prepolymer required to achieve foaming at a specific density. Examination of the thermogram of the precured sample shows characteristics which are related to the chemistry of the polymer. The loss of weight observed at a temperature below 823°K is probably due to a continuation of the cure mechanism, plus a small contribution by end group reactions tending to produce small amounts of ammonia and phenol. As the polymer is cured at these higher temperatures, e.g., 800-823°K, the active hydrogen in the imidazole ring begins to react, leading to branching and crosslinking (Reference 6). Compressive strength of foam samples cured at these higher temperatures (800°K) is slightly higher than samples cured at the lower temperatures, as shown in Figure 3. However, it was noted that the resiliency of the foam is slightly reduced when the foam is cured at this elevated temperature. Beyond the temperature of 823°K, decomposition of the polymer occurs (Reference 4) with the principal degradation products being water, phenol, and ammonia (Reference 7).

The foregoing discussion emphasizes the fact that the thermophysical properties of the polymer are strongly dependent on its previous thermal history.

2.2 FOAM FABRICATION

The foam is produced inside a stainless steel pan which has been equipped with an aluminum foil insert coated with a high-temperature, mold release compound. The amount of prepolymer required to achieve foam of a specific density is determined by the following equation:

$$\text{Wt prepolymer} = \frac{(\text{designed density})(\text{mold volume})\left(1 - \frac{\text{designed \% fiber}}{100}\right)}{\left(1 - \frac{\text{\% volatiles}}{100}\right)}$$

The prepolymer is evenly distributed in the bottom of the insert; the assembly is then closed and purged with nitrogen prior to the application of heat. The polymer is heated to the maximum cure temperature of 740-800°K. The heating rate between 457°K, and 550°K which is the temperature at which foaming occurs, is 2°K per minute.

The sample is cooled to 420°K, at which point the nitrogen is shut off and the mold removed from the oven. This fabrication procedure can further be simplified by utilizing an oven having a circulating inert atmosphere from which the phenol would be continually removed. The percentage of volatiles lost during the foaming and curing process corresponds very closely to the thermogravimetric analysis results obtained, making it possible to predetermine the foam density desired.

The effect of the high temperature (800°K) cure on the physical properties of the foam has not been fully evaluated. The thermophysical properties of the foams described are from samples which had a final cure temperature of 740°K.

2.3 EFFECT OF ADDITIVES

The effect of additives on the physical properties of the foam was evaluated. High temperature silicone oil surfactants (Dow Corning DC-710 and General Electric SF-96) seemed to improve cell uniformity and shape but had no significant effect on the moisture pickup of the foam as shown in Figure 4. The surfactant addition (0.5%) is achieved by dropping the silicone oil into the prepolymer after it has been spread out in the mold pan.

The effect of fiber additives on the foam system was determined. Free-foaming blends of fiber and prepolymer result in a somewhat more dense foam with a correspondingly finer cell size. The relationship of fiber content to the density of the foam is shown in Figure 5. The percentage of fiber in the finished foam is directly proportional to the density of the foam. In the preparation of the foam, the chopped fiber is blended with the prepolymer prior to placing it in the mold. Fibers investigated included Refrasil®, Modmur II®, and polybenzimidazole. The effect of fibers on the thermophysical properties of the foam has not been fully evaluated as yet.

2.4 THERMOPHYSICAL PROPERTIES

2.4.1 PHYSICAL PROPERTIES

Characterization of the physical properties of the foam included compressive strength and modulus, dimensional recovery, tensile strength, and porosity. Compression samples were tested according to ASTM D1621-64. For testing at elevated temperatures, a thermocouple was imbedded 1/2 cm in the center of the side of the sample and the compression value recorded when the desired temperature was measured by the thermocouple. Figures 6 and 7 illustrate the compressive strength and modulus of foam samples of various densities. Compressive properties were measured at both 10% and 50% deformations and the values shown are average values from random samples. The high-temperature compressive strength and the modulus of foam with a density of 43 kg/m^3 are shown in Figures 8 and 9. The degree of compressive change at higher temperatures for foams of varying density was approximately the same. A minimum of degradation of compressive properties is observed up to 473°K. The dimensional recovery after 10% or 50% compression at ambient and elevated temperatures is shown in Figure 10. The dimensional recovery was reproducible on two or more cycles; it may be concluded from the data that the foam has excellent resilience characteristics up to 573°K for use in applications where compressive recovery is needed.

Tensile measurements were conducted according to ASTM D1623-64. The tensile strength perpendicular to the foaming direction was approximately 200-250 kN/m^2 for a foam with a density of 33 kg/m^3. Lower tensile values were obtained when specimens were pulled parallel to the foaming direction. Porosity measurements were conducted by measuring the volumes of specimens and determining the amount of solution volume increase when the sample was submerged in a 50% aqueous acetone solution. The foam has approximately 15-25% interconnected porosity.

2.4.2 THERMAL PROPERTIES

In optimizing the processing parameters of the PBI foam, the objective was to retain the typical thermal characteristics of a high-temperature polymer consistent with optimum physical properties. Thermal performance properties measured included thermal efficiency and conductivity, flame spread, ease of ignition and smoke obscuration. Figure 11 illustrates the thermal efficiency of the foam as measured on the Ames Research Center JP-4 fuel burner facility (Reference 8). Thermal conductivity was measured by the guarded hot plate method according to ASTM C177-45. The effect of temperature on the thermal conductivity of the foam and the specific heat of the cured polymer which has been ground is shown in Figure 12. Flame spread measurements were made on a modified Monsanto flame tunnel employing a specimen 61 cm × 9 cm inclined 45° from the horizontal. The initial flame front of the sample is compared with that of asbestos (0 flame spread) and that of red oak (100 flame spread). Polybenzimidazole forms a stable char and has essentially zero flame spread when tested in this manner. The ease of ignition was determined using the Fenimore-Martin oxygen index method. In this test, the sample is held vertically in a vertical glass tube and a mixture of oxygen and nitrogen is metered into the bottom of the tube. The sample is ignited at its upper end and the atmosphere that permits steady burning down of the specimen is determined. The limiting oxygen index is the minimum fraction of oxygen in the oxygen-nitrogen mixture which will just permit the sample to burn. Materials which have a limiting oxygen index greater than 0.21 are self-extinguishing after ignition in air. The limiting oxygen index ($\eta\ O_2/\eta\ O_2 + \eta\ N_2$) for polybenzimidazole foam is approximately 0.70. Smoke obscuration measurements were made using a National Bureau of Standards smoke chamber. In this chamber, openings are provided to accommodate a photometer and samples are subjected to a heat flux of 25 kW/m^2 for 15 minutes. Light transmission of 70% represents the level below which a red exit sign at 3.0 m cannot be seen. Foam samples when tested in this manner permitted almost 100% light transmission.

The results of these thermal tests indicate the potential use of polybenzimidazole foams in areas where low flame spread and low smoke generation is mandatory, such as in aircraft fuselages and interiors.

3.0 CONCLUSIONS

Low density polybenzimidazole foam possessing good thermophysical properties has been produced from prepolymer prepared from 3,3' diaminobenzidine containing 95% theoretical ortho-diamine groups. Foams produced from lower purity prepolymer have inferior physical properties. The effect of processing parameters on the thermophysical properties of the foam was determined. Foam density is controlled by prepolymer volatile content, curing schedule and the presence of solid additives, such as fibers. High temperature compressive strength is increased by curing the foam at 800°K. A minimum of loss of compressive strength and modulus is observed at 473°K, with practically no loss of the resilient properties of the foam up to 573°K. Excellent fire and thermal performance properties make this foam an attractive candidate as a fire and thermal insulation material.

ACKNOWLEDGEMENTS

The authors wish to thank R. J. Milligan, Whittaker Corp., for polymer characterization and R. H. Fish, NASA, for flammability properties determinations.

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MATERIAL	PYROLYSIS TEMPERATURE °K	PERCENT CHAR YIELD AT 1073 °K	FOAM FABRICABILITY
PHENOLIC	633	57	VERY GOOD
POLYIMIDE	753	58	FAIR
POLYQUINOXALINE	793	66	FAIR
POLYBENZIMIDAZOLE	843	76	GOOD
p-POLYPHENYLENE	873	82	POOR

Table 1. Comparison of thermal properties of polymers.

1 ELEMENTAL ANALYSIS

MATERIAL	WEIGHT, %			MOLE, %		
	C	H	N	C	H	N
PREPOLYMER	78.2	17.3	4.3	53.9	10.2	35.8
970° K CHAR	86.2	12.3	1.3	76.1	9.3	14.5
IDEAL PBI STRUCTURE	77.9	18.1	3.9	54.5	12.7	32.7

PBI STRUCTURE PER ANALYSIS: $C_{18.3}$, $H_{12\,2}$, $N_{3.5}$
IDEALIZED PBI STRUCTURE: C_{20}, H_{12}, N_4

2 POLYMER MELT TEMPERATURE: 360° K-410°K

3. WEIGHT LOSS AT 685° K 35%±5%

4 WEIGHT LOSS OF POLYMER AT 1275° K <30%

Table 2. Characterization of prepolymer.

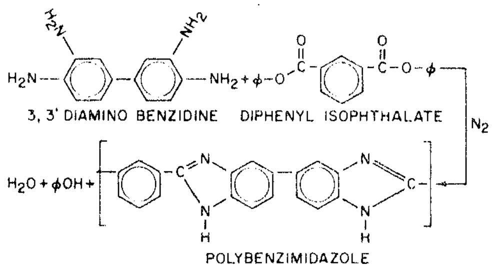

Figure 1. Reaction mechanism for polymerization.

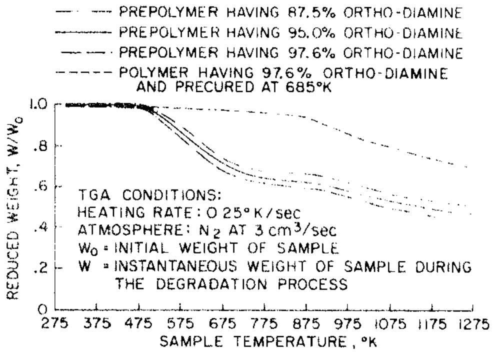

Figure 2. Dynamic thermogram for polybenzimidazole.

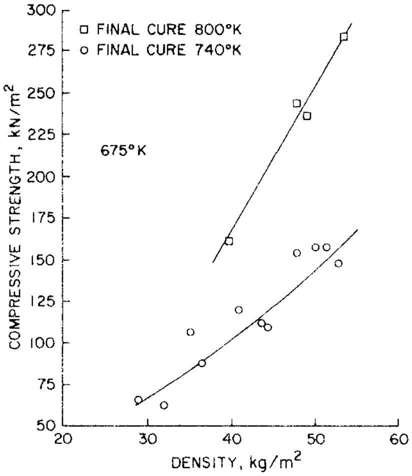

Figure 3. Effect of postcure temperature on compressive strength.

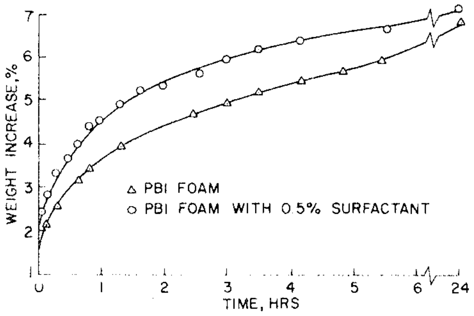

Figure 4. Moisture absorption.

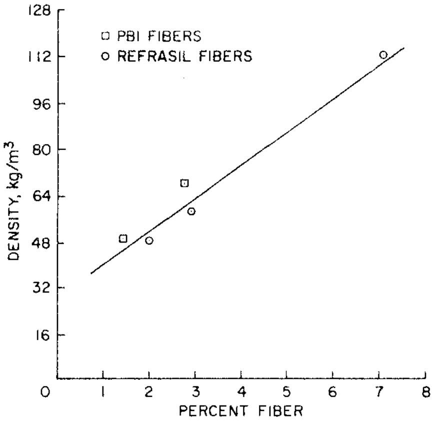

Figure 5. Effect of fiber additives on density.

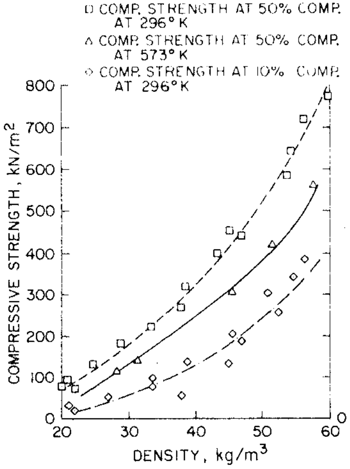

Figure 6. Effect of density on compressive strength.

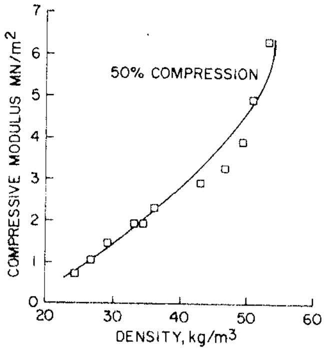

Figure 7. Effect of density on compressive modulus.

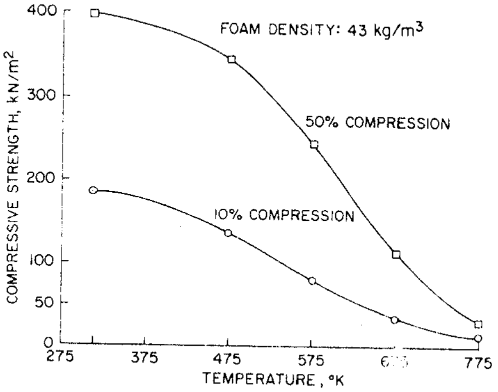

Figure 8. Effect of temperature on compressive strength.

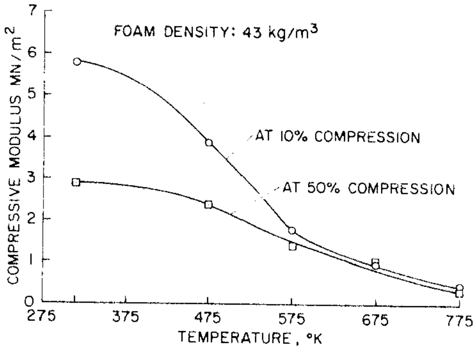

Figure 9. Effect of temperature on compressive strength.

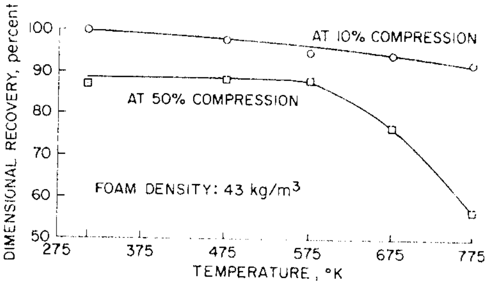

Figure 10. Effect of temperature on dimensional recovery.

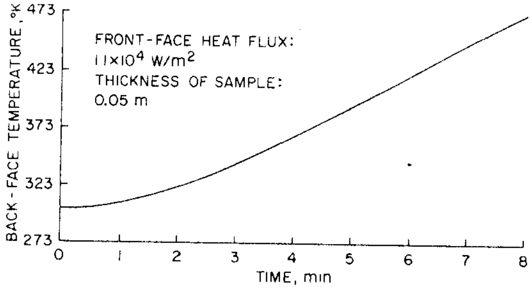

Figure 11. Thermal efficiency.

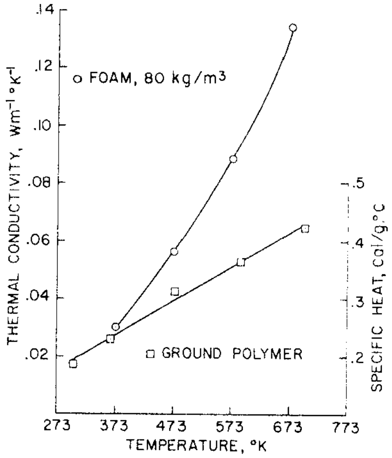

Figure 12. Effect of temperature on thermal conductivity and specific heat of PBI.