

Heat Resistance Properties of Poly(*p*-phenylene-2,6-benzobisoxazole) Fiber

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ABSTRACT: The high temperature properties of Poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fiber are examined and compared with those of the *p*-Aramid fiber. In particular, the temperature dependence of tensile strength of the PBO fiber is reported for the first time. The PBO fiber has 100°C higher decomposition temperature than the *p*-Aramid fiber, and the amount of toxic gases in combustion is much smaller than the *p*-Aramid fiber. Although the relative strength decreased proportionally in the range of room temperature to 500°C, the PBO fiber has 40% of the strength at room temperature even at a temperature of 500°C. After thermal treatment at 500°C for 60 s, the PBO fiber retained 90% of its original strength. The PBO fiber is expected to substitute for asbestos, which is still used as a heat resistant cushion material. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1031–1036, 1997

Key words: poly(*p*-phenylene-2,6-benzobisoxazole); PBO; Aramid; polybenzazole; high-temperature property

INTRODUCTION

PBO (poly(*p*-phenylene-2,6-benzobisoxazole) fiber has superior mechanical properties being stronger than carbon fiber, and excellent heat resistance and flame resistance but surprising flexibility and softness. The synthesis, polymerization, properties, and morphology of PBZ (polybenzazole) family have been reported¹ since PBZT (poly-*p*-phenylenebenzobisthiazole) was reported in 1979.²

The moduli of PBZT and PBO fibers have the highest values among the super fibers ever since a very early stage of development.^{1,3} The strengths, however, showed almost the same value as other super fibers such as *p*-Aramid at that time.^{1,3} Toyobo Company and Dow Chemical Company have performed joint research on the development of the PBO fiber and established the manufacturing technologies for the PBO fiber. As a result, the

strength of the PBO fiber has been increased to almost double that of *p*-Aramid.^{4,5}

Because PBZ was developed as a heat-resistant material, its properties of heat and flame resistance are well known.¹ However, a heat-resistant fiber has to show excellent mechanical properties at high temperature, which are not well known, except for the modulus at high temperature of PBZT,⁶ because of the difficulty of measurement. We recently built an apparatus for strength measurement at high temperature (up to 600°C) and measured the high temperature properties of the PBO fiber that was spun by our recent technology. In this study, the high temperature properties of the PBO fiber are compared with those of the Aramid fiber.

EXPERIMENTAL

Materials

Two types of PBO fiber, a regular type and a high modulus type (HM), both produced by Toyobo Co.

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Table I Mechanical Properties of Samples

	Denier	Tensile Strength (g/d)	Elongation at Break (%)	Tensile Modulus (g/d)
PBO fiber	500	44.1	4.0	1320
PBO(HM) fiber	490	42.1	2.6	1790
Aramid fiber	1450	23.1	3.5	610
Aramid(HM) fiber	1440	21.6	2.4	910

TF = 6.

Ltd., were used in this study. Commercial regular and high-modulus para-Aramid fibers (Kevlar[®]29 and Kevlar[®] 49) were also studied. The mechanical properties of these fibers were measured by using tensile tester (Orientec Tensilon Model RTM250). The samples were tested at a strain rate of 100%/min with gauge length of 200 mm. A specific twist level was applied to the fiber before the measurement. The applied twist factor (TF) calculated by using the following formula was 6, at which both strength and modulus showed adequately balanced value as at twisted yarn.

$$TF = 0.131 \times (\text{twist per inch}) \times (\text{denier})^{0.5} \quad (1)$$

Table I shows the physical properties of the samples.

Decomposition Behavior at High Temperature

Thermal gravimetry analysis using TG-DTA 2000S made by MAC Science Co. were performed under the heating rate of 20°C/min in air and in argon gas. The decomposition temperature was determined as the temperature at which 5% of weight loss occurred on the TGA curve. Isothermal weight loss was also measured by the following procedure. A sample was heated up to 500°C with a heating rate of 200°C/min then held at 500°C. Under this condition, the loss of weight was measured. Generated gases at high temperature (750°C) were measured in accordance with Japanese Industrial Standard (JIS) K7217 (Analytical Method for Determining Gases Evolved from Burning Plastics).

Measurement of Temperature Dependence of Strength

To obtain temperature dependence of strength, the single filament tensile tester was made as

shown in Figures 1 and 2, which has special jaws shown in Figure 3. Single filaments were selected at random from the fiber bundle. The single filament was mounted under a pretension of 1 g/d, and was heated in a heater chamber that was controlled at specific temperature. After 30 s the yarn temperature reached the heater temperature and a tensile measurement was taken. The heater chamber length (200 mm) was regarded as being gauge length, and the strain rate calculated by this gauge length was 100%/min.

High Temperature Modulus Measurement

A storage modulus was measured using a dynamic viscoelastometer (Orientec, Vibron model DDV-01FP). The samples were tested at a heating rate of 1°C/min from room temperature up to 400°C. Ten filaments from each fiber bundle were selected at random. Each end of the 10 filaments was glued on an aluminum substrate with an inorganic adhesive and then was subjected to measurement.

Strength Retention after Thermal Treatment

Strength retention after thermal treatment from 200 to 400°C was measured as follows. A sample was treated using a circulating air oven at the specific temperature. After the treatment, the tensile properties of the sample were measured at room temperature under the same condition as

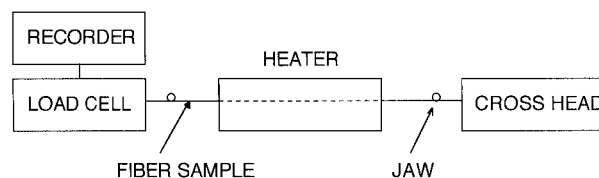


Figure 1 Schematic representation of high-temperature strength measurement apparatus.

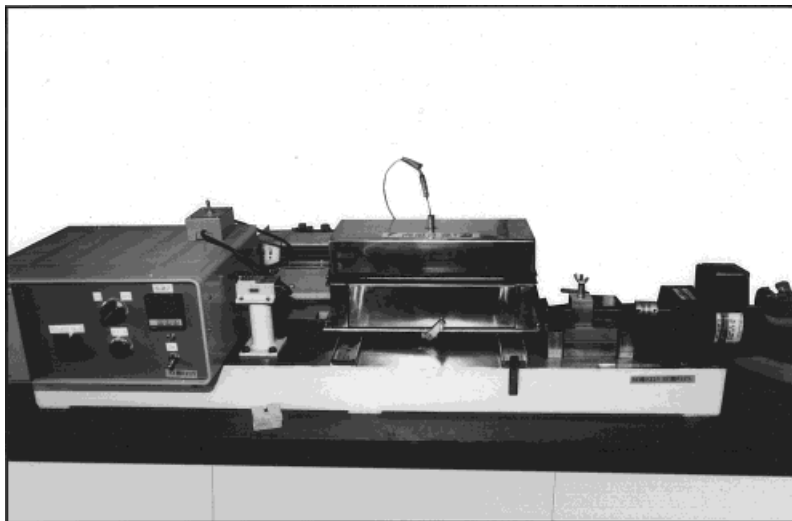


Figure 2 High-temperature measurement apparatus.

mentioned in the Materials section. The fiber was twisted before the thermal treatment. The twist factor was also 6. For the measurement of strength retention after thermal treatment at 500°C, the single-filament tensile tester as shown in Figure 1 was used. The strength measurement was conducted with single filaments.

RESULTS AND DISCUSSION

High Temperature Decomposition

Figures 4 and 5 show the results of thermal gravimetric analysis. PBO fiber has about 100°C higher decomposition temperature than Aramid fiber. Figure 6 shows the isothermal weight loss at 500°C of PBO and Aramid fiber. PBO loses weight very slowly even at 500°C in contrast with the very rapid decrease in weight of Aramid fiber. Generated gases at the temperature of 750°C are shown in Figure 7. The amount of toxic gases such as HCN, NO_x, and SO_x from the PBO fiber was small compared with the Aramid fiber.

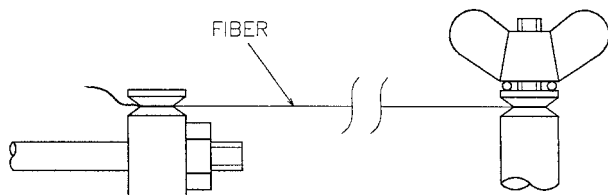


Figure 3 Jaw design of high-temperature measurement apparatus.

High Temperature Strength

The temperature dependence of strength of the PBO fiber and the Aramid fiber is shown in Figure 8. The relative strength of the PBO fiber decreased proportionally in the range of room temperature to 500°C. Even at the temperature of 500°C, the PBO fiber retained 40% of the strength at room temperature. A Yavrouian et. al. estimated tensile strength of the PBO fiber at 600°C from their TMA measurement.⁷ They indicated that relative strength at 600°C was 17% of the strength at room temperature. This value agrees well with the extrapolation to 600°C in our

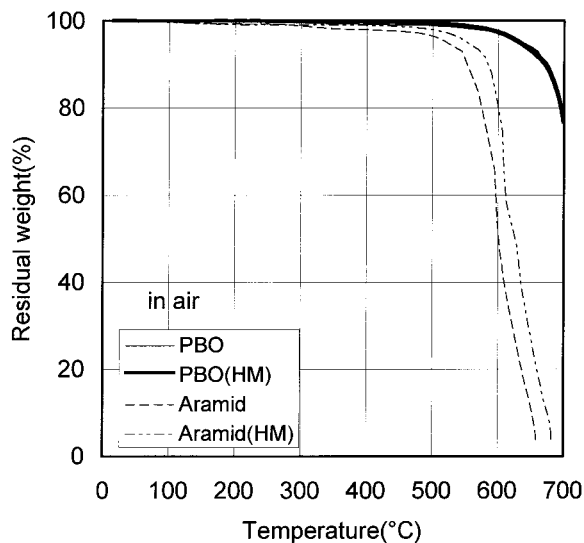


Figure 4 Decomposition behavior in air.

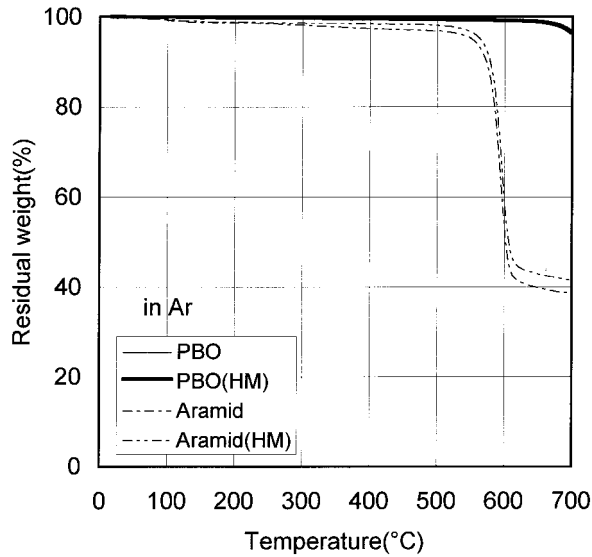


Figure 5 Decomposition behavior in Ar gas.

strength retention data. On the other hand, a steep decrease of relative strength over 300°C was observed for *p*-Aramid fiber. In so far as fiber type is concerned, no difference of temperature dependence of strength could be detected for the PBO fibers. In the case of Aramid fibers, however, the high modulus type had better retention over 300°C.

High Temperature Modulus

The temperature dependence of storage modulus of the PBO and the Aramid fiber was measured

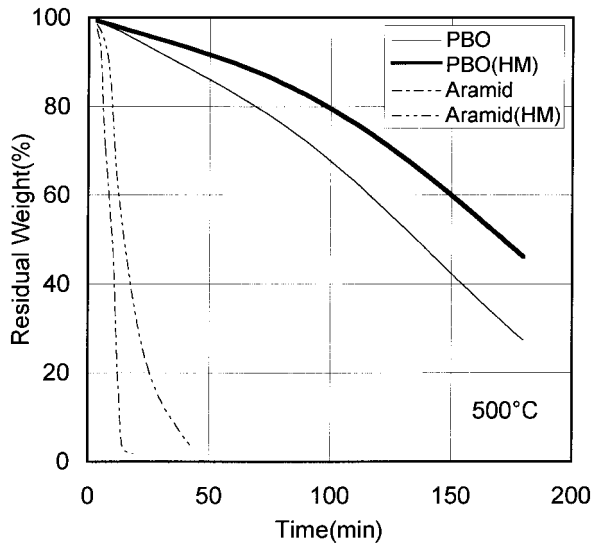


Figure 6 Isothermal weight loss at 500°C.

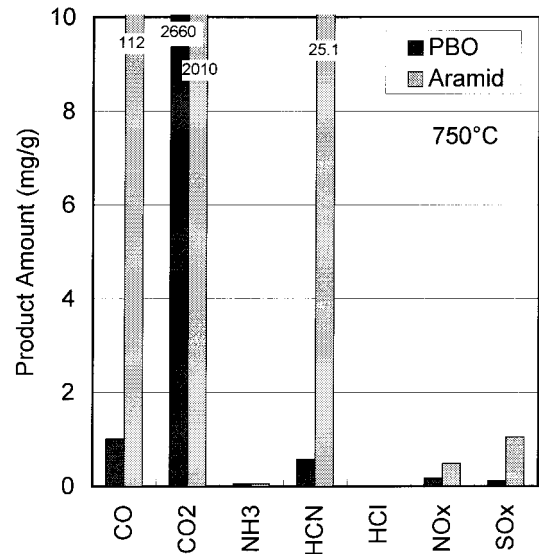


Figure 7 Gas generation from the PBO and Aramid fiber at 750°C.

only for the high modulus type fibers because both high modulus type fibers were obtained by the heat treatment of its regular type fiber and showed better thermal stabilities.

The temperature dependence of modulus in the range of room temperature to 400°C is shown in Figure 9. Even at 400°C the PBO fiber retained 70% of modulus at room temperature. The modulus of PBO fiber decreased gradually from around 300°C. According to the loss factor ($\tan \delta$) of the PBO fiber, the PBO fiber has a broad mechanical

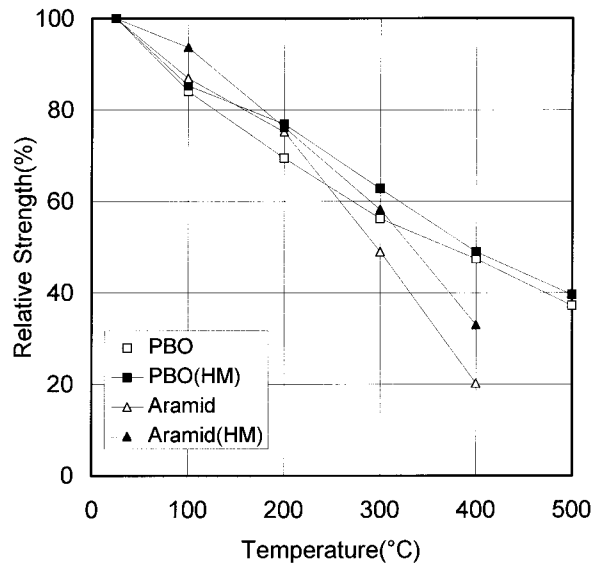


Figure 8 Temperature dependence of strength.

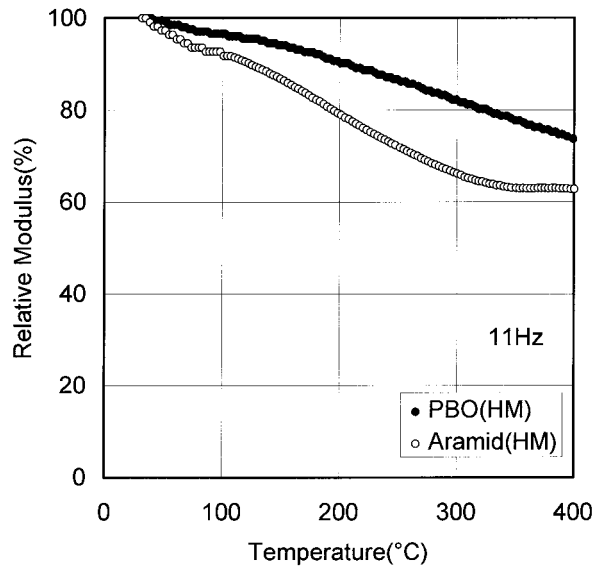


Figure 9 Temperature dependence of modulus.

relaxation around 300°C, as shown in Figure 10. Macturk et al. reported the molecular motion of PBZT crystal based on the torsion angle change between the phenyl and benzobisthiazole moieties over 300°C.⁸ However, the loss of modulus of fiber at high temperature is caused by the relaxation of the noncrystalline part of the fiber since Nakamae et al. showed that the crystalline modulus of the PBO and PBZT does not decrease up to 400°C.⁹

In the Aramid fiber, a certain relaxation was observed at around 200°C and the storage modu-

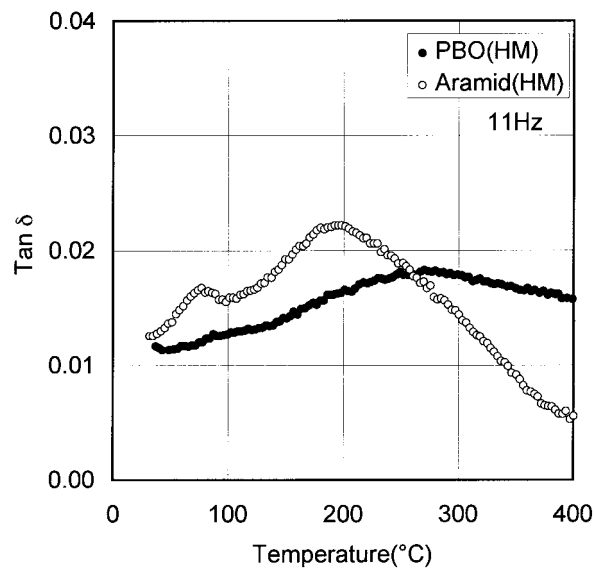


Figure 10 Dynamic loss factor of the PBO and Aramid fiber.

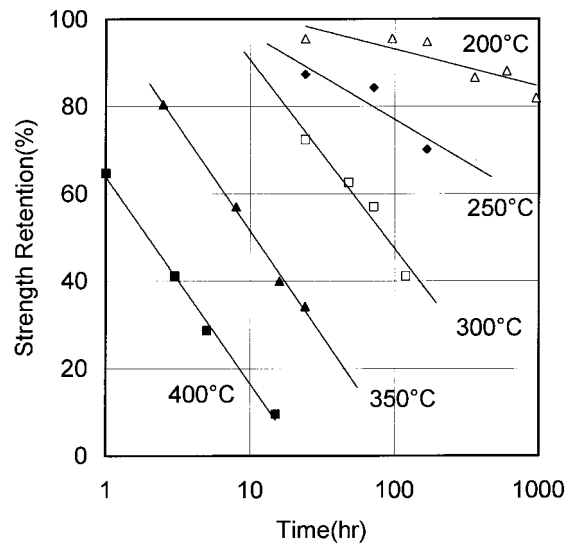


Figure 11 Strength retention after thermal treatment in air of the PBO (HM) fiber.

lus decreased to 70% of room temperature modulus at 300°C. The absorption around 100°C was assigned to the influence of water.

Strength Retention after High Temperature Exposure

The strength retention after thermal treatment of the PBO (HM) fiber in air atmosphere is shown in Figure 11 and is compared with the para-Aramid fiber in Figures 12–15. Compared with the regular Aramid fiber, both types of the PBO fiber

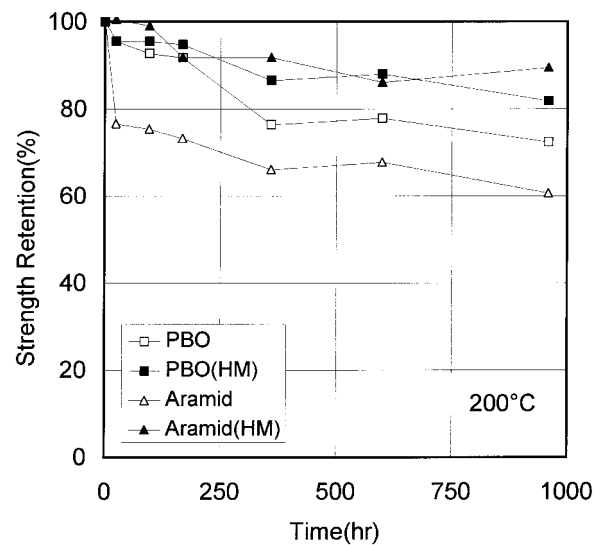


Figure 12 Comparison of strength retention after thermal treatment at 200°C.

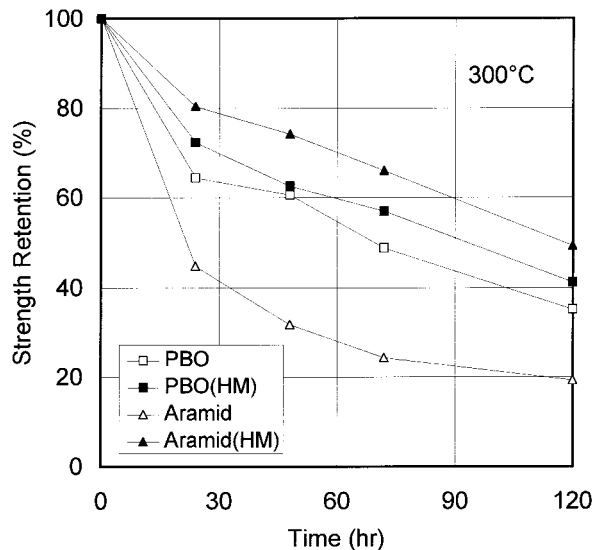


Figure 13 Comparison of strength retention after thermal treatment at 300°C.

had superior thermal stability in thermal treatment. However, the thermal stability of the high modulus Aramid fiber is improved like that of the PBO fiber up to 400°C. However, over 400°C, the PBO fiber showed definitely better thermal stability than the high modulus Aramid fiber.

CONCLUSION

The thermal stabilities of the PBO fiber were compared with those of the *p*-Aramid fiber, which was

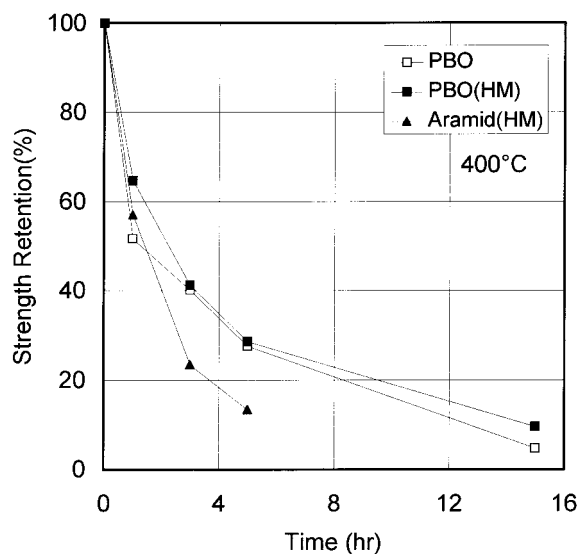


Figure 14 Comparison of strength retention after thermal treatment at 400°C.

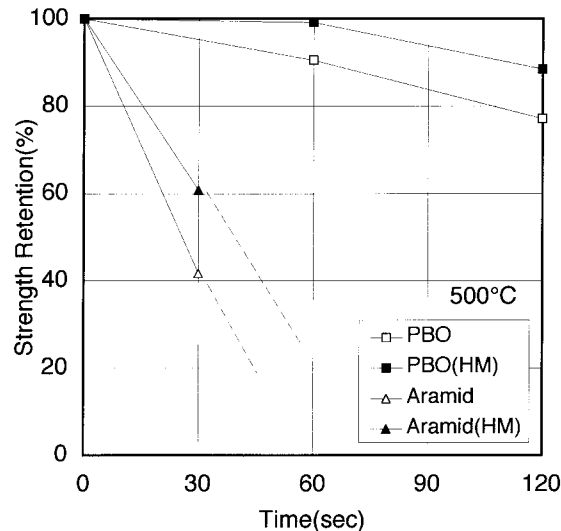


Figure 15 Comparison of strength retention after thermal treatment at 500°C.

used as a representative of heat-resistant organic fibers. The heat resistance of the PBO fiber is 100°C or higher than that of *p*-Aramid. The PBO fiber can be used as a tension member up to 350°C and further as a heat-resistant material up to 550°C or more. PBO can be expected to substitute for asbestos, which is still used as a heat-resistant cushion material for glass and metal manufacturing processes.

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REFERENCES

1. S. Kummar, *International Encyclopedia of Composite*, Vol. 4, S. M. Lee, Ed., VGH, New York, 1991, p. 51.
2. T. E. Helminiak, *ACS, Div. Org. Coat. Plast.*, 40 (1979).
3. J. F. Wolfe, *Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd ed., John Wiley, New York, 1988, p. 601.
4. J. Im, IFS'94, Yokohama (1994).
5. K. Yabuki, *Look Japan*, August 1995, p. 24.
6. H. Jiang, R. K. Eby, W. W. Adams, G. Lenher, *MRS Symp. Proc.*, **134**, 341 (1989).
7. A. Yavrouian, S. P. S. Yen, G. Plett, and N. Weissman, AIAA-95-1617-C (1995).
8. K. S. Mactuck, R. K. Eby, and B. L. Farmer, *Polymer*, **35**, 53 (1994).
9. T. Nishino, Y. Matsui, K. Nakamae, Y. Goto, and M. Nara, *Sen-i Gakkai Preprints*, **1995**, G-149 (1995).