Tensile and Fatigue Behavior of Poly-*p*- Phenylene Benzobisoxazole(PBO) Fibers

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Abstract. In this paper, tensile and fatigue strength of standard modulus type (As spun: AS) and high-modulus type (HM) poly-p-phenylene benzobisoxazole (PBO) fiber improved tensile modulus by heat-treatment have been investigated. The tensile tests of a monofilament were carried out at a gauge length of 12.5 mm and deformation rate of 0.5 mm/min. The fatigue tests of a monofilament were carried out to determine the S-N property at a frequency of 10 Hz with three stress ratios of 0.1, 0.5 and 0.7. It was found that the tensile strength of AS and HM fiber was well represented by a two-parameter Weibull distribution. The tensile strength of HM fiber was higher than that of AS fiber. The fatigue strength of HM fiber was higher than that of AS fiber over all fatigue lives because crystalline region in HM fiber increased by heat-treatment. In AS and HM fiber, the relation between the stress amplitude and fatigue life depended on the stress ratio. However, the relation between the maximum stress and fatigue life was independent of the stress ratio. Therefore, it was found that the maximum stress was useful to describe the fatigue lives at the different stress ratios. Additionally, in HM fiber, the factor governing fatigue fracture tended to vary from the mean stress to stress amplitude at the low stress ratio because crystalline regions increased by heat-treatment and fiber became brittleness. It was found by SEM observation that there were distinct differences between the surface image of tensile test specimen and that of fatigue test specimen, i.e., the splitting length in the fatigue test specimens was much longer than that in the tensile test specimens.

Introduction

In the field of polymeric fiber, PBO (Poly-p-Phenylene Benzobisoxazole) fiber has broadened its versatility and drawn the attention of customers for its properties that greatly surpass traditional fiber materials. One of the distinctive properties of this fiber, as shown in Fig. 1, is a high degree of strength and elasticity attributable to the rigid and highly linear polymer macromolecules laid out in the direction of the fiber [1]. Its versatility is expected to broaden further because its tensile strength is higher than that of carbon and aramide fibers and its tensile elastic modulus is comparable to that of carbon fibers. Currently, though, the PBO fiber is used mainly as a tension member in the axis of optic fiber cable [2] and as an adhesive tension sheet to repairing concrete beams [3]. Standard modulus type (AS) and high-modulus type (HM) of fibers with different degrees of elasticity are used widely at present. Well understood are fundamental properties of the fiber, such as relationship between the internal structure and deformation behavior [4], and its tensile strength [5]. Ambiguity remains about many of the properties of this relatively new material under specific conditions. Of the utmost

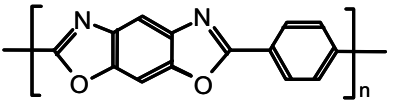


Fig. 1 Chemical structure of the PBO fiber.

importance is to understand the fatigue strength when it is used to reinforce composite material in machinery and structural members. This approach is indispensable to improve its properties, such as strength and elasticity, and widen its versatility. Under such circumstances, the authors have focused their research on the fatigue properties of PBO fiber. In their previous research, they reported on the fatigue strength properties of AS type PBO fiber [6]. By contrast, this report focuses on HM type PBO fiber with tensile elastic modulus increased thermal treatment and identifies its tensile and fatigue properties as found by relevant tests on monofilaments. The findings are compared with the results from the AS type PBO fibers reported in the previous report [6]. Examined are change in the relationship between the internal fiber structure and the tensile and fatigue strength

Experimental Procedure

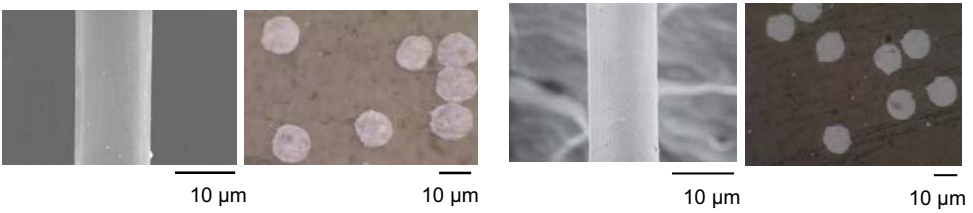
Test Materials and Specimens

PBO fibers, commercially available from Toyobo Co. in the brand name of Zylon®-HM is used for the experiment. This fiber is made of a polymer doping wet-day spun threads, a product of polymerized diamino-resorcitol and telephthalic acid, heat processed up to 600 C or above under tension. Fibers not heat processed this way are on sale as a standard type in the brand name of Zylon®-AS. In this report, such fibers are referred to as AS fibers as opposed to Zylon®-HM not heat processed to increase elasticity. The authors have reported on the tensile and fatigue properties of the AS fiber in a previous report [6]. For catalog data on both types of fibers, refer to Table 1 [7].

Figure 2 shows SEM images of the side surface and cross-sectional surface of HM and AS fibers.

Table 1 Mechanical properties of PBO fibers.

PBO Fiber	Tensile Elastic Modulus [GPa]	Tensile Strength, [GPa]	Filament Decitex	Density [g/cm^3]
HM Fiber	270	5.8	1.7	1.56
AS Fiber	180	5.8	1.7	1.54



(a) HM fiber. (b) AS fiber.

Fig. 2 Surfaces and cross sectional areas of two types of PBO fiber.

Cross-sectional images are shot of fibers buried in an acrylic resin, cut and polished in the diametric direction. The side surfaces of both fibers are relatively smooth with several ridges like streaks running in the direction of the fibers. But no macroscopic defects, such as cracks and holes, are spotted. Nor is spotted any disparity on both surfaces, caused by heat treatment. Cross-sectional images of both fibers present shapes that almost look like circles. Some types of fibers have odd cross-sectional shapes, and decision on the size of cross-sectional areas can affect the results of strength assessment. Since both types of fibers present almost circle-like cross-sections, however, the report assumes their cross-sections make circles. Diameters measured from the side-surface images are used to calculate fracture stress later on.

Figure 3 shows the shapes of the monofilament specimens used for the tensile and fatigue tests. Since the fibers are very thin, the test specimens are created with reference to JIS R7601. A rectangular piece of paper (approximately 0.3 mm thick) has its center cut open. A monofilament is placed on the opening with its both ends glued to the paper by an epoxy type adhesive. The gauge length is fixed to 12.5 mm in both the tensile and fatigue tests, taking into consideration responses of the fatigue tester. PBO fibers are reported [7] to deteriorate and decrease in strength from ultraviolet light and visible light. Therefore the test specimens are made in a room shielded from ultraviolet light and then stored in a dark room for one week until the adhesive dries out.

Monofilament Tensile Tests

A tensile strength test takes place on a monofilament in order to establish the standard to determine fatigue strength. For the test, a small desktop tensile strength tester was used. The tension rate is set at a constant 0.5 mm/min (8.3×10^{-3} mm/s). Load and cross-head variance are measured by a 5N capacity load cell. The number of specimens is set to 40 to allow for variance in tensile strength. Specimens that breaks off not within the gauge but at an adhesive point, is deleted from data collection, as in the monofilament fatigue case that takes place later.

Monofilament Fatigue Test

A 10N capacity electromagnetic fatigue tester is used for the monofilament fatigue test. The fatigue test takes place in a sine-wave load mode with controlled load. The frequency is set to f=10 Hz, and the stress ratio is set to R = 0.1, 0.5 and 0.7. The test stops in 10^7 cycles. As to load stress, the diameter of the fiber cannot be measured before the experiment because its surface can be injured in the measuring process. Therefore load stress is determined with reference to the average fracture load obtained in the monofilament tensile test. After the experiment, the diameter is measured to calculate the load stress. In order to prevent UV light and visible light from causing a decrease in strength, the tester as a whole is covered with a black covering during the test.

To examine fiber diameter, a field emission scanning electron microscope is used. Because SEM electron irradiation causes thermal damage to the surface of the fiber and a decrease in its strength, the diameter is measured after the experiment in a location sufficiently away from the spot of fracture within the gauge.

Results and Discussion

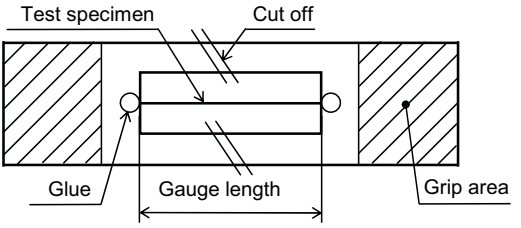


Fig. 3 Monofilament testing tab for tensile and fatigue tests.

Tensile Strength Distribution Properties

Figure 4 plots data on tensile strength obtained from the monofilament tensile test on Weibull probability paper. The symbol ● represents HM fiber, and ○ corresponds AS fiber, the comparative material. Both fibers make deviations from straight lines on the low strength side. Still, their movements can approximate to straight lines. The tensile strength of both the HM and AS fibers follows a 2-parameter Weibull distribution. The shape parameters for the HM and AS fibers are 7.68 and 7.22 respectively, no significant disparity in between. Their scale parameters, representing the strength, are 8.44 GPa for HM fiber and 5.76 GPa for AS fiber. The HM scale parameter is notably larger than the AS scale parameter. The average fracture loads are 699 mN for HM fiber and 521mN for the AS fiber. Again, HM load is higher than the AS load.

One of the authors identifies the internal structure of the AS fiber in a diagram shown in Fig. 5 [8]. The fiber is made up of micro-fibrils bound together in the fiber direction. The micro-fibrils are not fused with each other, separated by micro-voids running in the fiber direction. The density of the micro-voids changes little in the direction to the center. By comparison, no micro-voids are seen on the fiber's surface, which is made of a very thin skin layer, about 0.2 μm thick. A DF image analysis is made of the size of the fiber crystal in the X-ray scattering and TEM methods. The analysis shows that the HM crystal size, 160 A in the fiber direction and 110 A in the diametric direction, is about twice as large as the AS size, 96 A and 55 A in the respective directions. This means that the degree of crystal orientation in internal molecules of HM fiber is higher than that of AS fiber.

Polymeric fibers are generally known to increase rigidity with a rise in crystallinity [9]. Micro-voids and other defects are said to decrease or vanish in thermal extension and processing [10].

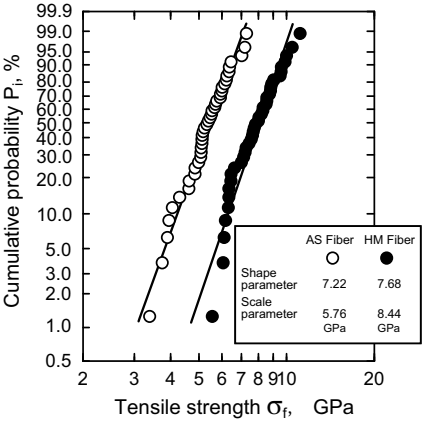


Fig. 4 Weibull distributions of tensile strength of HM and AS fibers.

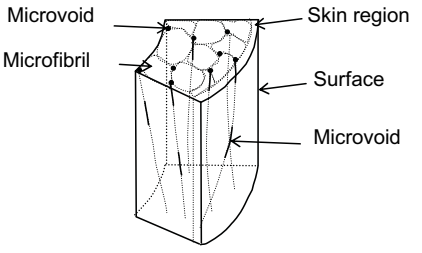


Fig. 5 Schematic illustration of internal structure of PBO fiber.

In HM fibers, the crystal area increases in thermal processing and the density also increases (Table 1), an indication of a significant decrease in micro-voids. These finding lead to the presumption that HM fibers become stronger than AS fibers, because internal molecules are crystallized and micro-voids and amorphous parts decrease or vanish in thermal processing.

Fatigue Strength Properties

Figure 6 shows fatigue test results of HM and AS fibers. The vertical scale marks stress amplitude σ_a while the horizontal scale marks the number of cycles to fracture N_f. Symbols of ●, ▲ and ■ give data when the stress ratio *R* is 0.1, 0.5 and 0.7. Data on fractures that occur in 10 cycles or less are not collected because such a small N_f indicates that fibers fracture before reaching the preset load waveform. Solid lines, broken lines and dotted broken lines plot results of linear regression of stress ratio data based on the weighted minimum square estimation. AS fiber stress ratio data are marked by symbols of ○, △ and □that represent 0.1, 0.5 and 0.7 in the stress ratio *R*. A narrow solid line, narrow broken line and narrow dotted broken line approximate the relationship between cumulative probability and tensile strength.

Regardless of variance in data on HM fiber stress ratios, Figure 6 shows that the ratios can be approximated to straight lines falling down from left to right on a single logarithm graph. With an increase in the stress ratio, strength at the same N cycles decreases and the approximation lines tend to decrease in angle. It is evident that HM fiber S-N properties, sorted out by stress amplitude σ_a, clearly

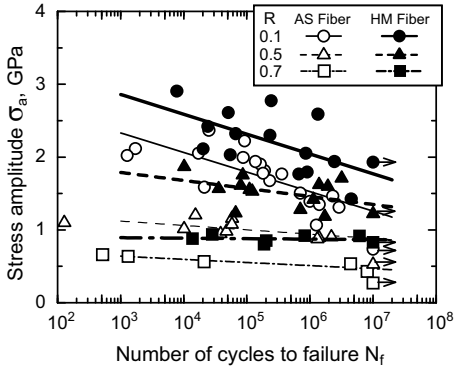


Fig. 6 S-N curves plotted stress amplitude in ordinate for HM and AS fibers.

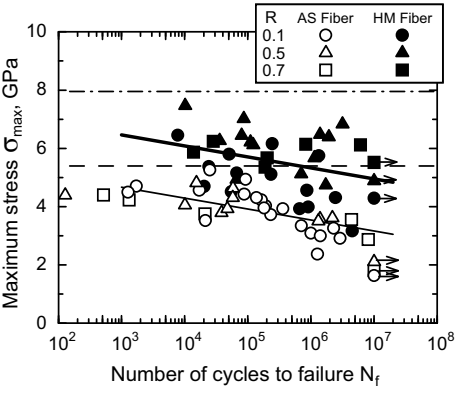


Fig. 7 S-N curves plotted maximum stress in ordinate for HM and AS fibers.

shows dependency on the stress ratio. Stress amplitude of HM fibers is larger than that of AS fibers at any stress ratio. Fatigue strength of HM fibers is higher than that of AS fibers, as is tensile strength. But stress ratio dependency of HM fibers is similar to that of AS fibers.

Figure 7 shows relationship between maximum stress σ_{max} and the number of cycles to failure N_f in HM fibers. The symbols of ●, ▲ and ■ in the chart gives data on 0.1, 0.5 and 0.7 in stress ratio the stress ratio *R* . Solid lines mark maximum stress regressed to them based on a weighted minimum square estimation. The thin dotted broken line shows average tensile strength, 7.93 GPa, equivalent to 10.91 μm, obtained in the previous section. The average diameter of fibers used for the fatigue test is 10.93 μm, very close to 10.91 μm, making any adjustment unnecessary. Data on maximum AS fiber stress are marked by symbols of ○, △ and □ corresponding to = 0.1, 0.5 and 0.7 in stress ratio *R*. The narrow line, as in HM fibers, plots all data regressed to the line based on a weighted minimum square estimation. The thin broken line gives the average tensile strength 5.39 GPa.

Variance in maximum stress in HM fibers is relatively large when the stress ratio *R* is 0.1, and becomes larger when *R* becomes smaller. Regardless of the stress ratio, maximum stress is plotted near the solid lines, meaning linear relationship established on a logarithm graph. Unlike in Fig. 6, where data are sorted out by stress amplitude σ_a, the maximum stress σ_{max} appears not as notably dependent on the stress ratio. In spite of some variance, fatigue strength of AS and HM fibers can be controlled primarily by the maximum stress. S-N properties of AS and HM fibers are affected more by the maximum stress than by stress amplitude. The solid line of HM fibers is higher than the AS solid line. Like tensile strength, fatigue strength of HM fiber marks high values.

Fatigue strength of polymeric material becomes higher with an increase in its crystallinity and an increase in molecular weight. HM fibers are stronger than AS fibers in fatigue because of progression of crystallization in thermal processing. There is no significant disparity between the two fibers as to effects of the stress ratio.

Figure 8 shows fatigue endurance limits corresponding to strength at different N cycles, obtained from Figs. 6 and 7. The vertical scale represents stress amplitude σ_a while the horizontal scale gives mean stress σ_m. The symbols of ●, ▲, ■ and ▼ shows strength at cycles of 10^4, 10^5, 10^6 and 10^7. The dotted broken line represents strength threshold limit ($\sigma_m + \sigma_a = 7.93$ GPa). AS fiber strength at N cycles are given by symbols of with ○, △, □ and ▽.

As shown by solid lines, HM fiber fatigue endurance limits corresponding to strength at individual N cycles bend like a Gerber curve with a decrease in the stress ratio. By comparison, AS fiber fatigue endurance limits looks like a modified Goodman line. This indicates HM fibers have stronger dependency on stress amplitude than AS fibers in all life spans with a decrease in the stress ratio. This is considered to be a factor in larger variance in maximum stress in HM fibers than in AS fibers, as in Fig.7.

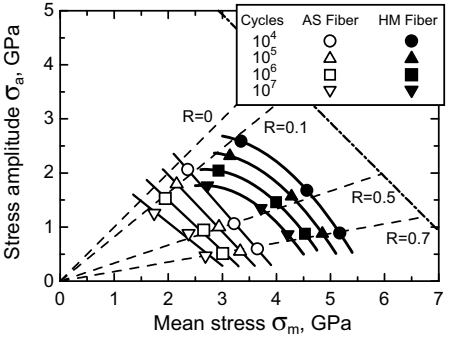
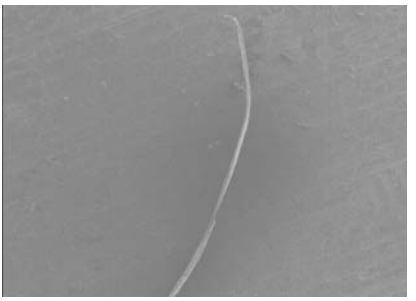


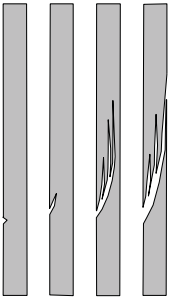
Fig. 8 σ_a-σ_m curves of HM and AS fibers.



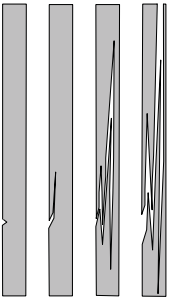
(a) Tensile fracture with a splitting.

(b) Fatigue fracture with multiple splitting in a PBO fiber.

Fig. 9 SEM photographs of tensile and fatigue fracture surface in AS type PBO fiber.



(a) Tensile fracture.



(b) Fatigue fracture.

Fig. 10 Schematic diagrams of tensile and fatigue fracture process in PBO fiber.

Fatigue behavior of HM fibers in a low stress ratio can be explained as follows. Non-crystallized areas decrease in HM fibers with crystallization underway in thermal processing. Molecules in such areas are aligned in one direction gradually by load until they play a role in reducing stress concentration. They are aligned relatively fast in high stress amplitude with the stress ratio of 0.1, for example. The mechanism of stress being reduced is restricted. As a result, it is presumed that dependency on stress amplitude, as seen in brittle material, becomes stronger.

Fracture Morphology

Figure 9 showed SEM photographs of tensile and fatigue fracture surface in AS type PBO fibers. Tensile and fatigue fracture specimens show long fracture with extensive splitting in a fiber direction. The splitting length in fatigue fracture specimen is longer than that of tensile one. These tendencies of AS fiber were similar to those of HM fiber.

Figure 10 shows schematic diagrams of tensile and fatigue fracture process in PBO fibers. The shear coefficient of elasticity and the shear strength of the fiber are very smaller than a tensile coefficient of elasticity and the tensile strength for the fiber direction is expected by fiber structure to show in Fig. 5. Therefore the crack develops in fiber direction. Because the crack develops slowly during cyclic loading, the splitting length in fatigue fracture specimen is longer than that of tensile one.

Summary

1. Tensile strength of HM fiber becomes higher than that of AS fibers, because internal molecules in fiber are crystallized and micro-voids and amorphous parts decrease or vanish in thermal processing.
2. S-N properties of HM fibers show clear dependency on the stress ratio when they are sorted out by stress amplitude σ_a. AS fibers show a similar tendency. But HM fatigue strength is higher than AS fatigue strength. There is no notable disparity between the two fibers in terms of effects of the stress ratio when their S-N properties are sorted out by maximum stress σ_{max}. In spite of variance, fatigue life of two fibers can be controlled by maximum stress σ_{max} effectively. Maximum stress σ_{max} can be a valid parameter to estimate fatigue lifespan.
3. HM fiber fatigue endurance limits corresponding to strength at individual N cycles bend with a decrease in the stress ratio like a Gerber curve. The endurance limits are subject to stress amplitude. But AS fibers show behavior like a modified Goodman line. This is probably because non-crystallized areas decrease in HM fibers with crystallization underway in thermal processing. Molecules in such areas are aligned in one direction gradually by load until they play a role in reducing stress concentration. They are aligned relatively fast in high stress. As a result, the mechanism of stress being reduced is restricted. It is presumed that dependency on stress amplitude, as seen in brittle material, becomes stronger.
4. Tensile and fatigue fracture specimens show long fracture with extensive splitting in a fiber direction. The splitting length in the fatigue test specimens is much longer than that in the tensile test specimens

References

[1] K. Yabuki, “Origin of the strength of super fibers”, Journal of the Textile Machinery Society of Japan, Vol. 48, No. 12, pp. 448-454 (1995).

[2] “Small-diameter high-strength optical drop and indoor cables with PBO-FRP strength member”, Furukawa Review, No. 29, pp.31-32 (2006).

[3] Z. Wu, J. Yin and H. Niu, “Some recent achievements in FRP bonding techniques”, FPR Composites in Civil Engineering, Vol. II, pp. 1021-1032 (2001).

[4] T. Kitagawa and K. Yabuki, “An investigation into the relationship between internal stress distribution and a change of poly-p-phenylenebenzobisoxazole (PBO) fiber structure”, Journal of Polymer Science: part B: Polymer Physics, Vol. 38, pp. 2901-2911 (2000).

[5] K. Kitagawa, K. Yabuki and R. J. Young, “An investigation into the relationship between processing, structure and properties for high-modulus PBO fibers. Part 1. Raman band shifts and broadening in tension and compression”, Polymer, Vol. 42, pp.

[6] N. Horikawa, Y. Haruyama, A. Sakaida and M. Ueda, “Fatigue strength of poly-p-phenylene benzobisoxazole (PBO) fibers”, Journal of the Society of Materials Science Japan, Vol. 54, No. 8, pp. 875-880 (2005).

[7] “Technical information (Revised 2005.6)”, p. 3 (2005) TOYOBO CO., LTD.

[8] T. Kitagawa, H. Murase and K. Yabuki, “Morphological study on poly-p-phenylenebenzobisoxazole (PBO) fiber”, Journal of Polymer Science: part B: Polymer Physics, Vol. 36, pp. 39-48 (1998).

[9] “Strength and fracture materials”, (2003) The Society of Materials Science, Japan.

[10] “Senikougaku II”, (1996) The Textile Machinery Society of Japan.