1. Introduction

High-strength fibers from liquid crystalline polymers are used for bulletproof vests and firefighting clothing because of their excellent impenetrable, anti-blade and heat-resistant properties, in addition to their high values of specific strength and specific elastic modulus. These fabrics are exposed to repeated deformation when they are being used, and the fatigue resistance is extremely important specifically for high-strength fibers from liquid crystalline polymers because these fibers have microfibrillar structures that tend to split because of repeated deformation.

The tensile fatigue process of various metals and plastics is as follows. Cracks are formed at a certain fatigue cycle number during tensile fatigue deformation and grow with increasing fatigue cycle number. Thus, the stress intensity factor at the crack tip increases. The tensile fatigue behaviour can be represented by the relationship between the crack growth rate, $dc/dN$ and the range of the stress intensity factor, $\Delta K$, which is defined as

$$\Delta K = K_{\text{max}} - K_{\text{min}}.$$  \hspace{1cm} (1)

Here, $c$ is crack length, $N$ is fatigue cycle number and $K_{\text{max}}$ and $K_{\text{min}}$ are respectively the maximum and minimum values of the stress intensity factor at the crack tip during each fatigue cycle. In many cases, the log($dc/dN$)-versus-log$\Delta K$ curves can be divided into three regions. In the region where $\Delta K$ is smaller than a certain critical value, the crack does not grow (region I). In the region where $\Delta K$ is remarkably large, log($dc/dN$) significantly increases, leading to unstable failure (region III). Between these regions, a region exists where log($dc/dN$) stably increases with increasing $\Delta K$ (region II). For various metals and plastics, the log($dc/dN$)-versus-log$\Delta K$ curves in region II generally follow Paris’ law [1], which is represented by
\[ \frac{dc}{dN} = a (\Delta K)^m. \]  

(2)

where \( a \) and \( m \) are material parameters.

For general-purpose plastics, shear deformation and formation of crazes and microvoids are the mechanisms for the progress of fatigue damages in region II. However, for high-strength fibers from liquid crystalline polymers such as poly(p-phenylene-2,6-benzobisoxazole) (PBO) and poly(p-phenylene terephthalamide) (PPTA), the fatigue damages are considered to progress in a completely different manner because of the microfibrillar fiber structure. Horikawa et al. [2] performed fatigue tests on the PBO fiber. They found that the fiber exhibits clear fatigue behaviour and that the fatigue strength decreases as the average load applied to the fiber during the test increases. Kobayashi et al. [3] investigated the effects of fiber folding on the tensile properties of the PPTA and PBO fibers. They reported that a severe drop-off in tensile strength and tensile strain at break occurs in the PBO fiber, whereas at most, a slight drop-off in these mechanical properties arises in the PPTA fiber. These experimental results have been interpreted with regard to the splitting of the microfibrils. In addition, they investigated the microvoid size and the fracture surface of the tensile fatigue tested PBO fibers [4]. From these experiments, they found that with increasing number of tensile fatigue cycle, the microvoid size perpendicular to the fiber axis direction increases and the bond between fibrils is weakened.

Although it has been noticed that the mechanical properties of the PBO fiber deteriorate due to fatigue as shown above, the influences of fatigue on the compressive strength and the growth of microvoids during tensile deformation are still unclear. Based on such a background, the present study investigated the progress of the tensile fatigue damages of the PBO fiber based on the structure analysis using the synchrotron radiation small-angle X-ray scattering (SAXS) and the measurement of the single-fiber axial compression strength. The single-fiber axial compression test was adopted for the experiment because the axial compression strength is considered to be sensitive to the splitting of the microfibrils.

2. Experimental

2.1 Tensile fatigue test

The PBO fiber used in the present study had tensile strength of 5.8 GPa, tensile modulus of 180 GPa, tensile strain at break of 3.5% and density of 1.54 g cm\(^{-3}\) (catalog data).

For the SAXS measurements of the fatigue-tested fibers, 10 filaments of the PBO fibers were aligned in parallel and bonded to a template using an epoxy resin at the gauge length of 25 mm. After the lateral sides of the template were cut, cyclic tensile stress was applied to the fiber bundle at a frequency of 10 Hz. The maximum stress applied to the fiber bundle during a fatigue cycle, \( \sigma_{\text{max}} \), was 4.0 GPa, and the ratio of the minimum and maximum stress was 0.25. The total number of fatigue cycles varied among \( 1.6 \times 10^4, 1.28 \times 10^5 \) and \( 1.0 \times 10^6 \).

For the single-fiber axial compression tests of the fatigue-tested fibers, cyclic tensile stress was applied to a single filament with the gauge length of 60 mm at a frequency of 10 Hz. The maximum stress, \( \sigma_{\text{max}} \), was 2.0 and 4.0 GPa, and the ratio of the minimum and maximum stress was 0.25. The total number of fatigue cycles varied among \( 4.0 \times 10^3, 1.6 \times 10^4 \) and \( 1.28 \times 10^5 \).

2.2 Small-angle X-ray scattering

The volume fraction of the scattering bodies such as microfibrils and microvoids in the fiber was determined by measuring the SAXS from the PBO fiber bundle using a diffractometer (Rigaku Denki) with a position-sensitive proportional counter. The incident beam was pinhole-collimated Cu \( K\alpha \) radiation, and the specimen-to-detector distance was 350 mm.

The volume fraction of the scattering bodies was determined by comparing the integrated SAXS intensities of the specimen and the standard specimen in accordance with the method proposed in our laboratory [5,6].

The SAXS measurements on the fatigue-tested fiber bundle in the static state and during tensile deformation used the beamline BL6A of the High Energy Accelerator Research Organization, Japan. The SAXS was detected using a CCD camera (C7300, Hamamatsu Photonics) attached with an image intensifier. The X-ray wavelength, beam cross-section sizes and specimen-to-detector distance were 0.15 nm, 0.3 mm \( \times \) 0.3 mm and 2.1 m, respectively.

The length of the microvoids measured in the fiber axis direction (axial microvoid length, \( L_3 \)) can be determined from the broadening of the azimuthal
SAXS intensity distribution of the fibers [7]. The microvoids were assumed to have a needle-like shape with a constant cross section along the longitudinal direction. Moreover, the intensity distribution caused by the orientation distribution of the microvoids was assumed to follow a Gaussian distribution. Then, the axial microvoid length was determined by using the following equations:

\[
[B_{\text{axial}}(s)]^2 = \frac{4\ln 2}{\pi L_3^2} + [B_{\text{void}}] s^2
\]

Here,

\[s = \frac{2}{\lambda} \sin \theta.
\]

\(\lambda\) is X-ray wavelength, \(2\theta\) denotes scattering angle, \(s\) represents the magnitude of the scattering vector and \(B_{\text{axial}}(s)\) denotes the full width at half maximum of the azimuthal SAXS intensity distribution along a circle with radius \(s\) around the centre of the pattern. Moreover, \(B_{\text{void}}\) represents the full width at half maximum of the intensity distribution caused by the orientation distribution of the microvoids.

2.3 Single-fiber axial compression test

The specimens utilised for the single-fiber axial compression tests were prepared in the following manner. A single fiber was bonded, using an epoxy resin cured at 40 °C for 24 h, to a small steel plate to ensure that the short length of the fiber end protrudes from the epoxy resin. These specimens were gold sputtered, and the protruding fiber ends were cut using a focused ion beam milling apparatus (FIB) at a protruded fiber length/fiber diameter ratio of 1.5.

Fig. 1 schematically illustrates the equipment used for measuring the single-fiber axial compression strength, consisting of an X-stage driven with a stepper motor for moving the specimen, an indenter with a mirror-finished surface, a load cell for measuring the compression load and an optical microscope for observing the specimen. The specimen was mounted on the stage, moved at 3µm min\(^{-1}\) toward the indenter and stopped just before the fiber touched the indenter. After adjusting the alignment of the specimen to ensure that the end faces of the indenter and fiber are set in parallel, the specimen was pushed to the indenter. For each fatigue condition, 10 specimens were tested.

3. Results and discussion

3.1 Changes in fiber structure owing to tensile fatigue

Fig. 2 illustrates the SAXS pattern of the original PBO fiber without a fatigue test, where the fiber axis is in the vertical direction of the figure. The scattering pattern is in the form of an elongated equatorial streak, indicating that the scattering bodies in the fiber have a large aspect ratio with a long axis highly oriented parallel to the fiber axis. In the production process of the PBO fiber, the PBO solution with nematic liquid crystalline characteristics is extruded through the spinneret into the solidification liquid, and during this process the swollen network of microfibrils with microvoids between microfibrils is formed [8,9]. The origin of this scattering has two possibilities, namely microfibrils and microvoids. However, the scattering bodies were determined as microvoids because the volume fraction of these microvoids was assumed to have a needle-like shape with a constant cross section along the longitudinal direction.
bodies was as low as 1.4%.

Fig. 3 illustrates the time variation of the axial microvoid length, \( L_3 \), in response to the variation of the tensile stress during the loading and unloading cycle of the original PBO fiber without a fatigue test. At the macroscopic fiber tensile strain of 2.3%, the increase in axial microvoid length is 21%. If the fiber undergoes the affine-like deformation, the local region of the fiber deforms similarly to the whole fiber and the increase in the axial microvoid length should be as small as 2.3%. The extremely large increase in the axial microvoid length is, therefore, due to the microfibril splitting. Once the microfibrils split, they don’t return to its original length when unloaded as is known from Fig. 3. As a result, the axial microvoid length increases steadily with increasing fatigue cycle number.

Fig. 4 illustrates the variation of the axial microvoid length with a fatigue cycle number for the PBO fiber, where the SAXS was measured without applying tensile deformation to the fiber. The increase in the axial microvoid length with increasing fatigue cycle number is due to the microfibril splitting. The comparison of Figs 3 and 4 indicates that the increment of the microvoid size caused by two times fatigue cycle is larger than that caused by \( 1.6 \times 10^6 \) times fatigue cycle. This is because the microvoids which have been present in the original fiber grow rapidly at the very beginning of fatigue, while many new microvoids with small sizes are formed thereafter. Thus the average microvoid size once decreases in the initial stage of the fatigue process.

Fig. 5 presents the variation of the axial microvoid length, \( L_3 \), in response to the tensile stress during tensile deformation for the original and fatigue-tested PBO fibers illustrated in Fig. 4. This figure indicates that the axial microvoid length increases not

![Fig. 3](image3.png)

**Fig. 3** Time variation of (a) the axial microvoid length, \( L_3 \), in response to (b) the tensile stress during loading and unloading cycle of the original PBO fiber without a fatigue test.

![Fig. 4](image4.png)

**Fig. 4** Variation of the axial microvoid length, \( L_3 \), with fatigue cycle number for the PBO fiber where the SAXS was measured without applying tensile deformation to the fiber. The maximum stress applied during the fatigue cycle, \( \sigma_{\text{max}} \), was 4.0 GPa.

![Fig. 5](image5.png)

**Fig. 5** Variation of the axial microvoid length, \( L_3 \), in response to the tensile stress during tensile deformation for the original and fatigue-tested PBO fibers illustrated in Fig. 4. The maximum stress applied during the fatigue cycle, \( \sigma_{\text{max}} \), was 40 GPa. The fatigue cycle numbers applied to the fibers are indicated in the figure.
only during the fatigue tests but also during the tensile deformation after the fatigue tests. The increase in the axial microvoid length during tensile deformation is smaller for the fibers fatigue tested with the larger fatigue cycle number. For the fibers fatigue tested with the largest fatigue cycle number, the axial microvoid length almost unchanged during the tensile deformation after the fatigue tests, which suggests that the axial microvoid length saturates to a certain value at the large fatigue cycle number. Meanwhile, for the fibers fatigue tested with a small fatigue cycle number, the axial microvoid length was remarkably lower than the saturated value, and an allowance exists for the axial microvoid length to increase during tensile deformation after the fatigue test.

3.2 Changes in single-fiber axial compression strength owing to tensile fatigue

To avoid flexural failure of the fiber during the single-fiber axial compression test, aligning the specimen is crucial to ensure that the end face of the indenter is set parallel to the fiber end face and perpendicular to the fiber axis. Fig. 6 presents the comparison of the load‒displacement curves of the single-fiber axial compression tests on the original PBO fibers, for which the flexural failure could and could not be avoided. The load‒displacement curve bends from the beginning of the test if the flexural failure could not be avoided. However, it follows a straight line if the flexural failure could be prevented. The axial compression strength can be calculated only with the latter case. The single-fiber axial compression strength of the original PBO fiber without a fatigue test was determined to be 197 MPa. This value is close to the reported values, that is, 190 MPa [10] and 200 MPa [11], of the axial compression strength of the PBO fiber.

Fig. 7 presents the SEM images before and after the single-fiber axial compression tests on the original PBO fiber, for which the flexural failure could be avoided. The figure shows that the kink band is formed when the fiber failed due to axial compression.

Fig. 8 presents the variation of the single-fiber axial compression strength of the PBO fiber with the fatigue cycle number. The PBO fiber fatigue tested by applying the maximum stress of 2 GPa (35% of the tensile strength) during the fatigue cycle did not indicate a marked reduction in the axial compression strength. By contrast, the fiber tested for fatigue by applying the maximum stress of 4 GPa (70% of the tensile strength) decreased to 15% at the cycle number of $1.28 \times 10^5$.

Based on the SEM images of Fig. 7, we propose that the PBO fiber fails under axial compression in the following manner (Fig. 9). The microfibrils in the fiber are not aligned completely in parallel to the fiber axis but have some misorientation. When the axial compression stress is applied to the misoriented microfibrils, they are compelled to increase the

![Fig. 6 Load-displacement curves of the axial compression tests on the original PBO fibers without a fatigue test. The flexural failure (a) could and (b) could not be avoided.](image)

![Fig. 7 SEM images (a) before and (b) after the single-fiber axial compression tests on the original PBO fiber without a fatigue test for which the flexural failure could be avoided.](image)
misorientation angle and the shear force arises at the interface between the neighbouring microfibrils. If the interface between the neighbouring microfibrils can bear the shear stress, the fiber is intact. However, if the axial compression stress is increased and the interface cannot bear the shear stress, splitting of the microfibrils and the growth of the already existing splitting take place which yields kink band and results in the axial compression failure of the fiber. The kink band is formed at the end face of the fiber since the shear deformation is easier to take place there.

Kim et al. [12] analysed the axial compression failure of the unidirectional fiber-reinforced composites and proposed an equation representing the axial compression strength of the composites when they fail along with the kink band formation because of the fiber-matrix interfacial failure in the region where the fibers are misoriented. The axial compression failure of the high-strength fibers from liquid crystalline polymers can be analysed similarly by regarding the microfibrils and their splitting for the high-strength fibers from liquid crystalline polymers as the fibers and the fiber-matrix interface failure for the unidirectional fiber-reinforced composites. Then, the axial compression strength of the high-strength fibers from liquid crystalline polymers, \( \sigma_c \), can be represented by the following equation, which can be derived by modifying the equation representing the axial compression strength of the unidirectional composites.

\[
\sigma_c = \left( \frac{1}{\tan \phi_o} + \frac{E_t}{G} \tan \phi_o \right) \tau_i / c_0, \tag{5}
\]

where \( \phi_o \) is the misorientation angle of the microfibrils from the fiber axis, \( E_t \) is the lateral modulus of the fiber, \( G \) is the shear modulus of the fiber with regard to the shear stress in the fiber axis direction, and \( \tau_i \) is the shear stress of the microfibrils when they split. This equation suggests that the increase in microvoid length causes the reduction in the axial compression strength of the PBO fiber as follows. If the microvoid length increases, the intact portion of the contact area between neighbouring microfibrils decreases. This causes the reduction of the resistance of the interface between neighbouring microfibrils against the shear stress which leads to the decreases in \( \tau_i \) and the axial compression strength. This equation also suggests that the axial compression strength of the PBO fiber reduces when a large tensile stress is applied to the fiber since the axial microvoid length increases in response to the tensile
stress as shown in Fig. 5. In order to improve the fatigue resistance of the PBO fiber, it is essential to increase the bonding strength between microfibrils.

4. Conclusions

The progress of the fatigue damages for the PBO fiber has been investigated based on the structure analysis using the synchrotron radiation SAXS and the measurement of the single-fiber axial compression strength. The microvoids formed by the splitting of the microfibrils due to the tensile fatigue deformation yield the elongated equatorial streak in the SAXS pattern. The axial microvoid length increased with increasing fatigue cycle number owing to the splitting of the microfibrils, thereby causing a reduction in the axial compression strength of the fiber. The axial microvoid length also increased during the tensile deformation after the tensile fatigue deformation. The axial compression failure of the single PBO fiber was accompanied by the formation of the kink band. Moreover, an equation representing the axial compression strength of this type of fiber has been proposed. Thus, the bonding strength between microfibrils must be increased to improve the fatigue resistance of the PBO fiber.

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