Effect of Alkali-Treatment on Tensile Properties of Kenaf Long Fibres using Data-based Cross-sectional Area Approximation Method

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Abstract

A cross-sectional area evaluation method for multi-cell type natural fibres treated in a highly concentrated alkali solution was proposed using kenaf fibres. Cross-section of kenaf fibres was drastically changed by the alkali treatment compared to the untreated fibres. Conventional data-based approximation (DBA) method for evaluating cross-sectional area was not sufficient, because it was based on cross-sectional area data of the untreated fibres. Therefore, DBA for alkali-treated multi-cell type fibres was newly developed on the assumption that each cell in the fibre is an elliptical shape. Results showed that the tensile strength was greatly improved, compared to the strength values estimated by untreated fibre-based DBA.

1 Introduction

Nowadays, global environmental problems about CO_2 emission become serious concerns, and therefore a number of biomass-based material researches are increasingly being developed. Environmentally friendly green composite using kenaf fibre and polylactic acid (PLA) is the promising material in the field of composite materials. It has already been used in cellular phones and automobile interior parts. However, practical kenaf/ PLA composites are often produced as an injection-moulded material, in which the morphology of reinforcement is short fibres. On the other hand, it has not been enough reported about the mechanical properties of a long kanaf fibre/ PLA composite. In the field of natural fibre-reinforced composites, a certain chemical treatment is applied to natural fibres to improve interfacial properties between natural fibres and resin. Alkaline treatment is one of the most typical chemical treatments, and often changes mechanical properties of the fibres. Kawahara, et al. [1] explored the mechanical properties of alkali-treated kenaf fibre by changing concentration of the aqueous solution of NaOH in the relatively low range, i.e. 1 to 7 %. The results showed that tensile strength of the treated fibres did not change so largely. On the contrary, alkali-treated kenaf fibre reinforced composites indicated high flexural strength and modulus [2]. It is guessed from the above that, although low concentration alkali-treated kenaf fibres can improve mechanical properties of the composites, this is mainly caused by interfacial improvement. When single-cell type natural fibres such as ramie are mercerized by high concentration alkali solution, the mechanical properties are dramatically changed, especially in fracture strain [3]. On the other hand, the effect of mercerization has not been explored sufficiently for multi-cell type natural fibres such as kenaf.

Meanwhile, Fig. 1(a) shows a cross-sectional microphotograph of a kenaf fibre. As observed in the figure, the shape of the fibre cross-section is not circle, but quite complicated. Cross-sectional area of general natural fibres including kenaf has often been estimated as a circle through measurement of the fibre projection width. This estimation is clearly different from actual cross-sectional area, and results in bringing over- or under-estimation in strength. To correct such wrong estimation, a cross-sectional area estimation method called DB-based approximation method (DBA) was proposed [4]. DBA method is based on the database for a distribution of actual area obtained from cross-sectional images of natural fibres. Although this method was proposed for untreated natural fibres, the shape of cross-section is often changed by alkali treatment. Therefore, the conventional DBA is needed to be modified.

The purpose of this study is to investigate the effect of high concentration alkali treatment on the tensile properties of kenaf fibres. In addition, a new methodology for cross-sectional area measurement of alkali-treated multi-cell fibres is proposed.

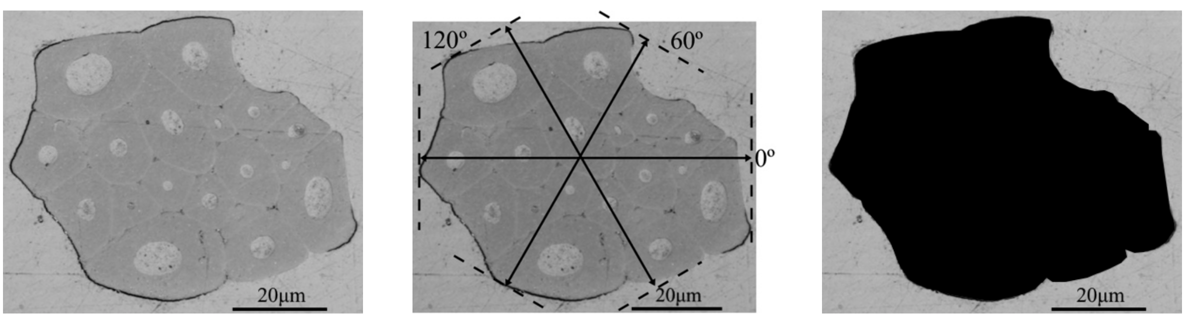
2 Experimental

2.1 Materials

Kenaf fibres (Hibiscus cannabinus), harvested in Vietnam was used in this study. Alkali treatment was applied at room temperature to the fibres in a 10wt%NaOH solution for two hours or a 15wt%NaOH for one, two, four or six hours. Hereinafter, untreated fibres are denoted as UT, and alkali-treated fibres are denoted as AT followed by (concentration) - (treating time). For example, AT15-2 means alkali-treated fibres in a 15wt%NaOH solution for two hours.

2.2 Cross-sectional area measurement

The methodology of DBA used in this study is such that the fibre cross-section is first approximated as a shape of hexagon, as presented by broken line in Fig. 1(b). It consists of three diagonal lines corresponding to three projective widths, measured from 0º, 60º, and 120º as shown in Fig. 1(b). Next, as indicated in the image painted in black in Fig. 1(c), the actual cross-sectional area of the fibre is measured using an image analysis. In this case, the hexagon area was calculated as 15,701 μm^2, while the actual cross-sectional area was analyzed as 12,615 μm^2. Therefore, this approximated area is needed to be revised, as mentioned later. Approximated shapes of the cross-section in this study were a circle, ellipse, octagon, dodecagon and icositetragon, in addition to hexagon. Hereinafter, the actual cross-sectional area is denoted as A_f, and the approximated area is denoted as $\tilde{A}_f$. The relations between the actual cross-sectional area, and the circle, ellipse and four polygonal-approximated areas are shown in Figs. 2(a) - (f) in filled circle, respectively. It is proved that circle- and ellipse-assumed $\tilde{A}_f$ in the figs (a) and (b) vary more widely than polygon-assumed $\tilde{A}_f$ in the figs. (c),



(a) Micrograph of cross-section (b) Hexagonal-assumed image (c) Painted image

Figure 1. Optical micrograph of cross-section on a kenaf fibre and methodology for measurement of cross-sectional area.

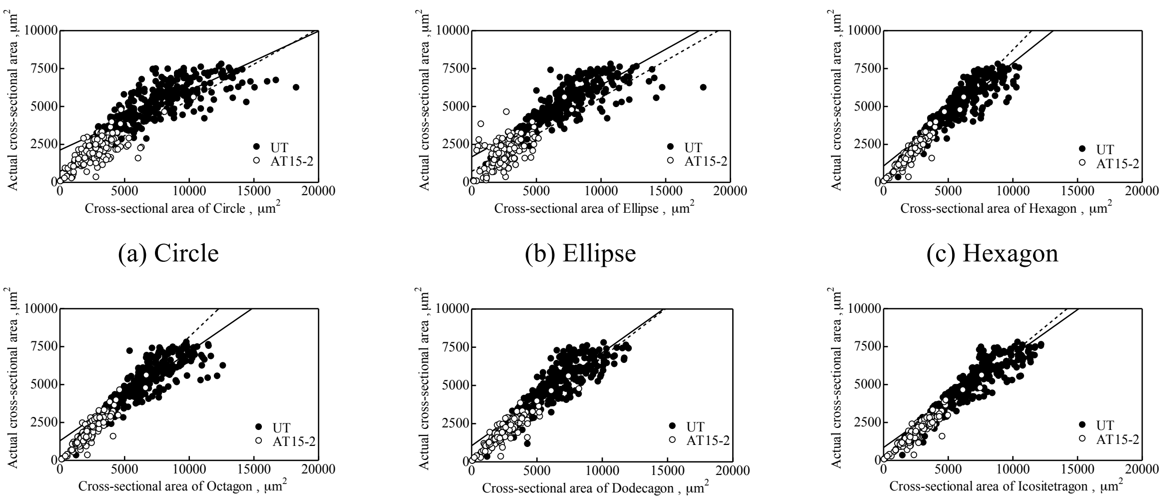
(d), (e) and (f). Table 1 shows average values of the cross-sectional areas, and correlation coefficients between A_f and $\tilde{A}_f$. It is found that, while all averages of $\tilde{A}_f$ are larger than A_f, any polygon-approximated $\tilde{A}_f$ is more correlated with A_f, as compared to circle- and ellipse-assumed $\tilde{A}_f$. Correlation coefficients are relatively high in hexagon- and icositetragon approximations. In the case of hexagon-approximated area, the linear relation between A_f and $\tilde{A}_f$ is given as:

$$A_f{}^* = 0.680\tilde{A}_f + 1080 \quad (1)$$

Where, A_f^* is an estimated cross-sectional area as a function of $\tilde{A}_f$. We suppose first that eq. (1) is applicable for alkali-treated kenaf fibres as well as untreated ones.

2.3 Tensile test

Single fibre tensile tests were carried out using a tension and compression testing machine developed in the authors' laboratory, to which a 20N load cell was attached. The gauge length of the tensile specimen was 25 mm, the tensile speed was 1.0 mm/min and the number of samples in each condition was ten. The projective widths of the specimen were measured



(a) Circle (b) Ellipse (c) Hexagon

(d) Octagon (e) Dodecagon (f) Icositetragon

Figure 2. Relationship between actual cross-sectional area and each assumed cross-sectional area for kenaf fibres.

Shape	A_f or $\tilde{A}_f$ [μm^2]	Correlation coefficient
Actual	5010	-
Circle	7356	0.800
Ellipse	7045	0.840
Hexagon	5783	0.900
Octagon	6338	0.880
Dodecagon	6494	0.871
Icositetragon	6865	0.909

Table 1. Correlation between actual cross-sectional area (A_f) and various assumed cross-sectional areas ($\tilde{A}_f$) for kenaf fibres.

from three directions of 0, 60 and 120 degrees at 0.1 mm interval along its axial direction, using a laser scan micro-meter (LSM-500S, Mitutoyo Corporation, Japan). Then, the shape of cross-section was approximated as a hexagon. Displacement during tensile test was measured using a laser displacement meter (KEYENCE, LS-7500).

2.4 X-ray diffraction approach

High concentration alkali treatment for natural fibres metamorphoses their crystalline structure from Cellulose I to II, called mercerization [3]. Mercerized ramie fibres decrease in strength and stiffness because of the decrease in the crystallinity index and the occurrence of Cellulose II. After metamorphosis into Cellulose II, this crystal structure brings the less elastic modulus into the fibres [5], but toughness of the fibres are improved because of partial disappearance in binder (hemicellulose) [3]. In this study, X-ray diffraction analysis of the alkali-treated kenaf fibres was conducted to identify the change in fibre structure using the X-ray diffraction apparatus (RINT-2500HF; Rigaku Corp.). The Cu Kα radiation (40 kV and 200 mA) was irradiated on the specimen with symmetric transmission geometry. These measurements were taken for a 2θ range from 5º to 35º. In this study also, *CrI* of UT and AT fibres was calculated using the following equation.

$$CrI = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100 \qquad (2)$$

Where, I_{002} is the maximum intensity of diffraction of the (002) lattice peak at a 2θ angle between 22° and 23°; I_{am} is the intensity of diffraction of the amorphous part, which is taken at a 2θ angle between 18º and 19° where the intensity is at a minimum [6].

3 Result and Discussion

3.1 Tensile properties

Hexagon-approximated $\tilde{A}_f$ were represented as an average of hexagonal area data measured at a 0.1 mm interval. Tensile strength was calculated using this average $\tilde{A}_f$. The average was further changed into A_f^* through eq. (1), and the corresponding tensile strength was estimated. The results are shown in Table 2. Because A_f^* is less than the average $\tilde{A}_f$, the estimated strength becomes higher. The latter strength using A_f^* is given more exactly because the fibre cross-sectional area is more appropriately estimated through DBA.

Table 4 shows results of tensile test for AT fibre specimens. Tensile strength of AT10-2 fibres and AT15 series fibres decreased compared to that of UT fibres. A15 fibres also decrease in tensile strength with treating time. Young's modulus of AT15 fibres was furthermore lowered to one-fifth to one-fifteenth less than that of UT fibres. The degree of the decrease in modulus is more intense than that of ramie [3]. On the other hand, AT15 fibres increased in fracture strain, in the same way as single-cell type natural fibres such as ramie. Especially, AT15-1 fibres show the largest fracture strain of all samples. From the viewpoint of toughness improvement, AT15-1 fibres exhibit three times higher in fracture energy than UT fibres. Fig. 4 indicates typical stress-strain curves of UT and AT fibres. Through the alkali treatment, the fibres decrease in strength and stiffness, as mentioned above. Especially, AT15-4 and AT15-6 fibres show a milder behavior in its slope at the initial stage, as compared to other fibres. It is guessed that lignin existing between cells was almost removed through the long time alkali treatments. Therefore, it is estimated that the initial mild behaviour arises from the unbalanced stress distribution in the separated cells.

3.2 X-ray diffraction approach

Figure 4 shows X-ray relative intensity of UT and AT fibres. Results show that the peak intensity of UT fibres exists at the diffraction angle 2θ of 16° and 22.5°, and also that the AT10 fibre shows the peak at the same diffraction angles. These diffraction angles are

	$\tilde{A}_f$ or A_f^* [μm²]	**Tensile strength [MPa]**
Hexagonal approximation	4517	260
Corrected by eq.(1)	3734	320

Table 2. Cross-sectional area and tensile strength calculated from hexagon-approximated cross-section and DBA.

Fibre type	A_f^* [μm²]	σ_f [MPa]	E [GPa]	ε_f [%]
UT	3734	320	30.8	1.28
AT10-2	2537	235	7.77	2.64
AT15-1	2987	263	6.67	6.14
AT15-2	2792	196	4.52	4.94
AT15-4	2748	198	5.21	3.57
AT15-6	3049	155	2.01	5.15

σ_f: Tensile strength, E : Young's modulus, ε_f : Fracture strain.

Table 3. Tensile properties of UT and AT fibres.

known to correspond to the peak intensity of Cellulose I being the crystal of untreated kenaf fibre [7]. However, the peak intensity of AT15 series fibres is in progress at the diffraction angles of 22°, corresponding to the peak intensity of Cellulose II [8], although the peak at 16° remains in the diagram. Therefore, mercerization is not perfectly completed under the given alkali-treatment conditions, but it occurs partly in the fibres. Table 4 shows the crystallinity index of UT and AT kenaf fibres. AT10 fibre shows roughly equal values to those of the UT fibre. However, the crystallinity index of any AT15 series fibre decreased about 25% less than that of UT fibre. It is considered that such a decrease in the crystallinity index as well as partial mercerization causes a more severe decrease in the fibre stiffness. We estimate that hemicelluloses between cellulose microfibrils (CMFs) as well as lignin in a kenaf fibre are at least partly removed through the alkali treatment, which engenders relative slippage between CMFs during tensile loading to the fibre. Therefore, it increases the fracture strain.

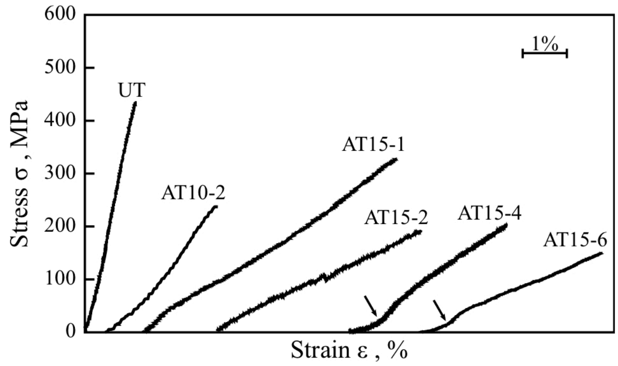


Figure 3. Typical stress-strain curves of UT and AT fibers.

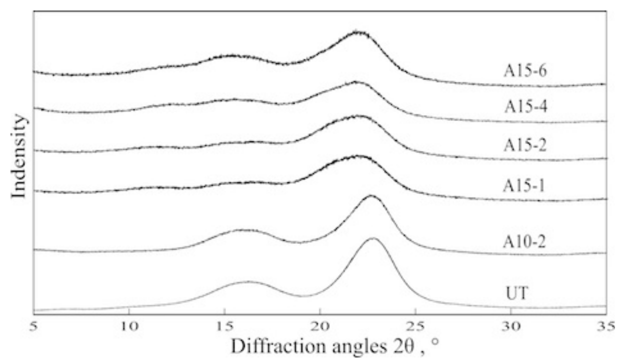


Figure 4. X-ray diffraction diagrams of UT and AT fibres.

	UT	Alkali-treated conditions				
		10-2	15-1	15-2	15-4	15-6
***CrI* [%]**	76.0	70.6	49.3	49.7	49.4	49.3

Table 4. Effect of NaOH concentration on the crystallinity index of kanaf fibres.

3.3 DBA for alkali-treated kenaf fibres

Cross-sectional shape of kenaf fiber was drastically changed by high concentration alkali treatment, as shown in Fig. 5(a). Many gaps between cells occurred due to removal of lignin. Thus, alkali-treated kenaf fibres should be reconsidered in evaluating cross-sectional area. In this study, DBA for alkali-treated fibre is newly proposed as follows:

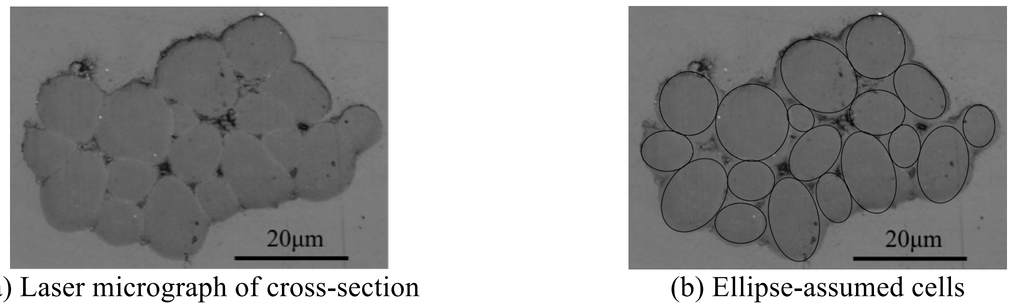
(1) Cross-section of each cell is approximated as an ellipse as shown in Fig. 5(b), and each area is summed up. This is defined as actual cross-sectional area.
(2) $\tilde{A}_f$ obtained from projection widths is estimated similarly to the conventional DBA.
(3) $\tilde{A}_f$ obtained in (2) is correlated to the actual cross-sectional area A_f obtained in (1), which leads to estimation of a linear approximation equation.

One hundred fifty nine micrographs of AT15-2 fibre cross-section were used to obtain the approximation equation. The results are added to Figs. 2 (a) – (f) by open circle. Results show that any open circle occupies less cross-sectional area. Any variation of polygon-approximated $\tilde{A}_f$ is less than that of circle-approximated and ellipse-approximated $\tilde{A}_f$, similarly to the case of filled circles. Table 5 shows average values of A_f and $\tilde{A}_f$ for AT15-2 fibres and their correlation coefficients. Results show that any average of $\tilde{A}_f$ is larger than A_f, and also any polygon-approximated $\tilde{A}_f$ is more correlated with A_f, as compared to circle-approximated and ellipse-approximated $\tilde{A}_f$, as in the case of UT fibres; the correlation coefficients between A_f and polygon-approximated $\tilde{A}_f$ are all greater than 0.9. The approximation equation for the alkali-treated fibre cross-sectional area was estimated from the comparison between A_f and hexagon-approximated $\tilde{A}_f$ in Fig. 2(c), as in the below.

$$A_f{}^* = 0.868\tilde{A}_f + 57 \qquad (3)$$

Because this evaluation method is DBA for AT15 series fibres, it is hereinafter denoted as DBA-AT. Tensile test results corrected by DBA-AT are presented in Table 6. The estimated area A_f^* is about 20% smaller than $\tilde{A}_f$ in Table 3, and results in increasing tensile properties of AT15 series fibres. From the comparison between original DBA and DBA-AT, it is proved that A_f^* estimated by the latter is about 16% smaller than the former. Therefore, the tensile strength and Young's modulus of AT series fibres increase from the original values. Figure 6 shows stress–strain curves corrected by DBA-AT. The AT15-1 fibre strength is comparable to that of UT fibres.

It is guessed that A_f^* obtained by DBA-AT is underestimated because gaps between cells are often evaluated exaggeratedly when drawing elliptical cells. Therefore, the whole fibre cross-section was painted in black and evaluated again as an actual cross-sectional area using image analysis. This method might be called an upper bound in estimating actual cross-sectional area because every gap separating cells is evaluated as an extra contained area. Comparison between the gap-contained and elliptical cell-based evaluations for cross-



(a) Laser micrograph of cross-section (b) Ellipse-assumed cells

Figure 5. Laser micrograph of cross-section on an alkali-treated kenaf fibre and ellipse approximation.

Shape	A_f or $\tilde{A}_f$ [μm^2]	ρ
Actual	2009	-
Circle	2731	0.751
Ellipse	2640	0.625
Hexagon	2249	0.944
Octagon	2444	0.918
Dodecagon	2604	0.909
Icositetragon	2762	0.937

ρ : Correlation coefficient

Table 5. Correlation between actual cross- sectional area (A_f) and various assumed cross- sectional areas ($\tilde{A}_f$) for alkali-treated kenaf fibres.

Fibre type	A_f^* [μm^2]	σ_f [MPa]	E [GPa]
AT15-1	2510	354	9.00
AT15-2	2211	250	5.90
AT15-4	2186	274	7.37
AT15-6	2862	187	2.54

σ_f: Tensile strength, E : Young's modulus

Table 6. Cross-sectional area and tensile properties by DBA-AT of AT15 series fibres.

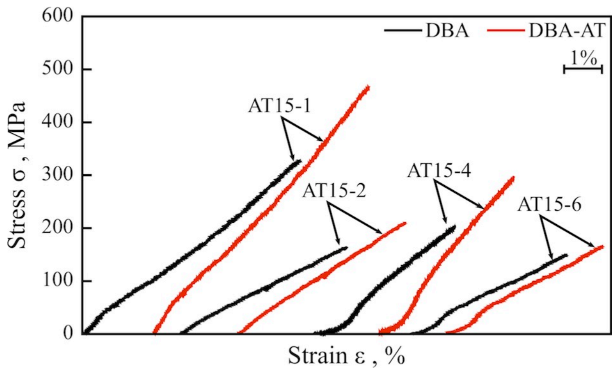


Figure 6. Corrected stress-strain curves of AT15 fibers by DBA-AT.

	Gap-contained	Elliptical cell-based
Average [μm^2]	2067	2009
Standard deviation [μm^2]	958	912

Table 7. Comparison between cross-sectional areas by gap-contained and elliptical cell-based estimations.

sectional area is shown in Table 7. The average area corrected by the former is slightly larger than the latter, but it is statistically considered that this difference is quite small. The correlation coefficient between the gap-contained and hexagon-approximated cross-sectional areas is 0.948. The approximation equation was obtained as presented below.

$$A_f^* = 0.916\tilde{A}_f + 7.75 \quad (4)$$

DBA-AT using the gap-contained estimation is hereinafter denoted as DBA-AT(UB), because it gives an upper bound of the actual cross-sectional area as mentioned above. In contrast, the elliptical cell-based estimation described above is a lower bound. It is also denoted as DBA-AT(LB). The fibre cross-sectional area was re-calculated through eq. (4). Results show that the ratio of cross-sectional area estimated from DBA-AT(UB) was 1.04 to that from DBA-AT(LB). Such slightly larger cross-sectional area estimation brought 4% less tensile strength and 6% less Young's modulus. DBA-AT(LB) or (UB) proposed here is expected to realize a more correct evaluation in strength of multi-cell type natural fibres treated in a highly concentrated alkali solution.

4 Conclusion

A cross-sectional area evaluation method for multi-cell type natural fibres treated in a highly concentrated alkali solution was proposed using kenaf fibres. Tensile tests of the alkali-treated kenaf fibres were carried out. Although the fracture strain of alkali-treated fibres increases dramatically, which is an inherent property of mercerized fibres, the magnitude of stress level was evaluated much less than untreated fibres based on the usual DBA. Cross-section of alkali-treated fibre had drastically changed from a polygon shape to an elliptical one, accompanied with many gaps between cells. Therefore, the DBA used here was insufficient for the alkali-treated cross-sectional area evaluation, because it was estimated based on untreated fibres' cross-section. Through image analysis, the actual cross-sectional areas were estimated again on the assumption that the shape of each cell in the alkali-treated fibres was an ellipse. And then the actual areas were correlated with hexagon-approximated cross-sectional area. This is the newly proposed data-based approximation method (DBA-AT). Tensile properties were recalculated through DBA-AT. Results show that the tensile strength is greatly improved. Particularly, the alkali-treated fibre on the condition of 15wt%NaOH for one hour is comparable to that of untreated fibre.

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