

CRYSTAL MODULUS OF TWARON AND TECHNORA FIBRES

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Abstract

Synchrotron radiation was used to follow the change of *c*-spacing of meridional reflections with applied tension which allowed the crystal strain to be calculated. The crystal modulus values of Technora, Twaron 81 and 83 fibres were determined and compared to the fibre tensile modulus values. The crystal moduli of both Twaron 81 and 83 had similar values of 200 GPa where as that of Technora fibre was much lower at 105 GPa.

Keywords: Crystal modulus, Technora fibre, Twaron fibre

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Introduction

Crystal affects the strength, modulus and durability of fibres in the chain direction. Crystallinity depends on polymer structure and processing conditions. Gel spun high density polyethylene (HDPE) and polyethylene terephthalate (PET) make high modulus fibres. The modulus of HDPE is 324 GPa, PET is 110 GPa, Kevlar is 194 GPa and that of poly(p-phenylene benzobisoxazole (PBO) is 477 GPa. PBO is a rigid rod aromatic fibre with extended chain and has a tensile modulus of 318 GPa. (Gupta & Radhakrishnan, 1991) X-ray diffraction uses to characterize crystal scale behavior and microstructure of substances. X-ray synchrotron radiation was chosen for this work because its many orders of magnitude are more powerful than normal X-ray produced from laboratory sources such as that obtained from Cu K α radiation. The wavelength of the X-ray synchrotron is suitable for studying the atomic structures of the molecule and the radiation has high intensity and high collimation. X-ray synchrotron was used for deformation study of electrospun fibres with varying composition of the fibres (Huang et al., 2021). Single crystal modulus of lanthanum gallium silicate was also studied (Gureva et al., 2020) and it was utilized to observe micromechanical behavior of alloy. (miller et al., 2020) This work includes the deformation study of Twaron 81, 83 and Technora fibres under tension. It provides informations of the crystal related to processing condition or behavior of the fibres in service condition under tension.

Objective

This work aims to identify the crystal modulus of Twaron 81, 83 and Technora fibres using X-ray synchrotron.

Research Methodology

1. Materials

1.1 Twaron Fibres

Twaron 81 and 83 fibres were specially prepared and supplied by Teijin-Twaron Ltd., Arnhem, The Netherlands All of the Twaron fibres were found to have a light yellow colour. Figure 1 shows the chemical structure of Poly(p-phenylene terephthalamide)(PPTA) fibre.

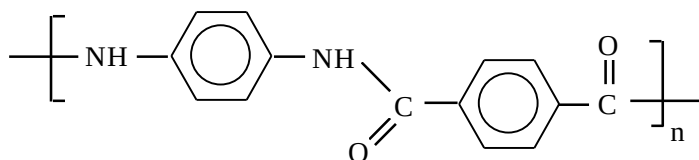


Figure 1 Poly(p-phenylene terephthalamide)(PPTA).

1.2 Technora Fibres

Untreated commercial Technora fibres were supplied by Teijin-Twaron Ltd., Japan. Technora fibres were found to have a yellow-gold colour. The manufacturing details of all fibres mentioned above are confidential to the manufacturers. The chemical structure of Technora fibre is illustrated in Figure 2.

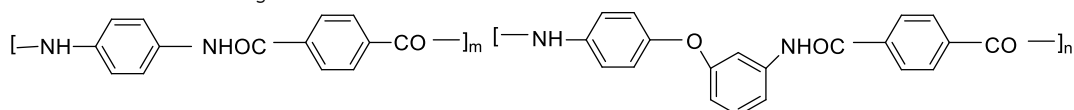


Figure 2 Copolyamide of terephthaloyl chloride, *p*-phenylenediamine and 3,4'-diaminodiphenyl-ether (Technora fibre).

2. Sample preparation

2.1 X-ray synchrotron specimens of Twaron and Technora fibres for determination of crystal modulus

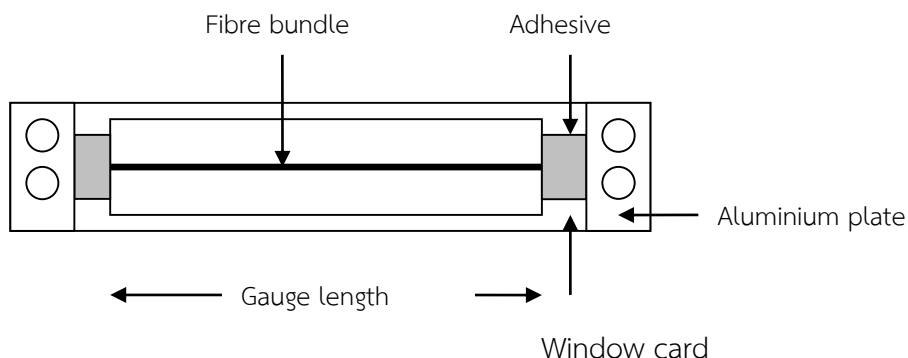


Figure 3 Bundle fibre specimen.

The synchrotron radiation specimens were prepared by mounting a bundle of fibres on 50 mm window cards using cold-setting epoxy resin, then 1x2 cm rectangular aluminium plates with two 0.5 cm diameter holes were fixed on both ends of each sample using cyanoacrylate adhesive as shown in Figure 3. They were left at room temperature for the resin to cure for 7 days.

2.2 X-ray synchrotron radiation for determination of crystal modulus

The synchrotron radiation experiment was undertaken at Station 14.1, Daresbury Laboratory (SRS), UK. The beamline was configured with a multi-pole wiggler (an insertion device) to enhance the beam characteristics which provided 10 times the flux of the bending magnet

stations. The wavelength of the X-ray used was $1.488 \text{ \AA}$, the focal spot size was less than $0.3 \times 0.4 \text{ mm}^2$, the flux was $5 \times 10^2 \text{ photons/sec}$, and the intensity was $5 \times 10^{13} \text{ photons/sec/mm}^2$. The diffraction patterns were collected by ADSC Quantum 4R CCD detector with the beam stop placed in front of it to prevent damage. The experimental setup is illustrated in Figure 4. Samples with 50 mm gauge length prepared by the method mentioned in section 2.1 were placed and clamped on the deformation rig. The position of the fibre bundle was adjusted by using a portable microscope. The load cell of the transducer was calibrated using a known weight prior to testing. Ten different known weights (1-8 N) were hung on the load cell and the readings from the transducer were recorded. A linear calibration curve was obtained from the plot of transducer readings versus loads as shown in Figure 5. The initial load was read from the transducer connected to the deformation rig. The tension was applied onto the fibre bundle and the load at each level of stretching was recorded. After the experiments were finished, paraffin wax was applied onto the fibre bundle and the X-ray diffraction pattern was taken. This allowed the sample-to-detector distance to be determined.

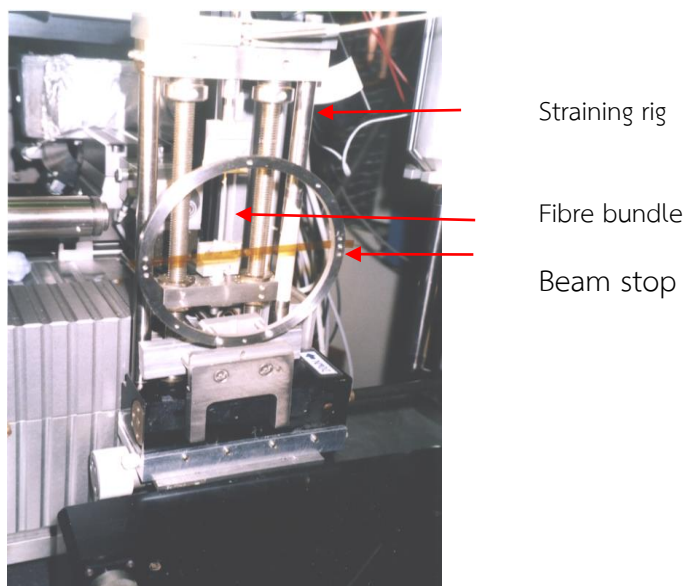


Figure 4 Experimental setup for determination of crystal modulus of Twaron and Technora.

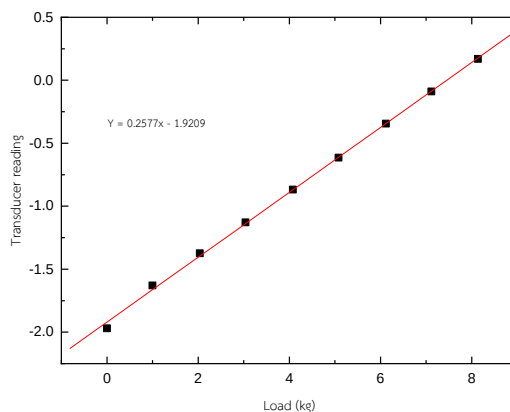


Figure 5 Load cell calibration curve of deformation rig for crystal modulus determination.

All of the X-ray patterns were analysed using *Fit2D* software. The program was used in this work to visualise the diffraction patterns, convert them to two dimensional diffraction intensity profiles and analyse the diffraction pattern obtained from the specimen coated with paraffin wax for calibration purpose. The diffraction pattern was firstly loaded into the program, and then a Cake function performed to choose the area of interest to be integrated. In this case, a particular meridional reflection was chosen. After that, the pixels intensity of the chosen Cake was integrated, and then the resulting two-dimensional intensity diffraction profile was attained and ready to be fitted using GRAMS-32™ software.

The specimen-to-detector distance (r') was determined by analysing the diffraction pattern of paraffin wax (Figure 6). The diffraction pattern was analysed by choosing the calibrant menu in *Fit2D* program. This allowed positions on the ring to be chosen and the beam centre is calculated. The specimen-to-detector distance was calculated following Equation 1, obtained from the geometry of the experiment as shown in Figure 7, where j is the radius of the inner ring and 2θ is obtained from the known paraffin wax standard.

$$r' = \frac{j}{\tan 2\theta} \quad (1)$$

The intensity profile of the reflection obtained from Twaron fibres was fitted using a Gaussian function, $G(x)$.

$$G(x) = I \times \exp \left[- \left(\frac{x - P}{w_m} \right)^2 \right] \quad (2)$$

where P is the band position, w_m is the full width at half maximum intensity and I is the intensity of the raw data. The intensity profile obtained from Technora fibres was fitted

using mixed Gaussian and Lorentzian function. The Lorentzian function, $L(x)$, is shown in Equation 3.

$$L(x) = \frac{I \times w_m^2}{[(x - p)^2 + w_m^2]} \quad (3)$$

The “goodness of fitting” can be measured from a chi-squared parameter, χ^2 , a measure of the difference between the fitted curve and the raw data given by:

$$\chi^2 = \frac{\sum (I_R - I)^2}{n'} \quad (4)$$

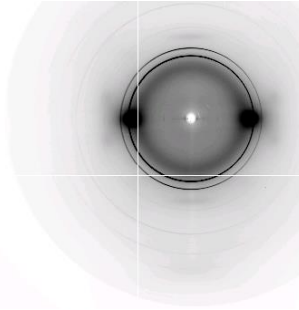


Figure 6 Diffraction pattern of paraffin wax on the Twaron fibres for calibration. of the synchrotron radiation experiment.

where I_R is the intensity of the data and n' is the number of data points. During the curve fitting procedure, GRAMS-32™ software continuously adjusted the fitting parameters in order to minimise the chi-squared value. The c -spacing of each X-ray diffraction pattern can be calculated from the following formula (Arridge et. al., 1976).

$$c = \frac{l' \lambda}{\sin^{-1}(h_l / r')} \quad (5)$$

where l' is the order of the layer line; $l' = 0$ for the equatorial line and $l' = 1$ for the first layer line etc., λ is the wavelength of the X-ray, h_l is the radius of the l' layer line and r' is the sample-to-detector distance. Uniform stress across the fibre bundle is assumed and it is assumed that the stress subjected to the crystal is the same as that applied to the fibre bundle. The crystal strain can be calculated from the change of c -spacing and the stress can be obtained from conversion of the load to stress. Finally, the crystal modulus (E_c) was calculated from the ratio of stress over strain following Equation 6.

$$E_c = \frac{F/A_b}{\Delta c/c_0} \quad (6)$$

where F is the load, A_b is the cross-sectional area of the fibre bundle and Δc is the amount of crystal elongation and c_0 is the initial c -spacing of the sample before any load is applied. The experiments were performed at room temperature.

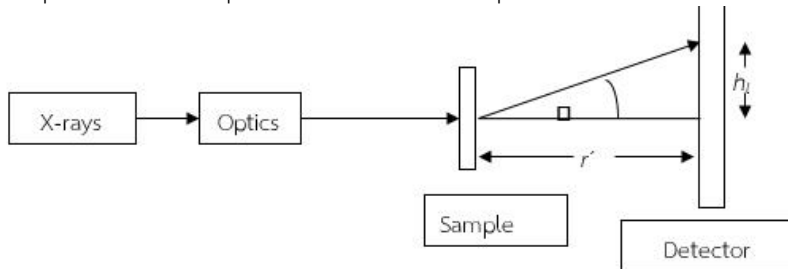


Figure 7 Schematic illustration of the formation of the diffraction pattern.

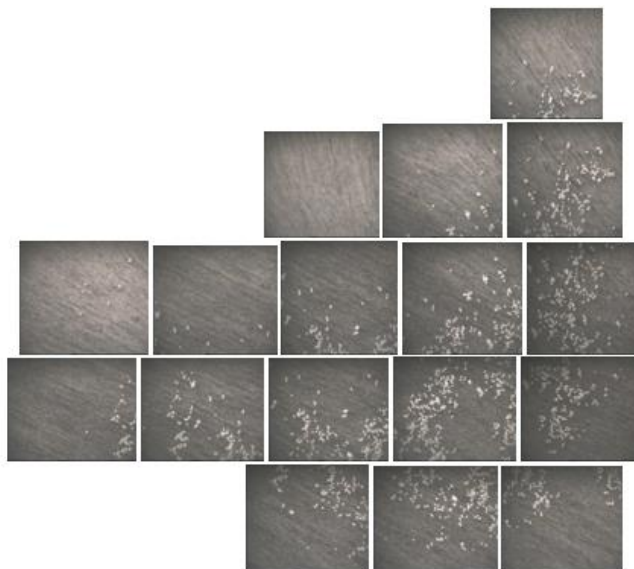


Figure 8 Twaron 81 fibre bundle under optical microscope observed using a $\times 20$ objective lens.

2.3 Determination of the number of fibres in bundles of Twaron and Technora Fibres.

The number of fibres in each bundle sample was determined by embedding the fibre bundle in epoxy resin and leaving it to cure for 7 days. After that, the resin block was cut across the fibre cross-section using a band saw and polished using a fine silicon carbide disk (number 4000) under water. Once the fibre surface cross-section was clearly seen and smoothed, it was wiped by tissue paper to dry the resin block. The resin block was then placed under an optical microscope and the $\times 20$ objective lens was used to observe and count the

number of fibres. Micrographs of the resin block containing fibres were taken and assembled as shown in Figure 8 in order to count the number of fibres in the bundle. The number of Twaron 81, 83 and Technora fibres were determined using the same method mentioned above.

Results and discussion

Tensile properties of Twaron and Technora fibres.

Tensile modulus of Twaron and Technora fibres were obtained. Figure 9 shows that the modulus of both fibres increased with an increase in the gauge length. This resulted from the end effects, machine softness and gripping system (Arridge et.al, 1976). The accurate tensile modulus of all fibres studied can be obtained from extrapolating the plots to infinite gauge length to eliminate the end effects. The results are summarised in Table 1.

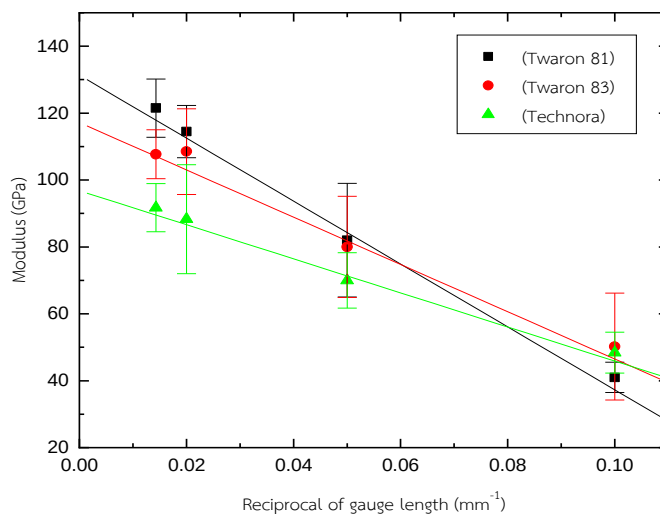


Figure 9 Relationship between the Young's modulus and the reciprocal of gauge length of the Twaron and Technora fibres.

Table 1 Summary of diameters and extrapolated tensile modulus values of the Twaron and Technora fibres.

	Twaron 81	Twaron 83	Technora
Diameter (μm)	12.1 $\pm$ 0.8	12.5 $\pm$ 0.5	12.6 $\pm$ 0.5
Tensile modulus (GPa)	131.4 $\pm$ 12.0	116.4 $\pm$ 10.6	96.4 $\pm$ 6.5

Number of fibres in the bundle

The average number of fibres in each of the Twaron and Technora bundles was determined for calculating stress in the fibre bundles. The results are as shown in Table 2.

Table 2 Numbers of the fibres in each Twaron and Technora fibre bundles.

Fibre	Numbers of fibres
Twaron 81	997 ± 24
Twaron 83	988 ± 30
Technora	994 ± 35

Calculation of meridional crystal strain and determination of crystal modulus

Crystal Structure of Twaron and Technora Fibres

Figure 10 shows the diffraction patterns obtained from the Twaron and Technora fibre bundles with the axis of the bundles aligned with the vertical axes of the patterns. The white cross wires superimposed on the patterns are from the detector system. The X-ray patterns were converted to diffraction profiles following the method described earlier. The peak position was attained by fitting the curves using a Gaussian function for Twaron fibres and mixed Gaussian and Lorentzian functions for Technora fibre in the *Gramm32™* program as described in that section.

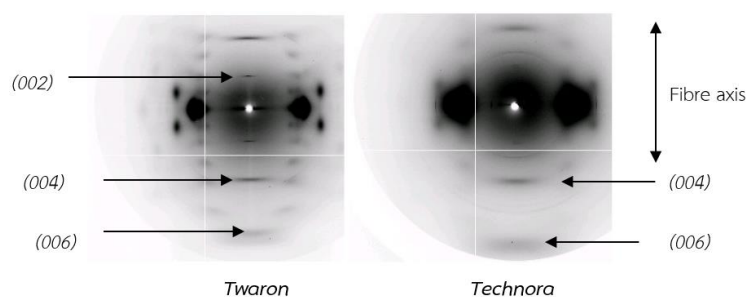


Figure 10 Synchrotron X-ray diffraction patterns of the Twaron and Technora fibres.

The X-ray pattern from the Twaron fibres showed that the material was more highly oriented compared to the Technora fibres. Both the equatorial and meridional reflections of Twaron fibres appeared sharper than those of the Technora fibres which indicated that the material had a larger crystallite size. It was found that the X-ray pattern of PPTA fibre obtained using a single fibre and a bundle fibre were similar in terms of reflection intensity and position

(Chu et.al, 1990). The strong equatorial reflections arose from the (110) and (200) crystal planes (Northolt, 1974). The meridional reflections were from the (002), (004) and (006) planes in the Twaron crystals.

The X-ray pattern for the Technora fibres indicated that it had some three-dimensional order. There were three sharp low intensity rings on the pattern that might have arisen from contaminations picked up during fibres processing. The two diffuse meridional (004) and (006) reflections (Tashiro et.al, 1987) corresponded to planes with *c*-spacings of about 3.37 and 2.20 angstrom respectively. The length of the arcs and their diffuse nature implied that the crystallite size was small and that they were weakly oriented with respect to the fibre axis. This was also consistent with the broad diffuse equatorial reflections. The (004) reflection was chosen to be used to study the fibre deformation due to the appearance of both above and below positions with respect to the beam centre on the diffraction pattern which allowed the average value of radial distance to be obtained for further crystal modulus calculation. The reflections and crystal plane spacings are summarised in Table 3.

Figure 11 shows that both the Twaron and Technora fibres showed a decrease in meridional radial distance (the distance from the beam centre to each particular reflection) corresponding to an increase in *c*-spacing after being subjected to tensile stress. The reflections were also sharper which indicate an improvement of chain orientation with deformation. This was similar to other fibres, for instance PBO which showed better orientation when subjected to tensile stress (Davies, 2002).

Figure 12 shows the plots of azimuthal scans of reflection intensity versus radial distance from the beam centre of the fibres studied. It could be seen that the reflection profile of Technora fibres was broader than those obtained from both types of Twaron fibres. This indicates the smaller crystallite size of Technora fibres (Barton, 1985-1986), (Rao et.al., 2001). The profiles of the (002) and (004) planes of the Twaron 83 fibres showed a higher intensity and were sharper compared to those of the Twaron 81 fibres. This indicated that the Twaron 83 fibres were more oriented than the Twaron 81 fibres.

It was found that the (004) intensity profile of the Technora fibres consisted of 2 layer lines very close to each other (Figure 12). These layer lines had *c*-spacings of 3.37 and 3.06 angstrom. The former had systematic change during deformations (Figure 13) while the latter did not change systematically. This may have been because Technora is a copolymer, thus it has a complex internal structure and behaviour under tension.

Crystal Modulus of Twaron and Technora Fibres

The crystal strain was calculated from the change in *c*-spacing after applying the tensile stress assuming uniform stress across the fibre bundle and that the stress subjected to the crystals was the same as that applied to the fibre bundle. The *c*-spacing is attained from Equation 5. The average diameters of all fibres used for calculating the stress are shown in Table

1. Figure 13 shows that the strain increases linearly with increasing stress. The crystal modulus was obtained from the slopes of the plots. The summaries of crystal modulus obtained are shown in Table 4. It can be seen that the crystal modulus of both Twaron 81 and 83 fibres obtained from the (002) and (004) reflections were similar which was approximately 200 GPa, which agreed with the reported crystal modulus, 200 GPa (Tashiro et.al., 1987). The crystal modulus of the Technora fibre, 105 GPa was also comparable to the reported value of 91 GPa (Nakamae et.al., 1987). The comparison between the crystal modulus of Twaron and that of Technora fibres showed that Technora fibre had a lower value. This is because the structural repeat unit of the Technora chain is less linear, less oriented and more flexible due to the ether linkage as can be seen from its chain structure, which is a combination of the segments presented in Figures 2 compared to that of Twaron chain (Figure 1)

Table 3 Crystal planes of Twaron and Technora fibres obtained from equatorial and meridional reflections.

Fibre	Reflection	Crystal spacing (angstrom)
Twaron 81	(110) ^e	4.44±0.02
	(200) ^e	3.87±0.04
	(002) ^m	6.43±0.03
	(004) ^m	3.17±0.01
	(006) ^m	2.08±0.02
Twaron 83	(110) ^e	4.29±0.03
	(200) ^e	3.86±0.02
	(002) ^m	6.43±0.10
	(004) ^m	3.18±0.02
	(006) ^m	2.07±0.02
Technora	(004) ^m	3.29±0.02
	(006) ^m	2.20±0.02

e and *m* designate equatorial and meridional reflections, respectively.

The standard deviation of the experimental results obtained from both Twaron and Technora fibres (Table 4) may have been due to variation of c-spacings which occurs due to averaging over a number of filaments with different crystal orientations.

All fibres had higher crystal modulus than their tensile modulus (Table 1). This is because of paracrystalline orientation for the whole crystals that lowers the value of the macroscopic modulus i.e. tensile modulus and maybe also from defects and voids and chain ends distracting the orientation of the crystals within the fibre. The tensile modulus of Twaron 81 fibre was slightly higher than that of the Twaron 83 fibres. This indicated that the polymer chains of Twaron 81 fibre were better oriented. Again, Technora fibres had a lower tensile modulus compared to Twaron fibres. This resulted from the same reason that the overall structure is much less oriented compared to both Twaron fibres.

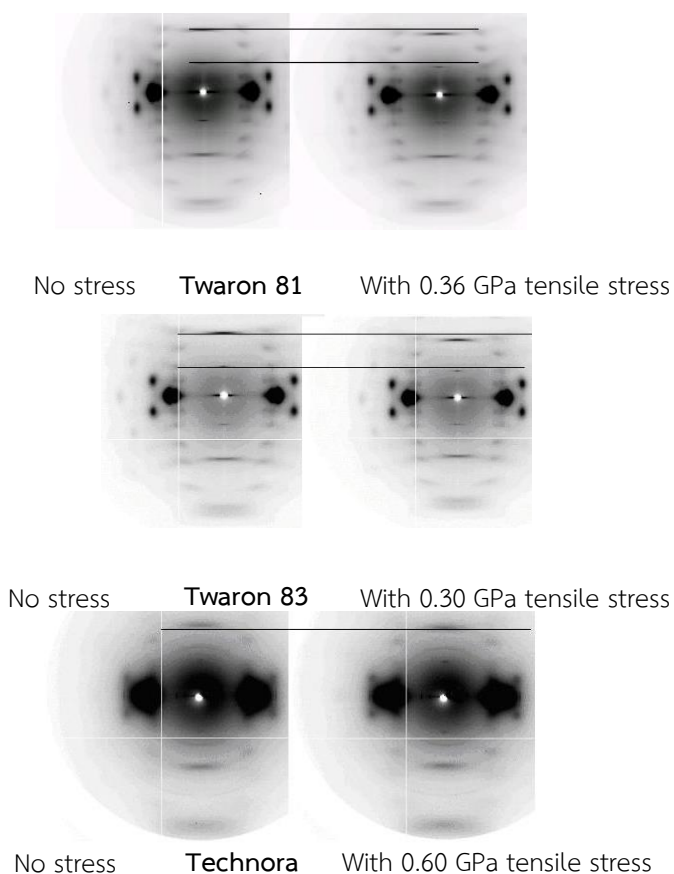


Figure 11 The decrease in radial distance of the layer line from the beam centre of Twaron 81, Twaron 83 and Technora fibres with tensile stress.

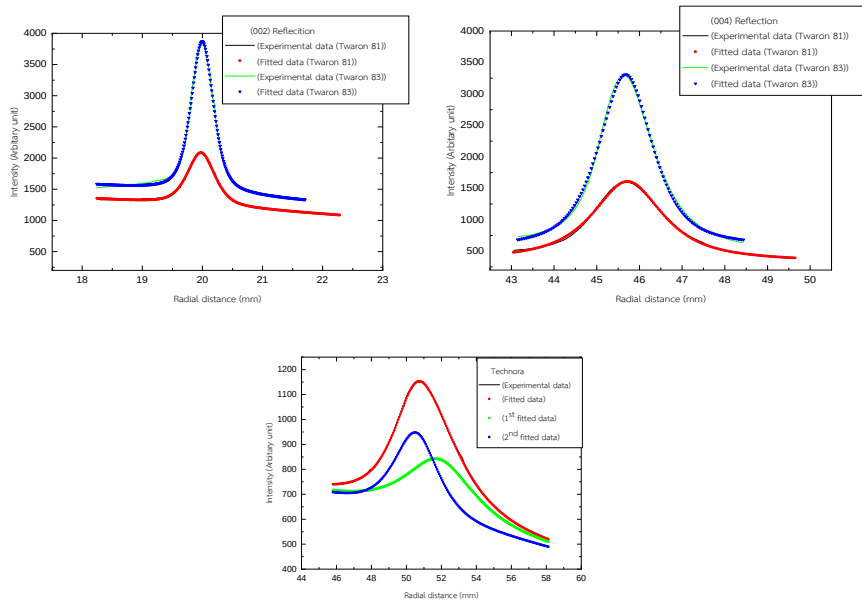


Figure 12 Azimuthal scans of intensity versus radial distances from the beam centre of Twaron 81, Twaron 83 and Technora fibres obtained from the X-ray synchrotron experiment.

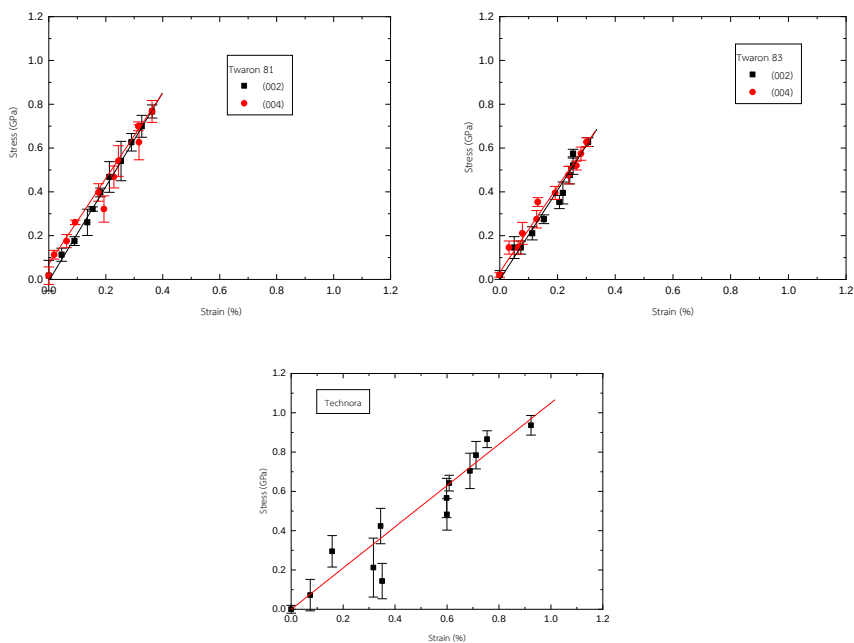


Figure 13 Stress/strain curves of Twaron 81, Twaron 83 and Technora fibres obtained from change in meridional c-spacings.

Table 4 Summary of the crystal modulus values of the Twaron 81, 83 and Technora fibres.

	Twaron 81	Twaron 83	Technora
Crystal Modulus (GPa)	214.5±5.1	203.4±14.9	105.0±12.5
	((002) reflection)	((002) reflection)	
Crystal Modulus (GPa)	195.0±10.0	194.9± 14.0	
	((004) reflection)	((004) reflection)	

Conclusions

The crystal moduli of both Twaron 81 and 83 had similar values of about 200 GPa whereas that of Technora fibre was much lower at 105 GPa. This is because the crystal modulus depends on orientation or linearity and flexibility of the structural repeat unit. Technora has more flexible units in its polymer chain and is less oriented, thus it has a lower crystal modulus compared to that of Twaron fibres. The tensile modulus is controlled by overall orientation of all polymer chains in the fibre. The x-ray synchrotron can be successfully used to monitor the deformation study of the fibre under tension providing information of the crystal under loading.

Future work

Future work can be carried out with various fibres by comparing processing parameters and the crystal modulus that will be obtained for each studied process.

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