Introduction

Carbon fiber reinforced plastics (CFRPs) have been applied in a wide range of engineering fields because of their light weight and good mechanical properties. Recently, CFRPs have been adopted as standard constituent materials in new aircraft structures. Among the potential application targets is lightweight automotive structures for reducing CO2 emissions [1]. Carbon fiber reinforced thermoplastics (CFRTPs) are expected to be recycling materials [2]. Considering the cost, discontinuous carbon fiber reinforced thermoplastics (D-CFRTPs) might be suitable for application to general automotive structures [1]. In recent years, new D-CFRTPs, such as those produced by the long fiber thermoplastic direct (LFT-D) method have been developed for applications as automotive structural materials [1, 3]. In the LFT-D method, the continuous carbon fibers (CFs) and the melted thermoplastic resin are blended and extruded directly [1, 3]. The mechanical properties of fiber reinforced plastics (FRP) depend on the length and orientation of the reinforcements [4, 5]. For example, the tensile modulus of the angle plied laminate depends on the off-axis angle [5]. The mechanical properties of
discontinuous FRPs also depend on the orientation of the reinforcements [6]. CFRTPs fabricated by extrusion have a wide distribution of fiber lengths because of fiber breakage caused during processing [3, 7, 8]. A new method has also been developed in order to measure the fiber length distribution more precisely and more efficiently [9].

On the other hand, it has been reported that the reinforcements are oriented during the molding process with the flow of the matrix resin in the LFT-D method [1]. For example, the fiber orientation during LFT-D compaction processing was predicted by a CAE tool called “3D-TIMON” [1]. The mechanical properties of the test piece are known to strongly depend on the location where the test piece was cut out from the CFRTP plate prepared by the LFT-D method [1, 3]. It was considered that the strong dependence of the mechanical properties on the location of the CFRTP plate is caused by the dependence of the fiber orientations on those in the previous works [1, 3].

As mentioned above, fiber orientation is an important parameter for the development of CFRTPs, just like fiber length [1, 9]. Hence, it is necessary to develop a method for accurately and efficiently measuring fiber orientation in CFRTPs. X-ray computed tomography (CT) scanning is well known as one of the most powerful techniques for investigating fiber orientation in CFRPs [10]. A high-resolution measurement of three-dimensional fiber orientation is possible using the X-ray CT scanning method. However, the measurement and analysis times are quite long [9]. Furthermore, the measurement area in X-ray CT scanning is considered to be too narrow to investigate the dependence of the fiber orientation on location in a large CFRTP plate. For example, the large mother plate prepared by the LFT-D method is 800 mm wide by 1400 mm long [1]; therefore, its area is much larger than the measurement area in X-ray CT scanning. On the other hand, the new thermal diffusion method known as “laser spot periodic heating method”, is effective for measuring the fiber orientations over a large area [1, 11]. However, practical improvements in this measurement system are now being undertaken [1].

In order to develop CFRTPs more efficiently, it is necessary to analyze the fiber orientation more easily in a short time using a general apparatus. It is known that an X-ray diffraction (XRD) peak from the reflection of the (002) crystal plane in graphite can be observed [12‒16]. It is also known that CFs comprise the preferentially oriented carbon hexagonal net layer stacks and microvoids to fiber axis and that XRD peak from the 002 reflection of the carbon net layer stacks can be characterized its structure and orientation [14‒16]. Hence, it is expected that the orientations of CFs in CFRTP could be investigated by the observation of the 002 reflection of graphite via XRD. It can be easily observed using a general X-ray scattering analysis system in a short time. In the case of potassium titanate fiber reinforced plastics, the fiber orientations were observed by XRD [17, 18]. Therefore, XRD is expected to be an easy and effective method for analyzing the fiber orientation in CFRTPs in a short time.

Recently, CFRTPs using polyamide 6 (PA6) as a matrix have been investigated to apply to automotive structures [1, 3]. Hence, the purpose of this work is the development of an easy and effective technique to analyze CF orientation in CFRTPs reinforced with PA6. For this purpose, we report CF orientations in CFRTPs reinforced with PA6 observed by XRD, and discuss the effectiveness of XRD for the measurement of the CF orientation in CFRTPs.

**Experiment**

**Sample**

**I) CFRTP**

In this study, a uni-directional CFRTP (UD-CFRTP), a twilled cloth CFRTP (c-CFRTP) and D-CFRTP were prepared. CF derived from polyacrylonitrile (PAN) was used as a reinforcement. The used CF tow was TORAYCA® T700S (Toray Industries, Inc.). PA6 was used as a matrix resin. The details are described below.

1) **UD-CFRTP**

UD-prepreg sheets were laminated in a mold with dimensions of 25 mm width × 150 mm length and then pressed at 230 °C. The dimensions of the prepared UD-CFRTP were 25 mm width × 150 mm length × 3 mm thickness. The prepreg sheet was purchased from Ichimura Sangyo Co., Ltd.. CFs were reinforced along the longitudinal direction.

2) **c-CFRTP**

C-CFRTP was purchased from Ichimura Sangyo Co., Ltd. The dimensions of the c-CFRTP were 25 mm width × 200 mm length × 3 mm thickness.
3) D-CFRTP

Short CFs with a length of 18 mm and PA6 were blended by melt mixing in a single-screw extruder (SEPICS, MEIKI CO., LTD.) at 260–275 °C. The mixing volume ratio of CF and PA6 was 35/65. The prepared compound was a sheet with dimensions of 300 mm width × 400 mm length in the molding direction (MD). This kneaded sheet was set in the center of a mold with dimensions of 400 mm width × 500 mm length and then pressed at 240 °C in order to obtain a D-CFRTP plate. The obtained D-CFRTP plate was demolded at 140 °C. The dimensions of the prepared D-CFRTP were 400 mm width × 500 mm length × 3 mm thickness. A schematic diagram of the kneaded sheet and the obtained D-CFRTP is shown in Fig. 1. In order to simplify the following discussion, the direction transverse to the MD is hereafter abbreviated as TD. Test pieces of 25 mm width and 200 mm length for XRD and tensile tests were cut out from the D-CFRTP plate, as shown in Fig. 1. The test pieces named MD1 to MD6 were used for tensile tests in the MD direction of and those named TD1 to TD6 were used for tensile tests in the TD direction. The test pieces named MD1–MD6 and those named TD1–TD6 are hereafter referred to as MDs and TDs respectively. The longitudinal direction, i.e., the tensile direction, was defined as the x-direction and the amplitude direction was defined as the y-direction. The used CF tow (TORAYCA® T700S) and PA6 (CM1006, Toray Ind., Inc.) were purchased from Toray Industries, Inc.

The volume fraction of CF (Vf) of UD-CFRTP and c-CFRTP were 46.9% and 49.5%. The average Vf of the D-CFRTP was 44.0%. Those were estimated based on the density. We considered the density of CF and PA6 to be 1.80 and 1.14 respectively [2].

(2) CF mat

A mat of CFs with a length of 3 mm was provided by Toray Industries, Inc. It was used as a control sample of randomly oriented CFs.

(3) PA6 plate

A PA6 plate was prepared by injection molding. The dimensions were 25 mm width × 100 mm length × 3 mm thickness.

Measurements

(1) X-ray diffraction (XRD)

XRD patterns were obtained using an X-ray scattering analysis system with a flat imaging plate (R-AXIS IV, Rigaku Co., Ltd). The camera distance was 165 mm. The CuKα source was operated at a voltage and current of 40 kV and 40 mA, respectively, to generate the X-ray beam in this work. The wavelength (λ) of a CuKα beam is 1.5418 Å and the diameter of the beam is approximately 0.3 mm. The incident X-ray beam was used to irradiate to the molding surface of the prepared samples for 10 min. In the case of the CFRTP, the incident X-ray was positioned at the center of the test piece, which is the adhesion position of the strain gage. A schematic diagram of the XRD measurement system of the test piece in the CFRTP is shown in Fig. 2.

(2) Tensile modulus

The tensile tests were carried out using Auto Graph (AG-X plus 100 kN, Shimadzu Co., Ltd). The tensile strain was measured by a strain gage, BFLA 5-8-1-L (Gage length: 5 mm, Tokyo Sokki Kenkyujo Co., Ltd). The strain gage was adhered to the center of the test piece. The span length was 100 mm and the cross head speed was 1 mm/min. Before the tensile tests, the test pieces were dried at 80 °C for 12 h at a pressure of approximately 1 Torr in a vacuum dryer.

![Fig. 1 Schematic diagram of D-CFRTP.](image)

![Fig. 2 Schematic diagram of measurements of CF orientations in the test pieces of CFRTPs by X-ray diffraction.](image)
Results and Discussion

(1) XRD patterns of CF mat, PA6, UD-CFRTP and c-CFRTP

The two-dimensional (2D) XRD pattern of the CF mat, PA6 plate, UD-CFRTP and c-CFRTP are shown in Fig. 3. The assignments of the diffraction features shown in this figure are described in the following. A circular small-angle X-ray scattering (SAXS) was observed in the center of the XRD image of CF mat. There are two diffraction rings in the XRD pattern of the PA6 plate. Two diffraction rings, a diffraction spot and SAXS were observed in the XRD pattern of the UD-CFRTP. A diffraction spot and SAXS were observed on the meridian line. Two diffraction rings, three diffraction spots and SAXS were observed in the XRD pattern of the c-CFRTP. The diffraction spots and SAXS were observed on both of the equatorial and meridian lines. In the range of the azimuth (φ) = −130°~−180° and that of φ = 130°~180°, the XRD image could not be observed because of the shadow of the beam stopper on the X-ray detector.

The 002 reflections of graphite in the CF derived from PAN fiber are observed to directions along approximately φ/c₀₀₃ ± 90° to the fiber direction [16]. Therefore, the XRD image of CF could be assumed to symmetric to rotation by 180° and we can discuss the XRD of the CFRTP in the range of φ = −90°~90° below.

The XRD intensity at a point with a diffraction angle of 2θ and an azimuth of φ is defined as I(2θ, φ). The integrated value of I(2θ, φ) in the range from φ = −90° to 90° is defined as XRD profiles (I(2θ)). I(2θ) is shown in the following formula:

$$I(2\theta) = \int_{-\phi}^{\phi} I(2\theta, \phi) d\phi$$  \hspace{1cm} (1)

The I(2θ) of the CF mat, PA6 plate and UD-CFRTP obtained from the XRD patterns shown in Fig. 3 are shown in Fig. 4. The assignments of the diffraction peaks and shoulders are shown in this figure. When the CuKα line is used as the X-ray beam, the diffraction peaks at 2θ = 20° and 2θ = 24° were assigned to the 200 reflection and 002 and 202 reflections of an α-type PA6 [19, 20] and the diffraction peak and shoulders at 2θ ≈ 26° were assigned to the 002 reflection of graphite [12]. The diffraction peaks at 2θ = 20° and 2θ = 24° correspond to the diffraction rings in the XRD of the PA6 plate, UD-CFRTP and c-CFRTP in Fig. 3. The diffraction peak and shoulder at 2θ = 26° correspond to the diffraction ring and spots in the XRD of CF mat and UD-CFRTP in Fig. 3, respectively. The I(2θ) of the UD-CFRTP showed a profile consisting of CF and PA6. Comparing the I(2θ) of PA6, CF mat and the UD-CFRTP, the I(2θ) of the CFRTPs contained contributions from both PA6 and CF in the 2θ range below 25°. The I(2θ) of CFRTPs was composed almost entirely of the contribution from CF in the 2θ range from 25° to 33°. Therefore, we discuss the dependence of the 002 diffraction intensity on φ in the range from 2θ = 25° to 33° in the following.

The integrated value of I(2θ, φ) in the range from 2θ = 25° to 33° is defined as I(φ) shown in the following formula:

$$I(\phi) = \int_{25°}^{33°} I(2\theta, \phi) d\phi$$

Fig. 3 XRD pattern of the CF mat, PA6 plate, UD-CFRTP and c-CFRTP. a: X-ray diffraction ring of PA6 200 reflection. b: X-ray diffraction ring of PA6 002 and 202 reflections. c: X-ray diffraction ring of graphite 002 reflection in CF. d: SAXS from CF mat and UD-CFRTP. e: Shadow by beam stopper.

Fig. 4 XRD profile I(2θ) of the CF mat, PA6 plate and UD-CFRTP.
\[ I(\phi) = \int_{-\infty}^{\infty} I(2\theta, \phi) d(2\theta) \quad (2) \]

In this study, \( I(\phi) \) is normalized values, that is to say, \( \int_{-\infty}^{\infty} I(\phi) d\phi \) equal to 1. The dependences of \( I(\phi) \) of the UD-CFRTP and c-CFRTP on the azimuth are shown in Fig. 5. \( I(\phi) \) of the UD-CFRTP and c-CFRP are defined as \( I_{\text{UD}}(\phi) \) and \( I_{\text{c}}(\phi) \) respectively. \( I_{\text{UD}}(\phi) \) showed its maximum value at \( \phi = 0^\circ \), which is perpendicular to the CF direction. CFs are not perfect graphite crystals [14‒16, 21] and the distribution of \( I(\phi) \) of CF depends on the crystallinity, orientation, sizes and stacking regularity of graphite crystals [14‒16]. Therefore, \( I_{\text{UD}}(\phi) \) depends on disorder of both those crystal structures in CF and CF orientation in UD-CFRTP. Hence, we performed only relative comparisons of \( I(\phi) \) of the other CFRTPs with that of UD-CFRTP. \( I(\phi) \) of the UD-CFRTP showed its maximum value at \( \phi = -90^\circ, 0^\circ \) and \( 90^\circ \). The diffraction peak at \( \phi = 0^\circ \) is considered to be the graphite 002 diffraction of the CFs oriented along the x-direction in the c-CFRTP which are oriented along the parallel direction to the CFs in the UD-CFRTP. On the other hand, the diffraction peaks at \( \phi = -90^\circ \) and \( 90^\circ \) are considered to be the graphite 002 diffraction of the CF oriented along the y-direction which are oriented to the perpendicular direction to the CFs in the UD-CFRTP. \( I_{\text{c}}(\phi) \) in the range of \( \phi = -120^\circ \sim -180^\circ \) and \( \phi = 120^\circ \sim 180^\circ \) are assumed to be \( I(\phi+180) \) and \( I(\phi-180) \) respectively. The predicted \( I_{\text{c}}(\phi) \) is defined as \( I_{\text{c,predicted}}(\phi) \). It shows the experimental \( I(\phi) \) in the range of \( \phi = -120^\circ \sim 120^\circ \) and shows \( I(\phi+180) \) and \( I(\phi-180) \) in the range of \( \phi = -120^\circ \sim -180^\circ \) and \( \phi = 120^\circ \sim 180^\circ \) respectively. \( I_{\text{c}}(\phi) \) rotated by 90° is defined as \( I_{\text{rotated c}}(\phi) \). It was estimated by the following.

\[
I_{\text{rotated c}}(\phi) = I_{\text{rotated c}}(\phi+90) \quad (3)
\]

\[
I_{\text{rotated c}}(\phi) = I_{\text{rotated c}}(\phi-270) \quad (4)
\]

\( I_{\text{c,predicted}}(\phi) \) predicted by that of UD-CFRTP is defined as \( I_{\text{predicted}}(\phi) \). It was estimated by the following.

\[
I_{\text{predicted}}(\phi) = \frac{I_{\text{UD}}(\phi) + I_{\text{rotated c}}(\phi)}{2} \quad (5)
\]

\( I_{\text{predicted}}(\phi) \) are shown as a broken line in Fig. 5. It showed approximately agreement with the observed one. Therefore, the CF orientation ratio in the c-CFRTP could be estimated based on the dependence of the 002 XRD intensity in the \( 2\theta \) range from 25° to 33° on the azimuth.

(2) XRD patterns of D-CFRTP

XRD patterns of MDs and TDs are shown in Fig. 6 and Fig. 7 respectively. The diffraction intensities outside of the outer rings and the SAXS patterns showed anisotropic in one or two directions along the yellow arrows shown in the figures. As above mentioned, the diffraction outside of outer ring

![Fig. 5](image)

Dependences of the 002 diffraction intensity in the range from \( 2\theta = 25^\circ \) to 33° on azimuth (\( \phi \)) in the case of UD-CFRTP and c-CFRTP.

![Fig. 6](image)

XRD patterns of the test pieces MDs of D-CFRTP.

![Fig. 7](image)

XRD patterns of the test pieces TDs of D-CFRTP.
was assigned to graphite 002 reflection from test piece. The anisotropy of the XRD patterns from those samples indicated that the CFs in those pieces were oriented anisotropically and not randomly.

The dependences of $I(\phi)$ of MDs and TDs on the azimuth are shown in Fig. 8 and Fig. 9 respectively. In the case of the MDs and TD6, the $I(\phi)$ showed their maximum values in the range of $\phi = -30^\circ \sim 30^\circ$ and the $I(\phi)$ at around $\phi = 0^\circ$ were higher than those at around $\phi = \pm 90^\circ$. Therefore, the CF orientation ratios in the parallel direction to the CFs in the UD-CFRTP ($x$-direction) were higher than those in the perpendicular direction to the CFs in the UD-CFRTP ($y$-direction). Main orientation angles of CFs in those were the range of $-30^\circ \sim 30^\circ$ to $x$-direction. On the other hand, the $I(\phi)$ of TD1~TD5 showed their maximum values in the range of $\phi = -60^\circ \sim -90^\circ$ and $\phi = 60^\circ \sim 90^\circ$ and the $I(\phi)$ at around $\phi = 0^\circ$ were higher than those at around $\phi = \pm 90^\circ$. The CFs in those were oriented to the $y$-direction (perpendicular to the CFs in the UD-CFRTP) rather than to the $x$-direction. The distributions of the $I(\phi)$ of MDs and TDs were wider than that of the UD-CFRTP. Therefore, the distributions of CF orientations in the D-CFRTP were wider than that in the UD-CFRTP. Especially, the distributions of CF orientations in TD6 and MD5 were wider than those in the others. The $I(\phi)$ of MD2 and TD2 showed bidirectional orientations as like the yellow allows shown in Fig. 6 and 7. Therefore, the $I(\phi)$ showed the orientation directions and distributions of the test pieces.

Considering both the distribution and direction of CF orientations, we estimated the orientation order parameters using the $I(\phi)$ obtained from the XRD data. In this paper, the orientation parameter of $I(\phi)$ to the azimuth ($\phi_0$) is defined in Formula (6) [22]:

$$ S(\phi_0) = \frac{3\langle \cos^2(\phi - \phi_0) \rangle - 1}{2} $$(6)

The graphite layers in CFs are oriented nearly parallel to the fiber axis, however, the orientations of the graphite layers are distributed [14‒16, 21]. Therefore, $I(\phi)$ of the CFRTP depends on the distributions of both the crystal orientation of graphite layers in CF and the CF orientation in CFRTP. That is to say, $S(\phi_0)$ estimated by $I(\phi)$ are contributed by both graphite crystals orientations in CFs and CF orientations in CFRTP. Hence, we could perform only relative comparisons of CF orientations by $S(\phi_0)$. In the following, the fiber orientation order parameter was estimated by $S(\phi_0)$ and $I_{UD}(\phi)$.

The fiber orientation ratio is defined as $f(\phi)$. $f(\phi)$ is also assumed to be normalized. The fiber orientation order parameter is defined as $F(\phi_0)$ as shown in Formula (7).

$$ F(\phi_0) = \frac{3\int f(\phi)\cos^2(\phi - \phi_0) d\phi - 1}{2} \quad (7) $$

$F(\phi_0)$ of UD-CFRTP is defined as $F_{UD}(\phi_0)$ as shown in Formula (8).

$$ F_{UD}(\phi_0) = \frac{3 \cos^2 \phi_0 - 1}{2} \quad (8) $$

Therefore, $F(\phi_0)$ is shown in Formula (9).

$$ F(\phi_0) = \int f(\phi) F_{UD}(\phi - \phi_0) d\phi \quad (9) $$

$I(\phi)$ is shown in Formula (10).
\[ I(\phi) = \int f(\phi) I_{UD}(\phi - \phi_0) d\phi, \quad (10) \]

\[ S(\phi) \text{ of UD-CFRTP is defined as } S_{UD}(\phi_0). \]

\[ S_{UD}(\phi_0) \text{ and } S(\phi_0) \text{ are shown in Formula (11) and (12).} \]

\[ S_{UD}(\phi_0) = \frac{3\int I_{UD}(\phi_0) \cos^2(\phi - \phi_0) d\phi - 1}{2} \quad (11) \]

\[ S(\phi) = \frac{3\int f(\phi) I_{UD}(\phi_0) \cos^2(\phi - \phi_0) d\phi - 1}{2} \]

\[ = \frac{3\int f(\phi) I_{UD}(\phi_0) \cos^2(\phi - \phi_0) d\phi - \int f(\phi) d\phi}{2} \]

\[ = \int f(\phi) [3\int I_{UD}(\phi_0) \cos^2(\phi - \phi_0) d\phi - 1] d\phi \]

\[ = \int f(\phi) S_{UD}(\phi_0 - \phi_0) d\phi. \quad (12) \]

\[ S_{UD}(\phi_0) \text{ and } S(\phi_0) \text{ were estimated by the Formula (6) and (11) by the integration range of } \phi = -90^\circ \sim 90^\circ. \]

\[ I_{UD}(\phi) \text{ and } I(\phi) \text{ were experimental values shown in Fig. 5, 8, 9. The correlation between } S_{UD}(\phi_0) \text{ and } F_{UD}(\phi_0) \text{ is shown in Fig. 10. They showed approximately linear relationship as shown in Formula (13).} \]

\[ F_{UD}(\phi_0) = A S_{UD}(\phi_0) + B \quad (13) \]

\[ A \text{ and } B \text{ are constant. In this case, they are 2.39 and -0.34 respectively.} \]

From Formula (9), (12), (13), the relation between \( F(\phi_0) \) and \( S(\phi_0) \) is shown in Formula (14).

\[ F(\phi_0) = \int f(\phi) F_{UD}(\phi - \phi_0) d\phi \]

\[ = \int f(\phi) [A S_{UD}(\phi - \phi_0) + B] d\phi \]

\[ = A \int f(\phi) S_{UD}(\phi - \phi_0) d\phi + B \int f(\phi) d\phi \]

\[ = A S(\phi_0) + B \quad (14) \]

\[ \] Therefore, \( F(\phi_0) \) could be estimated by \( S(\phi_0) \). \( F(\phi_0) \) of test pieces of the D-CFRTP were estimated by \( S(\phi_0) \) of those.

In this section, the azimuth \( (\phi_0) \) at which \( F(\phi_0) \) showed its maximum value was defined as \( \Phi_{max} \). As above mentioned about the XRD of UD-CFRTP, the direction of orientation is perpendicular to that of diffraction in the case of CF. We defined the direction perpendicular to the \( \Phi_{max} \) as the average orientation direction. The diameter of X-ray beam was 0.3 mm, hence, the average orientation direction obtained by the \( \Phi_{max} \) is considered to be the average one in the area of 0.3 mm diameter at the center of the test piece. The average orientation directions of the test pieces are shown in Fig. 11. The CFs in all test pieces except TD6 were almost oriented to MD.

Stress–Strain curves (SS curves) of the test pieces of D-CFRTP are shown in Fig. 12. The tensile modulus of the test pieces were estimated by the inclinations of the SS curves in the range from 0.05% to 0.15% strains. The relation between the tensile modulus and the fiber orientation order parameters in the tensile direction \( (F(0)) \) is shown in Fig. 13. The correlation between the tensile modulus and \( F(0) \) can be seen in this figure. Therefore, \( F(0) \) may be an effective parameter for discussing the relationship between the tensile modulus and the CF orientation in D-CFRTPs. However, the obtained \( F(0) \) is considered to be the fiber orientation order parameter in the area of 0.3 mm diameter at the center of the test piece, therefore, XRD measurements at multi points or X-ray CT are considered to be miscarly for the detailed discussions about the correlation between CF orientations and tensile modulus.

As shown in Fig. 8 and 9, the SAXS patterns of the test pieces of the D-CFRTP showed similar

![Fig. 10](image1)

Fig. 10 Correlation between the orientation order parameters of the fibers and those estimated by the XRD of UD-CFRTP.

![Fig. 11](image2)

Fig. 11 Average orientation directions of the test pieces in D-CFRTP.
anisotropies to their 002 reflection patterns. Hence, it is considered that the SAXS patterns depend on the CF orientations just as the 002 reflections do. However, SAXS pattern depends on many kinds of structural factors, such as the crystal size, morphology, and surface state [23]. Therefore, it seems to be difficult to estimate the CF orientations by the SAXS patterns because of their dependence on many kinds of structural factors induced from both CF and PA6 in this case.

**Conclusion**

In this study, we investigated the CF orientation in a CF mat, a UD-CFRTP, a twilled cloth-CFRTP (c-CFRTP) and a discontinuous CFRTP (D-CFRTP) reinforced PA6 based on XRD patterns obtained with CuKα beam of 1.5418 Å. The following conclusions could be drawn.

1. The PA6 200, 002, 202 reflections and graphite 002 reflection were observed from XRD of the CFRTPs. It was found that the XRD pattern of CFRTP in the 20 range from 25° to 33° was almost completely dominated by contributions from the CF.
2. The graphite 002 reflection and SAXS pattern in XRD images showed anisotropies caused by CF orientations in CFRTPs.
3. The dependence of the 002 XRD intensity in the 20 range from 25° to 33° on the azimuth (f(φ)) of c-CFRTP predicted that of UD-CFRTP showed approximately agreement with the observed one. Therefore, the CF orientation ratio in the c-CFRTP could be estimated based on the f(φ).
4. The direction and distribution of the CFs in the D-CFRTP could be estimated based on the f(φ). Each test piece showed a variable orientation direction and distribution. It was also found that the distribution of the CF orientations in the D-CFRTP were wider than that in the UD-CFRTP.
5. The orientation order parameters (S(φ)) were estimated from the XRD patterns of the D-CFRTP. The CF orientation order parameters (F(φ)) and S(φ) showed approximately linear relationship. The constants of the linear relationship could be the correlation between F(φ) and S(φ) of UD-CFRTP. Therefore, F(φ) of D-CFRTP could be estimated by S(φ) of D-CFRTPs and that of UD-CFRTP.
6. It was found that the CFs in the D-CFRTP were almost oriented in molding direction. The tensile modulus was correlated with the fiber orientation order parameters (F(φ)) estimated from S(φ) which were obtained by the XRD patterns of the D-CFRTP.

We were able to obtain these results by examining a UD-CFRTP, a c-CFRTP and a D-CFRTP with a general XRD system for 10 min by performing easy measurements. Therefore, XRD may be the one of the effective methods for the estimation of CF orientations in CFRTPs.

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Disclosure statement

No potential conflict of interest was reported by the authors.

References

1. T. Ishikawa, K. Amaoka, Y. Masubuchi, T. Yamamoto, A. Yamanaka, M. Arai, and J. Takahashi, *Composite Science Technology* **155**, 2018, 221-246
2. Y. Wan, T. Ohori, and J. Takahashi, 20th International Conference on Composite Materials Copenhagen, 2015
3. K. Rohan, T. J. McDonough, V. Ugresic, E. Potyra, and F. Henning, Mechanical study of direct long fiber thermoplastic carbon / polyamide 6 and its relations to processing parameters. Composite World 2015, June 1.
4. J. L. Thomason. The influence of fibre length and concentration on the properties of glass fiber reinforced polypropylene: 5. Injection molded long and short fiber PP. Composites: Part A, 33 2002 1641-1652
5. S. Kobayashi, *Mechanics of composite materials. Introduction to engineering beginners*. 3rd ed., edited by Seamus H, Baifukan, 2015, 99-100
6. M. Hashimoto, T. Okabe, T. Sasayama, H. Matsutani, and M. Nishikawa, Composites Part A 43, 2012, 1791-1799
7. N. G. Karsly and A. Aytac, Tensile and thermomechanical properties of short carbon fiber reinforced polyamide 6 composites. Composites: Part B, 51, 2013, 270-275
8. Y. Masubuchi, M. Terada, A. Yamanaka, T. Yamamoto, and T. Ishikawa, *Composite Science and Technology*, **134**, 2016, 43-48
9. M. Terada, A. Yamanaka, Y. Kimoto, D. Shimamoto, Y. Hotta, and T. Ishikawa, *Adv Compos Mater*, **27**, 2018, 605-614
10. A. Yoshimura, R. Hosoya, J. Koyanagi, and T. Ogasawa, *Adv Compos Mater*, **25**, 2016, 19-30
11. R. Fujita and H. Nagano, *Composite Science and Technology*, **140**, 2017, 116-122
12. N. Iwashita, *Tanso*, **188**, 1999, 147-151
13. V. A. Tyumentsev and A. G. Fazlitdinova, X-ray diffraction analysis of the fine structure of carbon fiber. Russian Journal of Applied Chemistry, 86, 2013, 760-764
14. Y. Tanabe, E. Yasuda, H. Machio, and S. Kimura, *Tanso*, **132**, 1988, 2-5
15. M. Shioya and A. Takaku, *Tanso*, **139**, 1989, 189-198
16. M. Shioya and A. Takaku, *SEN-I Gakkaishi*, **50**, 1994, 433-442
17. H. Takeda and Y. Seino, *Seikei-Kakou*, **1**, 1989, 88-94
18. H. Takeda and Y. Seino, *Seikei-Kakou*, **1**, 1989, 197-204
19. D. R. Holmes, C. W. Bunn, and D. J. Smith, *Journal of Polymer Science*, **17**, 1955, 159-177
20. M. Tsuruta, M. Yamamoto, A. Hanawa, and M. Hirami, *Kobunshi Kagaku*, **23**, 1966, 391-394
21. T. Hiramatsu, Carbon fiber composite. The Nikkann Kogyou Shinbun, 2015, 16-18
22. K. Araki, *Shikizai*, **62**, 1989, 683-690
23. K. Tashiro, X-ray small angle scattering. Introduction to Polymer Analysis. ed. by T. Nishioka, Kodansha press, 2010, p184 in Japanese