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Table of Contents Graphics

Change of crystallinity and long period of PEF during the process of uniaxial deformation at 200 °C.
Simultaneous WAXS/SAXS Study on Semi-crystalline Poly(ethylene furanoate) under Uniaxial Stretching

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Abstract

A time-resolved study of uniaxial deformation processes of semi-crystalline poly(ethylene furanoate) (PEF) at 200 °C was carried out using synchrotron simultaneous wide- and small-angle X-ray scattering (WAXS/SAXS) techniques. The stretching was able to dissociate existing lamellar crystal assemblies in the early stages of stretching (for strains less than ≈0.6), causing a slight decrease of crystallinity, and an increase of inter-lamellar distance. As stretching proceeded, an increase of crystallinity and at the same time a decrease of inter-lamellar distance was observed. Preferred orientation behavior in the early stages of stretching was complex, but could be approximated using oblique b-axis orientation associated with intra-lamellar slip along the [100] plane. In the late stages of deformation, new lamellar crystals were formed with their normal, i.e., the c-axis direction, parallel to the stretching direction.

Keywords: poly(ethylene furanoate); scattering; deformation.
Introduction

Research seeking for bio-based alternatives for conventional petroleum-based polymer has been intensively conducted for decades, owing to growing awareness of depletion of fossil fuel reserves. Among these efforts, success in synthesis of poly(ethylene-2,5-furanoate) (PEF), from the bio-derived monomers of furan-2,5-dicarboxylic acid (FDCA) or dimethyl furan-2,5-dicarboxylate (DMFDCA), is showing promise as a replacement for poly(ethylene terephthalate) (PET).[1] Recently, it has been shown that carbon dioxide (CO$_2$) can be used as feedstock to synthesize the building block monomer, FDCA, which makes PEF even more attractive as a renewable polymer that can be produced entirely through green chemistry.[2]

From a polymer chemistry point of view, synthesis of PEF (and other FDCA-based polyesters) had been successfully realized back in the 1950s. Given the length of time these polymers have existed it is perhaps surprising, that the characterization of their physical properties, has lagged somewhat behind. It has only fairly recently, that a series of detailed investigations of PEF’s molecular dynamics and its relationship to gas permeation behavior have been reported.[3–6] A model for its crystal structure has also been proposed.[7] In a separate paper, we have reported temperature dependent in situ wide- and small-angle X-ray scattering (WAXS/SAXS) studies on amorphous PEF during uniaxial deformation.[8] In that study, strain induced fibrillar crystals with a high degree of orientation were observed, although the overall induced crystallinity only reached a maximum of $\sim$ 5%. The structural development during stretching has been precisely mapped to stress-strain curves. Parallel study on amorphous PEF has also been reported recently by Stoclet et. al.[9]

In this paper, as a follow-up to the previous study, we report on in situ WAXS/SAXS studies from semi-crystalline PEF being uniaxially stretched at elevated temperatures. Although PEF is known to show a very low propensity to crystallize, it is however possible by thermal treatment over a prolonged time to obtain PEF samples with $\sim$ 25% crystallinity under quiescent conditions. Time-resolved WAXS/SAXS
(particularly as in this case when the two techniques were applied simultaneously) is very useful for characterizing processes, such as crystalline destruction and strain-induced crystallization to be observed over hierarchical length scales. By comparing structural development from the X-ray data with the mechanical properties derived from the stress-strain data provides direct insights into the molecular origin of the mechanical behavior of the polymer.

**Experimental**

**Materials and sample preparation**

The PEF polymer was provided by Coca-Cola Company. The weight and number molecular weights ($M_w$ and $M_n$) were determined to be 87,000 and 66,000 g/mol using multi-angle light scattering (MALS) and 110,000 and 47,000 g/mol using refractive index (RI) techniques, respectively, as calibrated using PMMA standards. Raw PEF pellet had a melting temperature of 219.2 °C, as determined by differential scanning calorimetry (DSC) with a heating speed of 10 °C/min; the glass transition temperature was 83.6 °C, which was determined in the subsequent cooling ramp, at a cooling rate of 30 °C/min. The DSC melting traces of the semi-crystalline films before and after being stretched (at the break strain of $\approx 1.7$) are shown in Fig. S1, in the Supporting Materials. A Carver hot press machine was used to make PEF films for the subsequent X-ray scattering experiments. The PEF pellets were vacuum dried at 140 °C for 3 days before use.

The dried PEF pellets were pressed and melted at 240 °C for 2 min. The temperature of the hot press machine was then reduced to 165 °C, and the film was annealed at this temperature for 1 h, after which time the film was removed from the press and allowed to cool down naturally to room temperature. Films obtained using this two-step annealing process were opaque indicating the presence of crystallinity in the sample. PEF samples used for in situ scattering-deformation experiments were cut from the larger samples and had dimensions of 6 mm × 26 mm × 0.8 mm.
**In situ WAXS/SAXS experiments**

WAXS/SAXS experiments were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline located at Sector 5-ID of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The beam line has three Rayonix CCD cameras installed in-line downstream of the sample to collect successively small- (SAXS), medium- (MAXS) and wide-angle (WAXS) X-ray scattering data simultaneously. The sample-to-detector distances were 197 mm, 1012 mm, and 7496 mm, respectively. The X-ray beam energy was set at 17 keV, corresponding to a wavelength of 0.7293 Å. Typical exposure time was 2 s.

A Linkam TST350 tensile stage was mounted vertically in the sample position at the beamline, so that the PEF films were perpendicular to the incident X-ray beam. X-ray scattering patterns were collected *in situ* during uniaxial stretching of the PEF sample at elevated temperatures. The stretching speed of the samples in all experiments was $50 \mu\text{m} \text{s}^{-1}$. Stretching experiments were carried out at 200 °C. The reason for using this relatively high temperature was that the force limit for Linkam machine was 200 N, and for the semi-crystalline films the tensile force exceeded the load limit at lower temperatures. In addition, at lower temperatures, we found the semi-crystalline films were very brittle and failure occurred at very small strains.

**Results and Discussion**

When PEF was annealed at 165 °C after cooling from the molten state, quiescent crystallization was observed to take place. However, after annealing for 1 h the PEF sample could only achieve a crystallinity of $\sim 25\%$ (as estimated from the WAXS profile by calculating the ratio of sum of the scattering intensities from all the detected diffraction peaks over the total scattering intensity; details will be discussed later). WAXS/SAXS patterns of these samples were isotropic, and the films were opaque and brittle at room temperature, and consequently stretching was only possible at elevated temperatures. The WAXS/SAXS patterns of semi-crystalline PEF film stretched at 200 °C are shown in Fig. 1, where the major diffraction
peaks have been indexed based on previous crystallographic studies.[7] By comparing the WAXS and SAXS patterns that PEF crystals and crystal lamellae had very different orientation modes in the early and late stages of the stretching processes. WAXS/SAXS patterns at different stages in the stress-strain curve is shown in Fig. S2 in the Supporting Materials.

The WAXS/SAXS patterns in the late stage of stretching (e.g., patterns at $\varepsilon = 1.67$ in Fig. 1) are the easiest to explain qualitatively. From the WAXS patterns it can be seen that all the $(h00)$ peaks appear along the equator. It indicates that the $a$ and $b$ axes of the unit cell are perpendicular to the strain direction. It follows that the polymer backbone, which is parallel to the $c$-axis of the unit cell, is parallel to the stretching direction. The corresponding SAXS pattern at high strains, consists of equatorial streaks and two diffuse scattering maxima that are symmetrically positioned in the meridian direction above and below the beam center. The equatorial streaks were attributed to polymer chain bundles and fibrillar crystals, whilst the maxima in the meridian direction are due to periodic stacking of amorphous phase and crystal lamellae. From the position of these maxima in the SAXS profiles, the inter-lamellar repeating distance was found to be $\approx 15$ nm. Higher order peaks were not observed due to low crystallinity and disorder. It should be pointed out that for strain-induced crystallization in amorphous PEF, crystallinity was much lower ($\sim 5\%$), and no ordered lamellar stacking could be identified using SAXS.[8]

By comparison, the scattering patterns during the early stages of deformation from the initially isotropic sample, however, are not so straightforward. At a strain of 0.60, scattering patterns are clearly no longer isotropic and in the WAXS patterns the $(020)$ peak has begun to center around the equator, indicating that on average this plane is parallel to the strain. However, the $(101)$ and $(1\overline{1}0)$ peaks become centered around the meridian, $i.e.$, these planes are perpendicular to the strain, meaning that the polymer chains in the crystals are clearly not oriented in the strain direction. At this strain, a four-lobe pattern is observed in the SAXS, a feature, which is sometimes called a ‘butterfly’ pattern, which indicates that equal proportions of the lamellae are at an angle to the strain direction. As strain increased, $i.e.$, at intermediate strain, the SAXS four-lobe pattern collapsed into the characteristic two-lobe structure that persists to
higher strains. The presence of a two-lobed pattern means that the lamellae are perpendicular to the strain, but at intermediate strains the inter-lamellar spacing is larger than seen at higher strain. At these intermediate strains the WAXS pattern shows that the crystalline alignment is complex. The (020) peak becomes further focused around the equator compared to lower strains, showing reduced distribution of crystal alignment, that is a greater degree of orientation of this plane parallel to the strain direction. In addition, the (110) peak has now split and there is intensity distribution around both the equator and meridian.

**Figure 1.** WAXS (top row) and SAXS (bottom row) patterns of semi-crystalline PEF film stretched at 200 °C, at three selected strains. The stretching direction is vertical for all images ($\phi = 0^\circ$). WAXS patterns at strain equaling to 0.60 and 0.92 are displayed on a linear scale; and all other images are in logarithmic scale.

To explain the observed orientation behavior, we first examine different types of orientation modes. To simplify the discussion, only simple fiber symmetry is used, which is often an excellent approximation of a polymer stretched at high strains. Although this assumption may fail at low strains, it can nevertheless still serve as a good starting point for qualitative discussions. Two rotation axes need to be employed to define the geometry of simple fiber symmetry. A principal axis of rotation (PA) is the rotational symmetry axis of the structural units, and an ensemble of the structural units has rotational symmetry...
around the fiber axis (FA).\textsuperscript{[10]} It needs to be pointed out that each structural unit does not necessarily have a circular shape to possess rotational symmetry around PA, the effect can also occur for an ensemble average as well. Three types of orientation modes can be defined for such a system, as shown in Fig. 2. When PA is parallel to FA, it is called \textit{parallel orientation}; and \textit{perpendicular orientation} refers to the situation when PA is perpendicular to FA. The last orientation mode is for \textit{oblique orientation}, where there is an oblique angle between FA and PA.

A function \( g(\beta) \) can be used to represent the orientation distribution function (ODF) in real space, defining the orientation state of the structural units. To calculate the 2D diffraction pattern, one needs to smear the scattering intensity for a given \((hkl)\) plane using a transformation kernel which is associated with \( g(\beta) \). Both the parallel and perpendicular orientations are simple cases where the diffraction intensity has an analytical form depending only on the polar angle \( \phi \), and modulus of scattering vector \( s \) \((s = (2/\lambda)\sin(\theta/2))\), with \( \lambda \) being the wavelength and \( \theta \) being the scattering angle), if an appropriate functional form of \( g(\beta) \) is selected. Computing diffraction patterns corresponding to oblique orientation is more complex, but can be achieved by employing the Legendre expansion technique (see detail in the Appendix).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Illustration of three orientation modes, categorized by geometric relationship between fiber axis (FA) and principle axis of rotation (PA) that are display parallel (a), perpendicular (b), and oblique (c) orientation to each other.}
\end{figure}
Figure 3 shows the computed fiber diffraction patterns of PEF assuming different orientation modes. The parallel orientation mode with the c-axis aligned with the fiber axis (in our case, the stretching direction) is shown in Fig. 3a. The calculated diffraction pattern explains the peak positions of all the \((hkl)\) planes in experimental data of the semi-crystalline PEF in the late stages of stretching, cf Fig. 1 at \(\varepsilon = 1.67\). When calculating diffraction patterns in Fig. 3, the effect of disorder was not considered, which could significantly weaken the large-angle diffraction peaks. This is the reason why more diffraction peaks are visible in the calculated patterns, and they appear more intense than those observed experimentally.

Clearly, Fig. 3a cannot explain the diffraction pattern collected in the early stages of stretching. It is therefore necessary to consider other oblique orientation modes to simulate the observed diffraction pattern. In the first case, oblique c-axis orientation is considered, meaning that the c-axis and PA are parallel, but have an oblique angle, \(\beta_0\), with respect to FA, as shown in Fig. 3b. In this case, all the \((hk0)\) planes are close to the equator, which is not what has been observed and can be ruled out. Figure 3c corresponds to the calculated diffraction pattern from oblique b-axis orientation. In this case, the b-axis is coincident with PA, which is at an oblique angle to FA. This orientation produces a broad \((020)\) arc close to the equator, and \((101)\) and \((110)\) arcs close to the meridian. This pattern seems to explain the experimental data shown in Fig. 1 at low strain. However, on closer inspection a major discrepancy in the position of the \((110)\) peak is evident, as it is closer to the meridian in experimental data than in the predicted pattern (Fig. 3c). An oblique [120] orientation, defined such that the [120] crystallographic direction is coincident with PA, but is oblique with respect to FA, is shown in Fig. 3d. In this case, both \((101)\) and \((1\overline{1}0)\) peaks are centered near the meridian. This structure is entirely consistent with the experimental diffraction pattern at low strains.
Figure 3. Calculated 2D WAXS patterns of PEF crystals with different orientation modes using the methods described in the Appendix. FA and PA stand for the fiber axis and principal axis of rotation, respectively. Pattern (a) was displayed in logarithmic scale. Patterns (b-d) are on a linear scale. See details in the text for the description of different types of orientation.

As has been pointed out, application of simple fiber symmetry is unlikely to be appropriate to explain orientation modes in the early stages of deformation, and indeed the real orientation condition is more likely to be a superposition of different modes. Therefore, we tend not to explicitly explore geometric relationship between crystallographic directions and PA. Nevertheless, Fig. 3 indicates that when PA is approximately perpendicular with respect to FA, and is nearly coincident with the $b$-axis of the unit cell, the fiber diffraction pattern in the early stage of stretching can be qualitatively explained. We show below that this orientation mode most likely originates from complex stress distributions induced by tensile force in the sample.
For an oblique orientation, the ODF in real space is centered at $\beta_0 \neq 0^\circ$; $\beta_0$ is the oblique angle where the majority population of the structural units is oriented nearby (see Fig. 9 in the appendix). Consequently, $(0k0)$ arcs will be off-axis from the equator. In the early stage of stretching, the intensity around the $(020)$ diffraction arc in the WAXS pattern has broad, symmetric distribution around the equator (see Fig. 1). Figure 4 shows three selected plots of the $\phi$-dependence of the scattering intensity of the $(020)$ diffraction peak in early stages where $\varepsilon < 0.6$. The broad maxima in Fig. 4 although centered on the equator, i.e., $\phi = 90^\circ$, cannot be fitted using a simple bell-shaped function. Fits to these data were only possible by considering oblique orientation modes through use of a Legendre expansion method. The broad maxima are actually due to a superposition of two off-axis intensity maxima with narrower peak widths, the fitting of which allows the determination of the oblique angle $\beta_0$ and degree of orientation.

![Figure 4. $\phi$-dependence of scattering intensity of the (020) arc, at different strains, in the early stage of stretching. Points are experimental data; and solid lines are fitted curves using oblique orientation mode. $\phi = 0^\circ$ is consistent with the stretching direction, as shown in Fig. 1.](image)

Of particular interest is the change of the oblique angle $\beta_0$ during the early stages of stretching. The value as determined through fitting the angular dependence of the $(020)$ arc in the WAXS data can be compared with orientation of the lamella determined from the SAXS data. From the SAXS data, $\beta_0$ was
directly measured from the position (in $\phi$-dependent scattering intensity) of the lobes in the four-point pattern, which provides the orientation angle of the crystal lamellae (from the normal of the lamella). Comparison of calculated values of $\beta_0$ derived from WAXS and SAXS analysis are shown in Fig. 5. Over the strain range from $\approx 0.25$ to $\approx 0.7$, the values of $\beta_0$ determined from both SAXS and WAXS increased by $\approx 15^\circ$, toward equatorial direction, showing that orientation of unit cells is consistent with that of crystal lamellae. However, there is a difference of $\approx 15^\circ$ between the values of $\beta_0$ determined from the SAXS and WAXS data. There are a number of potential reasons for this discrepancy. The first is the possibility that polymer chains along the $c$-axis are not normal to the plane of the lamellae. Given the complexity of the molecular and mesoscale rearrangement required for the system to adopt a defined oriented state from one that was entirely isotropic, a simple ODF might not be able to fully capture the real orientation process, leading to discrepancies between the SAXS and WAXS analysis. On the other hand, as a qualitative understanding, there is a possibility that polymer chains ($c$-axis direction in the unit cell) have a tilting angle with the normal of a crystal lamella.

Using this analysis procedure on the 2D WAXS and SAXS patterns, a physical model of the deformation process of the semi-crystalline PEF can be established. Keeping in mind that the initial crystallinity was very low, tensile forces was transmitted to the lamellar crystals through the amorphous network. In their initial state, lamellar crystals are locally stacked together, but the orientation direction of each stack are random relative to each other, making the system isotropic. Although generally agreed that tensile forces can cause both inter-lamellar and intra-lamellar slip, the interplay between these parameters in PEF is complex.[11–13] At the onset of strain, lamellae initially begin to rotate so that their normals point in the equatorial direction. Since equal numbers of lamellae rotate in the both positive and negative directions to the strain, this leads to the observed symmetric four-lobe SAXS pattern. These lobes show an increasing divergence as deformation increases, indicating that the lamellae continue to rotate until orientated parallel to the strain direction. Analysis of the WAXS pattern, however, shows that the (101) and (1\bar{1}0) move toward the meridian, whilst the (020) moves toward the equator, indicating a rotation around an
axis close to the $b$-axis. This can be understood by applying a qualitative examination. For example, if $c$-axis is the PA (see Fig. 2), then all $(h k 0)$ planes should reside on the equator. On the other hand, if $a$-axis is aligned with the PA, then the $(0 k 0)$ planes are observed as isotropic rings after intersecting the pole figure with the Ewald sphere. This behavior could be explained by intra-lamellar slip along the [100] direction (although it might not be exactly coincident with the plane). This type of slip has also been observed during uniaxial deformation of PET,[14,15] and polyolefins such as polyethylene (PE),[16–18] although whether inter-lamellar and intra-lamellar slip occurred in these polymers at the same time or successively is dependent both on the polymer and the processing conditions. In our case, intra-lamellar slip took place at the very beginning of stretching, which is consistent with the behavior that has also been reported when stretching PE.[12]

![Figure 5](image-url)

**Figure 5.** Change of oblique angles as a function of strain in the early stage of stretching. Both oblique angles derived through fitting the (020) arc in WAXS patterns, and that derived by direct measuring tilting angle of lobes in four-point SAXS patterns are shown.

As stretching proceeded in the intermediate strain regime, the existing association of lamellar crystals were largely destroyed. At the same time, analysis of the amorphous PEF chain conformation from the WAXS data shows that they are highly aligned with the stretch direction. This chain alignment and their close association explains the observation of the formation in the SAXS pattern of maxima in the
meridian. This indicates development of newly grown lamellae perpendicular to the stretch direction. The perpendicular lamellae alignment relative to the strain direction is also consistent with the WAXS patterns, which show that all the \((h00)\) planes are aligned in the equatorial direction, a behavior that is quite universal for most semi-crystalline polymers under uniaxial deformation.

The 1D sectional average of SAXS intensity including the lobes in four- and two-point patterns are shown in Fig. 6 for measurements at selected strains. The average inter-lamellar distance, i.e., the long period, can be determined by the position of the maximum for each curve. As the stretching process continues, intensity maximum moves toward small values of \(s\) (for strains less than 0.58), and then toward larger values of \(s\) (for strains greater than 0.82). This corresponds to an increase of inter-lamellar distance in the initial stages of deformation before it decreases in the late stages of elongation. Intensity decays in the large angles are in general close to the \(\sim s^{-4}\) asymptote, suggesting a relatively sharp boundary between crystalline and amorphous phases.

**Figure 6.** Selected 1D SAXS profiles of semi-crystalline PEF stretched at 200°C, at different strains. The dashed line shows a \(l \sim s^{-4}\) asymptote.

The instantaneous crystallinity in the semi-crystalline sample as a function of strain, can be determined by taking the ratio of integrated scattering intensity under all the diffraction peaks to that under the entire
scattering profile in WAXS data. The crystallinity determined using this method is accurately known as the relative crystallinity index, although we use the term crystallinity throughout this paper for simplicity. It is useful to plot the change of crystallinity (derived from the WAXS data) as a function of strain together with long period derived from SAXS data, which together are able to provide insights into structural development at multiple length scales. The benefits of simultaneous measurement of WAXS/SAXS and stress-strain data, are now apparent since results from the two techniques can be matched exactly. Figure 7 shows the engineering stress-strain curve (Fig. 7a), and the structural parameters during stretching (Fig. 7b) for the PEF sample deformed at 200 °C. Initially there is an increase in the long period, but at $\varepsilon \approx 0.6$ the trend changes and as strain increases the long period decreases. The change of crystallinity index, shows the reverse trend, with an initial drop of a few percentage and then for $\varepsilon \geq 0.6$, the crystallinity can reach an asymptotic value of approximately 32%.

For $\varepsilon < 0.6$, the decrease of crystallinity can be explained due to partial destruction of existing lamellar crystals. This is consistent with the trend of increasing in long period where the lamellae are increasingly pulled apart by uniaxial tensile forces. The deformation-induced destruction of the pre-existing lamellar crystal aggregates has been observed in many other polymeric materials.[12,19–23] Since the temperature of the measurements was only $\approx 20 ^\circ C$ below $T_m$, strain-induced crystallization can occur rapidly where the amorphous chains are highly aligned. Consequently, it can be assumed that at $\varepsilon \approx 0.6$ the amorphous chain alignment is optimal for onset of crystallization, creating new lamellae. It should be noted that the initial lamellae are not completely destroyed by the applied strain as evidenced by the crystallinity never dropping below 22%. However, the long period of the newly generated lamellae decreased from a maximum of $\approx 15\text{ nm}$ down to $\approx 12\text{ nm}$, which is the same dimension as that of the quiescent created lamellae. The decrease could in part be due to growth of these new lamellae between the pre-existing lamellae.[20,21,24–26]
Figure 7. Engineering stress-strain curve of PEF stretched at 200 °C (a); and relative crystallinity index determined by WAXS and long period determined by SAXS during the stretching process (b).

The stress-strain curve for a semi-crystalline PEF (shown in Fig. 7a) is very different from the behavior observed by amorphous PEF.[8] In the latter, stress slowly increased with strain until strain-hardening was observed due to the onset of crystallization. By comparison, in the current work, the stress-strain behavior of the semi-crystalline PEF shows an initially abrupt increase of stress at the initial application of strain, associated with a resistance to deformation produced by the existing semi-crystalline network. After this initial increase, stress increases at a much slower rate with strain due to the crystalline assemblies being continuously modified including as discussed above by lamellae rotation. At strains greater than $\varepsilon \approx 0.6$, newly formed strain-induced crystallinity starts to play a role, ultimately leading to the onset of strain-hardening. Unlike the observations in amorphous PEF, the strain-hardening regime for
semi-crystalline PEF is much broader. This is because the apparent stress-strain curve has two competing contributing processes, namely, the destruction of the existing network and crystalline aggregates, and formation of strain-induced crystallization.

For semi-crystalline systems, in addition to the long period, the lamellar thickness $l_c$ is also of interest, which can be derived using a 1D correlation function approach. The 1D correlation function can be defined as follows:[27]

$$
\gamma_1(r) = \int_0^\infty I(s)s^2 \cos(2\pi sr)ds / \int_0^\infty I(s)s^2ds
$$

Equation 4 is essentially a Fourier cosine transform of the Lorentz-corrected 1D scattering curve, normalized by the scattering invariant. To apply the transformation accurately, extrapolation of the data beyond the limits of experimental intensity to small and large values of $s$ needs to be carried out. In our case, a Guinier-type exponential function (Eq. 5) was used to account for the small-angle data extrapolation:[28]

$$
\lim_{s \to 0} I(s) = k \cdot \exp(-bs^2)
$$

In Eq. 5, $k$ and $b$ are fit parameters used to extrapolate the data to scattering angles close to the beam stop. Extrapolation to high values of $s$, was not necessary as the high-angle data collected by the small-angle detector (SDD=7496 mm) coupled with the small-angle data collected by the mid-angle detector (SDD=1012 mm) provided data up to values of $s \approx 0.8 \text{ nm}^{-1}$. In reality, the SAXS data reached baseline values at $s \approx 0.5 \text{ nm}^{-1}$. Given our high-angle data collection range exceeds the limit at which background is observed, large-angle data extrapolation was not necessary in this case. Calculated 1D correlation functions as a function of (real space) distance, $r$, at three strains are shown in Fig. 8. We should point out that only the first-order scattering maximum could be observed in all SAXS patterns, the correlation between crystal lamellae was weak. Therefore, no effort was made to apply correlation function analysis to all data frames continuously collected during stretching, to produce a continuous spectrum of correlation curves. Instead, correlation functions at three critical points, namely, before
stretching, \( i.e., \varepsilon = 0 \), at \( \varepsilon = 0.62 \) (near the turning point of crystallinity index and long period change), and in the late stage of stretching (\( \varepsilon = 1.67 \)) was evaluated, as shown in Fig. 8.

In Fig. 8, \( \gamma_1(r) \) first decreases monotonically, reaches a minimum and starts to increase and then reaches the first maximum. After that, it starts oscillating, with a decaying amplitude until reaching a constant value at \( \gamma_1(r) = 0 \). The position of the first maximum corresponds to long period. The first zero point, \( r_0 \), namely, the distance where \( \gamma_1(r) \) first intersect with \( \gamma_1(r) = 0 \), is of importance. It is related to lamellar thickness through the following relationship (assuming volume crystallinity is less than 50%, which is valid in our case)[29]

\[
\frac{r_0}{L} = \nu_t (1 - \nu_t)
\]  

(6)

where \( L \) is the long period and \( \nu_t \) is the so-called linear crystallinity, which is the ratio between the lamellar thickness and the long period. The calculated lamellar thicknesses for the three strains are given in Table 1. It is clear that stretching did not cause much change in lamellar thickness, though a fairly large variation of inter-lamellar distance has been observed.
Table 1. List of linear crystallinity and lamellar thickness at three selected strains, determined using 1D correlation function method.

<table>
<thead>
<tr>
<th>$\varepsilon$</th>
<th>$\nu_l$</th>
<th>$l_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.33</td>
<td>4.0</td>
</tr>
<tr>
<td>0.62</td>
<td>0.29</td>
<td>4.2</td>
</tr>
<tr>
<td>1.67</td>
<td>0.36</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The physical picture of deformation of semi-crystalline PEF at high temperature merges, after integrating WAXS/SAXS data and stress-strain curve. The tensile force first destructed existing crystalline assemblies, namely, lamellar crystals connected by inter-lamellar amorphous chains. Lamellae became more and more separated before $\varepsilon \approx 0.6$. Due to the high temperature, PEF chains were mobile enough to form new crystals as stretching proceeded. This caused increase of crystallinity. Some of newly-grown crystals could insert in between the existing lamellae, causing decrease of long period. During the entire process, lamellar thickness was kept unchanged.

Conclusion

By combing analysis of the stress-strain measurements with that from WAXS/SAXS data, the structural development of PEF during uniaxial stretching experiments can be correlated with the mechanical properties. The following major conclusions can be drawn from these in situ, time-resolved WAXS/SAXS study of semi-crystalline PEF polymer.

Uniaxial stretching was able to dissociate pre-existing crystal assemblies, causing them to become more separated. This caused an increase of long period (as revealed by SAXS), and a decrease of crystallinity (as revealed by WAXS), in the early stage of stretching when $\varepsilon$ was less than $\approx 0.6$. At strains greater than $\approx 0.6$, the deformation causes new strain induced crystals to form, and because of higher degree of chain orientation in the amorphous phases. This caused an increase in the crystallinity and decrease of the long period, as some of newly-grown lamellae are able to insert in between existing lamellae. Despite
these changes in crystallinity, the thickness of the lamella remains almost unchanged throughout the stretching process.

Appendix. Calculating fiber diffraction patterns for oblique orientation modes

For fiber diffraction patterns showing distinct Bragg peaks, the intensity distribution as a function of the \( \phi \)-angle at a given \( s \), can be written as:[16, 27]

\[
I(s, \phi) = I_{hkl} \cdot F(\phi_{hkl}, \phi)
\]  
(A1)

Where \( I_{hkl} \) is the powder-averaged intensity for a given \((hkl)\) plane, \( \phi_{hkl} \) is the polar angle (see Fig. 5), and \( F(\phi_{hkl}, \phi) \) is the transformation kernel smearing \( I_{hkl} \) along \( \phi \), which is transformed from the orientation distribution function (ODF), \( g(\beta) \).[16, 28, 29] For parallel and perpendicular orientation (see the main text for definition), \( F(\phi_{hkl}, \phi) \) has a simple analytical form if \( g(\beta) \) is chosen appropriately. For oblique orientations, where the ODF is centered at an off-axis position, no simple form of \( F(\phi_{hkl}, \phi) \) has been found so far. One might attempt to use \( g(\beta - \beta_0) \) to describe ODF, but it becomes immediately clear that \( g(\beta - \beta_0) \) will not be able to normalize in the range of \( 0 \leq \beta \leq \pi/2 \).[16]

It has been shown that the Onsager function is well-behaved, producing reasonable bell-shaped profile. It can be used to describe parallel orientation, and has the following form:[3, 12, 16]

\[
g_{ON}(\beta) = p \cdot \text{csch}(p) \cdot \cosh(p \cos \beta)
\]  
(A2)

where \( p \) defines the profile width. Applying a Legendre expansion to Eq. (A2) yields:

\[
g_{ON}(\beta) = p \cdot \text{csch}(p) \sum_{n=0}^{\infty} (1 + 4n)i_{2n}(p)P_{2n}(\cos \beta) \equiv \sum_{n=0}^{\infty} a_n P_{2n}(\cos \beta)
\]  
(A3)

where \( i_n(p) = \sqrt{\pi/(2p)}I_n(p) \), with \( I_n(p) \) being the modified Bessel function of the first kind of order \( n \).
Figure 9. Illustration of equatorial scattering intensity distribution due to oblique orientation for system possessing simple fiber symmetry.

We now construct the ODF with an oblique angle $\beta_0$, by applying another Legendre expansion based on Eq. (A3), written as

$$\tilde{g}(\beta, \beta_0) = \sum_{0}^{\infty} a'_n p_{2n}(\cos \beta)$$  \hspace{1cm} (A4)

where $a'_n = a_n p_{2n}(\cos \beta_0)$. Using $\tilde{g}(\beta, \beta_0)$ as the new ODF that accounts for the oblique angle, the transformation kernel can be expressed in expanded form as:

$$F(\phi_{hkl}, \phi) = \sum_{0}^{\infty} a'_n p_{2n}(\cos \phi) p_{2n}(\cos \phi_{hkl})$$  \hspace{1cm} (A5)

Substituting Eq. (A5) into Eq. (A1), the $\phi$-dependence of the scattering intensity for a given $(hkl)$ plane can be computed. For relatively broad line profiles, as those shown in Fig. 8, only a few terms of the Legendre polynomial are needed.

A typical feature of fiber diffraction patterns from a system with oblique orientations is apparent broad diffraction peaks. This effect can be understood with reference to Fig. 9. For a perfectly aligned system
(with respect to the fiber axis), the \((hk0)\) peaks occur at the equator. At a given \(s\), the fiber-averaged result is a \(\delta\)-ring at the equator. In the presence of an oblique angle \(\beta_0\), fiber-averaging yields a croissant-shaped broad intensity distribution close to the meridian.[10] The intensity minimum is exactly located on the equator. That is, the broad equatorial arc is actually composed of two off-axis intensity maximum close to the equator. When the orientation distribution is not too narrow, very often one cannot distinguish these two peaks, as can be seen in Fig. 8. But the profiles would not be able to be fitted by using one single bell-shaped function.

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**Reference**


**Highlights:**

1. Deformation of semi-crystalline PEF film was investigated *in situ* using X-ray scattering;
2. Orientation modes of PEF crystals could be modeled by applying 2D scattering pattern analysis;
3. Crystal destruction and strain-induced crystallization could be mapped to stress-strain curve.