Microstructural Evolution of *Isotactic*-Polypropylene during Creep: An *in-situ* Study by Synchrotron Small Angle X-ray Scattering

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Abstract: The structure evolution of *isotactic*-polypropylene during creep is investigated by *in-situ* synchrotron small angle X-ray scattering. During primary creep, strain grows nonlinearly to a value less than 15 %. The long period in loading direction ($L_{\parallel}$) increases with time, whereas the long period perpendicular to loading direction ($L_{\perp}$) decreases slightly. During secondary creep, strain increases linearly with time. $L_{\parallel}$ and $L_{\perp}$ shows the same tendency with strain. The increase of the long period is caused by lamellae thickening, which is a kind of cooperative motion of polymer chains with their neighbors at the lamellae surface. Moreover, the growth rate of $L_{\parallel}$ is larger than that of $L_{\perp}$, indicating that the orientation of molecular chains along loading direction decreases the energy barrier of the cooperative motion. During tertiary creep, strain grows dramatically in a short time. In this step the lamellae were tilted, rotated, and then disaggregated. In addition, a fibrillar structure is formed during lamellae breaking. The length of the fibrillar structure increases from 364 nm to 497 nm while its width stays at 102 nm with increasing creeping time.

1. Introduction

Polypropylene (PP) is a type of thermoplastic which is used in a wide variety of areas including packaging, textiles, laboratory equipment, automotive components, etc. According to a survey by Ceresana, the global market for PP was about 55 million tons in 2013.^[1] Considering its ever-increasing range of applications in our daily life and in the engineering field, it is of great significance to evaluate the microstructure response under mechanical load.^[2-7] Unlike to uniaxial drawing, compression and impact tests, creep test serves as an effective method for the long-term life time assessment of polymer materials. Creep is generally defined as a time-dependent deformation under constant load for a prolonged period at constant temperature. Generally, creep behavior can be elaborated well within the framework of linear viscoelasticity.^[8] The master curve of creep compliance can be constructed by using the time-temperature superposition concept based on the William-Landel-Ferry equation.^[6, 9] Satapathy and his colleagues studied the short term tensile creep behavior of PP/multi-walled carbon nanotubes composites employing time-temperature superposition. The results indicated that nanocomposites showed an increase in creep compliance with increasing temperature as a consequence of the temperature-activated motion of the polymer chains.^[6] A prerequisite for linear viscoelasticity is that the creep compliance is only a function of time and temperature, which could not be fulfilled all the time, unfortunately. When the strain is beyond a certain limit, the creep compliance becomes a function of time, temperature and stress.^[10] In that case, tensile creep should be considered as a non-iso free-volume process. Kolařík^[10-13] successfully proposed a procedure to transform the as-received creep data to a pseudo-iso free-volume state. This makes it possible to construct a generalized creep compliance curve under any selected stress in the range of reversible deformations. The procedure was utilized to explain the influence of crystallinity or rubber content on the creep compliance of PPs, including isotactic-PP (*i*PP), *i*PP blends

consisting of 88 % of *i*PP and 12% of ethylene/propylene rubber (EPR), rubber-toughened *i*PP, etc.

It is widely accepted that the crystalline structure and morphology of *i*PP has a significant effect on its creep behavior. Sliding of tie chains and their detachment from lamellar blocks play a key role in the time-dependent response of *i*PP.^[14, 15] The mobility of chain-segment in the amorphous phase influences the creep deformation of β -*i*PP.^[3] The increase of crystallinity, the presence of subsidiary lamellae in the amorphous region, and the integration of preexisting lamellar structure would enhance the creep resistance of *i*PP.^[16, 17] Liao^[18] found that well-developed spherulites with integrated crystalline structure, showed poor creep resistance. Bundle-like morphology, whose crystalline phase was imperfect, had a better creep resistance. Finally, needle-like morphology, in which the crystalline phase was disordered and the long spacing was the largest, shows the best creep resistance.

Despite the fact that considerable attentions have been applied, the microstructure evolution of *i*PP during creep is not yet well understood. In this study, the microstructural evolution of *i*PP during creep is characterized by *in-situ* synchrotron small angle X-ray scattering (SAXS) measurements. SAXS is employed because of its nondestructive feature and powerful detection ability for the microstructure with a size ranging from several nanometers to several hundred nanometers. In addition, modern synchrotron radiation sources enable us to get low-noise SAXS patterns with high time and spatial resolution, which greatly benefits *in-situ* study. The results reveal that the microstructural development in different creep stages differs from each other distinctly. The evolution of long period and lamellae thickness in secondary creep, as well as the lamellae disaggregation, and formation of fibrillar structure in tertiary creep are studied in detail.

2. Experimental Section

2.1. Materials and sample preparation

The *i*PP used in this study is a homopolymer, grade HD120MO, manufactured by Borealis (Linz, Austria). The weight-average and number-average molecular weights are $365 \text{ kg}\cdot\text{mol}^{-1}$ and $67.6 \text{ kg}\cdot\text{mol}^{-1}$ respectively, and the melt flow index is 8 g/10 min (at 230 °C and 2.16 kg) ^[19]. Compression molded plates with a thickness of 1 mm were produced by heating injection molded *i*PP plates to 210 °C for 5 min, and subsequently cool them down to room temperature at $15 \text{ K}\cdot\text{min}^{-1}$. Via this procedure the thermal history and anisotropy of the morphology should be erased.

2.2. Creep test

Creep tests were performed in a force-controlled mode on a custom-made miniature tensile machine designed by the Leibniz Institute of Polymer Research Dresden for *in-situ* studies at the synchrotron. During the measurement, both grips move simultaneously in opposite directions to keep the beam position on the sample at a fixed point. In any test, the specimens were loaded with a cross-head speed of 0.1 mm s^{-1} to the defined stress, and then the stress was kept constant. The true strain was determined optically by monitoring the deformation of a grid pattern ($0.35 \text{ mm} \times 0.35 \text{ mm}$) applied on the specimen surface. ^[20]

2.3. *In-situ* synchrotron small angle X-ray scattering (SAXS) measurement

In-situ synchrotron SAXS measurements were performed at the MiNaXS beamline at Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany. ^[21] The energy of the X-ray radiation was 11.5957 keV, resulting in a wavelength of 0.106917 nm. The patterns were recorded using a Pilatus 1M detector (981×1043 pixels with a pixel size of $172 \times 172 \text{ }\mu\text{m}^2$). The distance between the specimen and the detector was 4961 mm. A dynamic technique ^[22] was used to record SAXS data during the experiment, i.e., to catch pattern continuously

without stopping the stretching of the specimen. An exposure time of 0.5 s and a time interval between the measured patterns of 7.5 s were chosen to avoid burning of the specimen by X-ray. Data processing was performed by PV-Wave software package from Visual Numerics.^[20] All SAXS patterns were corrected with respect to air scattering.

3. Results and Discussion

3.1. Creep test results

Typical creep curve at 120 °C are shown in **Figure 1a**. It is obvious that the displacement (Δd , black triangle) and the true strain (ε , blue square) increase with time. According to the change of Δd and ε , the creep curve for a load of 8 MPa can be splitted into four intervals:^[7]

- (I) Primary creep, in this stage, ε grows quickly to 15 % within sufficiently small time (not more than 80 s). The deformation during primary creep can recover after releasing the force. It is caused by the visco-elastic deformation of polymer chains in the amorphous phase inside the hard crystalline skeleton.^[23]
- (II) Transition region, from 80 s to 280 s. In this stage, the strain rate ($\dot{\varepsilon}$) decreases with the increasing time, till the secondary creep is established.
- (III) Secondary creep, from 280 s to 1152 s. The creep process in this stage is a steady state. Δd increases nearly linear with time, and $\dot{\varepsilon}$ approaches to a constant value. The duration of the secondary creep is the longest period of the whole creep process. It is remarkably longer than the primary creep and the tertiary creep. The strain evolution during secondary creep can be described by the empirical function

$$\varepsilon(t, \sigma, T) = \varepsilon_e(\sigma, T) + \varepsilon_v(t, \sigma, T) + \varepsilon_p(t, \sigma, T), \quad (1)$$

where $\varepsilon(t, \sigma, T)$ is the strain during tensile creep, t is the creep time, σ is the creep stress, and T is the temperature, $\varepsilon_e(\sigma, T)$ is the reversible elastic component, $\varepsilon_v(t, \sigma, T)$ is the time-dependent viscoelastic part which is also reversible and $\varepsilon_p(t, \sigma, T)$ is the irreversible plastic part.^[11] Before plastic deformation happens within the creep process, the strain can be described as

$$\varepsilon(t, \sigma, T) = \varepsilon_e(\sigma, T) + \varepsilon_v(t, \sigma, T) \quad (2)$$

The secondary creep is a steady state, which means that the strain rate is nearly constant.^[7, 18] Secondary creep contributes mainly to $\varepsilon_v(t, \sigma, T)$. Therefore, the investigation of the structural evolution during secondary creep will help to get a better understanding of the mechanism of creep, which enables a better prediction of the lifetime of the polymer materials in use.

- (IV) During tertiary creep necking happens, whereby ε grows rapidly within a short time and the sample will fail.

The loading stress (σ) has a great impact on the speed of creep deformation.^[24] This can be understood by examining the data in **Figure 1b**. With a slight increase of σ , $\dot{\varepsilon}$ in secondary creep increases greatly and the creep failure lifetime decreases remarkably.^[25, 26] The higher the applied σ , the faster the creep deformation proceeds. Generally, the dependence of $\dot{\varepsilon}$ on σ during secondary creep can be approximated by the Eyring equation^[27]

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp[(\sigma V / k_B T)] \quad (3)$$

where $\dot{\varepsilon}_0$ is a pre-factor, k_B the Boltzmann constant, T the temperature, and V the activation volume. The linearity of $\ln \dot{\varepsilon}$ vs. σ is checked by linear regression, and the correlation coefficient is 0.99. The activation volume calculated from the slope of the fitted line in **Figure**

$1c$ is 2.12 nm^3 , which agrees well with the values provide by other studies (in the range between $2\text{-}4 \text{ nm}^3$).^[24, 27, 28] At the very end of the secondary creep a critical strain (ε_c) is reached, which decreases with the increase of σ . The decrease of ε_c indicates that the creep here should be treated as a non-linear viscoelasticity behavior. Otherwise ε_c should keep constant regardless of σ .^[4, 29-32] Generally, the non-linearity of tensile creep is mainly caused by the strain-induced free volume increment.^[10, 33]

Figure 1. (a) Creep curve of *iPP* under constant stress (8 MPa) at 120 °C. The black triangles show the displacement (Δd) and the blue square the true strain (ε); (b) Creep curves of *iPP* under various stresses (σ) at 120 °C; (c) plot of the strain rate $\ln\dot{\varepsilon}$ and the critical strain ε_c as a function of σ , the straight lines are obtained by linear regression.

3.2. *In-situ* SAXS results

In order to detect the microstructure evolution during creep, *in-situ* SAXS measurements were carried out on the specimen during creep at 8 MPa at 120 °C. **Figure 2** shows a few characteristic SAXS patterns during creep in different characteristic abovementioned stages. The signature of the 2D-SAXS patterns is associated with spatial ordering of the crystalline lamellae.^[34-37] The initial isotropic SAXS pattern results from randomly oriented lamellae before creep. During primary creep, the scattering intensity in the meridional direction enhances whereas the scattering intensity in the equatorial direction weakens slightly. This indicates a slight orientation of lamellae. In addition, dark arcs in the equatorial direction can be observed which are caused by the shift of the scattering in the meridional direction towards the center of the pattern, suggesting the change of the lamellae stacking in the meridional and the equatorial direction. A quantitative discussion about the change of lamellae stacking will be given in the following section. During secondary creep, the SAXS pattern changes to an anisotropic ellipse. The long axis of the ellipse is perpendicular to the loading direction. During tertiary creep, the SAXS patterns change from slight ellipses to distinct ellipses. This transition indicates that lamellae are tilted and rotated.^[38] After that, the SAXS patterns transforms from a distinct ellipse into a “two-spot” pattern, meaning that lamellae are preferentially aligned along loading direction. What’s more, a streak appears in the equatorial direction, which provides a hint that a highly oriented fibrillar structure is formed in this region.

Figure 2. Representative 2D-SAXS patterns in different states of creep, the size of the pattern is $\pm 0.0525 \text{ nm}^{-1} \times \pm 0.0525 \text{ nm}^{-1}$. The scale refers to the number of counted photons during the exposure time of 0.5 s. According to the much higher intensity in the center of the pattern each color change stands here for a repeated application of the scale.

3.2.1. Evolution of long period and domain thickness

In the spherulite of *i*PP lamellae grow radially along the radius, which is illustrated in **Figure 3**. When the sample is subjected to a uniaxial load, the deformation behavior of the lamellae in region P and region A is different. In region A, the normal direction of the lamellae is the same as with the loading direction. In region P the normal direction of the lamellae is perpendicular to the loading direction. In order to comprehensively investigate the crystalline structure evolution during creep, the long periods (L) in both regions are calculated from the peak position of 1D-SAXS curves:

$$L = \frac{1}{s_{max}} \quad (4)$$

$$s = 2\sin\theta/\lambda \quad (5)$$

s is the scattering vector, λ is the X-ray wavelength and θ is the scattering angle. The long period along the loading direction is labeled as $L_{\parallel}$ and the other one is labeled as $L_{\perp}$.

Figure 3. (a) Schematic diagram of an *i*PP spherulite and (b) the scattering pattern of the spherulite, the size of the pattern is $\pm 0.0525 \text{ nm}^{-1} \times \pm 0.0525 \text{ nm}^{-1}$. $L_{\parallel}$ can be obtained from the slice (the yellow strip) along s_z , and $L_{\perp}$ can be obtained from the slice along s_y . y and z stand for the equatorial and meridional directions in the scattering pattern, respectively.

The evolution of $L_{\parallel}$ and $L_{\perp}$ as a function of creep time are shown in **Figure 4**. It can be seen that for both $L_{\parallel}$ and $L_{\perp}$ the whole curve can be divided into 4 stages, which coincides very well with the evolution of macroscopic Δd in **Figure 1a**.

Figure 4. Evolution of long period along ($L_{\parallel}$) and perpendicular ($L_{\perp}$) to loading direction during creep under 8MPa at 120 °C.

In region I (primary creep), $L_{\parallel}$ increases linearly with creep time, whereas $L_{\perp}$ decrease slightly. As mentioned above, the deformation in primary creep is caused by the elastic deformation of the amorphous region which has a lower modulus compared to that of the crystalline region. The increase of $L_{\parallel}$ suggests that the polymer chains along loading direction are stretched,^[37] while the decrease of $L_{\perp}$ indicates that the molecular chains perpendicular to loading direction are compressed. The compression force comes from the squeeze of expanded lamellae along loading direction.^[39] Region II is the transition stage. In region III (secondary creep), the evolution of $L_{\parallel}$ and $L_{\perp}$ show a similar trend. Both of them increase with creep time. The rates of increase of $L_{\parallel}$ and $L_{\perp}$ obtained by linear fitting are $6.34 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$ and $4.81 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$, respectively. In the work of Li,^[4] the elongation of micron-scale spherulites along the loading direction, accompanying with the increase of nano-scale lamellar long period were also observed when ε_t is smaller than 17 %. Furthermore, in the work of Li^[4] $L_{\parallel}$ increases from about 17.7 nm before drawing to 20.5 nm at the end of secondary creep. This is different to the results of this work where $L_{\parallel}$ changes from 11.8 nm before loading to 13.74 nm at the end of secondary creep. The difference is caused mainly by differences in the sample preparation process. Nevertheless, the relative increase of long period is nearly the same: 15.8 % in the work of Li and 16.4 % in this work. In region IV (tertiary creep), $L_{\parallel}$ increases strongly while $L_{\perp}$ remains constant within the range of uncertainty. After 1232 s, no $L_{\perp}$ can be detected, because the lamellae are strongly aligned in tensile direction and the lamellae perpendicular to loading direction are fragmented.

In order to get a better understanding of the structural evolution during secondary creep, one-dimensional correlation function ($K(z)$) is employed to get the domain thickness of *i*PP

during creep, including crystalline region thickness (L^c) and amorphous region thickness (L^a).

$K(z)$ is given as follows,^[40]

$$K(z) = \frac{\int_0^\infty 4\pi^2 s^2 I(s) \cos(2\pi sz) ds}{\int_0^\infty 4\pi^2 s^2 I(s) ds} \quad (6)$$

where z represents the distance in real space with a unit of nm, $I(s)$ is the experimental scattering intensity as a function of s . L^c or L^a can be evaluated from the intersection of the straight line in the origin region with the baseline at the minimum of the correlation function.^[41] It must be mentioned that it is impossible to decide whether it is L^c or L^a that is read out directly from the correlation function without prior knowledge of the crystallinity. In the present study, the degree of crystallinity is higher than 0.5 (calculated from XRD and DSC, see **Supporting Information**), which ensures the assignment of the smaller value obtained from $K(z)$ to L^a . Then L^c can be obtained by

$$L^c = L - L^a \quad (7)$$

It can be seen in **Figure 5** that the domain thickness of *i*PP increases with creep time, the rates of increase of $L_{\parallel}$ and $L_{\perp}$ are $10.3 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$ and $7.52 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$, for $L_{\parallel}^c$ and $L_{\perp}^c$ they are $8.04 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$ and $6.28 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$. The very small rates of increase of $L_{\parallel}^a$ and $L_{\perp}^a$ are $2.29 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$ and $0.96 \times 10^{-4} \text{ nm} \cdot \text{s}^{-1}$, respectively. So, the increase of long period during secondary creep can be attributed to the thickening of lamellae.

Figure 5. Evolution of long period along and perpendicular to loading direction during creep ($L_{\parallel}$ and $L_{\perp}$) (a) and evolution of thickness of crystalline and amorphous regions ($L_{\parallel}^c$, $L_{\perp}^c$, $L_{\parallel}^a$, and $L_{\perp}^a$) (b).

For thin polymer crystals, the thermodynamic driving force capable for the thickening phenomena arises from the unequal free energies of the fold surface and the lateral surface, it moves the crystal in the direction of lowest free energy. By analogy to other irreversible processes, an appropriate phenomenological law for the rate of polymer crystal thickening can be expressed as ^[42]

$$\frac{dy}{dt} = \frac{2}{\tau} \left(\frac{1-y^{3/2}}{y} \right) \quad (8)$$

$$y = l/l^* \quad (9)$$

$$\frac{1}{\tau} = \frac{k\sigma_e}{l^{*2}} \quad (10)$$

where l is the thickness of lamellae, l^* is the equilibrium thickness, t is time, τ is the relaxation time, and k is a proportionality constant. The stress dependence of the lamellae thickening rate can enter the theory via k , by invoking a molecular mechanism that involves the cooperative motion of a certain minimum number of molecular chains which have attained “liquid-like” mobility. For one polymer chain in the crystal, the free energy fluctuation

needed to attain liquid-like mobility equal to the Gibbs free energy of melting, which in the simplest approximation is given by

$$\Delta G = \Delta H(T_m^0 - T)/T_m^0 = \Delta H \Delta T / T_m^0 \quad (11)$$

where ΔH is the heat of fusion per polymer chain and T_m^0 is the equilibrium melting point of the crystal. If v is the minimum number of polymer chains required for cooperative motion, then the probability that v molecular chains will simultaneously suffer a free energy fluctuation of ΔG is proportional to the product of the individual probabilities, or $\exp(-v\Delta G/RT)$, where R is the gas constant. Thus, k for this mechanism is given by ^[43]

$$k \propto k_0 \exp[-v\Delta H \Delta T / RT T_m^0] \quad (12)$$

It is well known that the structure of iPP can be well described by a skeleton of a crystalline phase with an amorphous phase between the crystallites.^[23, 44, 45] In a recent work by Sotta^[45] it is proved that the local tensile strain of lamellae is lower than the macroscopic one. The reduced local tensile strain must be compensated mainly by shear deformation in the amorphous phase causing an enhanced orientation of the chains within the amorphous phase. This enhances the probability for such cooperation and decreases the energy barrier, thus the rate for the increase of $L_{\parallel}$ is larger than that for $L_{\perp}$. This behavior is confirmed by the higher thickening rate along loading direction, shown in **Figure 5**.

3.2.2. Lamellae tilting and rotation

During tertiary creep, 2D-SAXS pattern changes from a slight ellipse into a distinct ellipse. For comparison, an isotropic 2D-SAXS pattern before creep is also provided, see **Figure 6a** and **Figure 6b**. **Figure 6c** presents the long period as a function of azimuthal angle (φ) with respect to the loading direction. The long period in all directions stays constant at 14 nm

before loading. For the elliptical pattern at 1208 s, the long period is greatest along loading direction and decreases gradually towards the direction perpendicular to loading direction.

Figure 6. (a) Isotropic 2D-SAXS pattern at 0 s and (b) elliptical 2D-SAXS pattern at 1208 s during tertiary creep, the size of the pattern is $\pm 0.0525 \text{ nm}^{-1} \times \pm 0.0525 \text{ nm}^{-1}$, color scale like in Figure 2; (c) long period as a function of azimuthal angle (ϕ) with respect to the loading direction.

Generally, the appearance of the elliptical pattern is related to lamellae tilting and rotation, caused by inter- and intra-lamellar slip.^[46] However, the quantitative interpretation of the elliptical reflections is still an on-going topic up to now. In the very recent work by Murthy and his coworkers,^[36, 38] models using an equilibrium distribution of molecular orientations and lamellar tilts are proposed which can predict elliptical reflections. Whereas, the models require some assumptions, these make the physical background of the fitting parameters unclear. So, a directly assignable structural basis for the parameters in their model is not possible yet. Therefore, the calculation of the lamellae tilting angle and rotating angle with respect to the loading direction remains unsolved in this work.

3.2.3. Lamellae orientation and formation of a fibrillar structure

At the transition to the phase of tertiary creep the SAXS pattern transforms from ellipse to a “two-spot” pattern (see **Figure 7**), indicating stress-induced crystalline block disaggregation after rotation and tilting of lamellae, forcing the lamellae to orientate along loading direction.

Additionally, the “spot” exhibits a pronounced broadening in the equatorial direction. Such a broadening might be due to either the misalignment of the lamellar structures with respect to the stretching direction or the limited lateral dimension of the lamellae making up the stacks.^[47]

Figure 7. (a) “Two-spot” SAXS pattern with a streak signal (shown by the arrow) at 1248 s, the size of the pattern is $\pm 0.0525 \text{ nm}^{-1} \times \pm 0.0525 \text{ nm}^{-1}$; (b) is the enlargement of the center region of (a) with a size of $\pm 0.0175 \text{ nm}^{-1} \times \pm 0.0175 \text{ nm}^{-1}$, color scale like in Figure 2.

Herman’s orientation function^[48] can be used for the calculation of the lamellae orientation degree along loading direction. It is given as

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{\pi/2} I(\theta) \cos^2(\theta) \sin(\theta) d\theta}{\int_0^{\pi/2} I(\theta) \sin(\theta) d\theta} \quad (13)$$

$$f_H = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (14)$$

φ is the angle between loading direction and the lamellae normal, θ is the azimuthal angle ranging from 0-360°. $f_H = 1$ means that all the lamellae are perfectly oriented parallel to the loading direction, $f_H = 0$ means that the lamellae are oriented randomly, and $f_H = -0.5$ means that the lamellae are oriented perpendicular to the loading direction. The lamellae orientation degree is 0.45 after yielding and it increases to 0.5 in the phase of tertiary creep.

Figure 8. Herman's orientation degree of lamellae after yielding, corresponding to a creep time from 1248 s to 1280 s. The creep temperature is 120 °C and the loading stress is 8 MPa.

In addition to the “two-spot” scattering signal, a streak (shown by the arrow) in equator direction can be found in **Figure 7**. The appearance of the streak indicates the formation of the fibrillar structure after yielding, which is aligned along the loading direction. However, only a very limited part of the streak can be observed and the signal in the center region of the pattern is covered by beamstop. To get full information about the streak, the scattering intensity in the blanked region in **Figure 7** must be extrapolated and fitted using the sum of two 2d-Gaussian functions

$$I(s) = p_{f0} \exp(-p_{f1}s^2 - p_{f2} \cos(2\phi) s^2) + p_{m0} \exp(-p_{m1}s^2 - p_{m2} \cos(2\phi) s^2) \quad (15)$$

$$\phi = \arctan \frac{i}{j} \quad (16)$$

i and j define the pixel position in 2D-SAXS patterns with respect to the beam center. The first Gaussian curve describes the fibrillar structure with three parameters. p_{f0} is the scattering intensity at the beam position, and as ellipse the axes are $p_{f1} + p_{f2}$ and $p_{f1} - p_{f2}$ respectively. The second Gaussian curve describes the scattering from the matrix. The raw pattern and the reconstructed one are given in **Figure 9a** and **9b**. One can see that the

extrapolation and fitting works well. The two Gaussian curves are provided in **Figure 9c** and **9d**.

Figure 9. Modelling of a scattering pattern by the sum of the signals of the fibrillar structure and the matrix according to Guinier's approximation. The pattern corresponds to the creep time of 1248 s. The size of the pattern is $\pm 0.026 \text{ nm}^{-1} \times \pm 0.026 \text{ nm}^{-1}$. The creep temperature is 120 °C and the loading stress is 8 MPa.

According to Ruland's streak method,^[49, 50] the integral width of the azimuthal peak profile of the streak B_{obs} can be estimated as function of s as

$$B_{obs}(s) = \frac{1}{I(s, \pi/2)} \int_{-\pi/2}^{\pi/2} I(s, \phi) d\phi \quad (17)$$

Under the assumption that the fibrillar structure is perfectly oriented, the length of the fibrillar (L_f) structure should be

$$L_f = \frac{1}{B_{obs}(s)} \quad (18)$$

From equation (13), we know that for the fibrillar structure

$$I(s, \phi) = p_{f0} \exp(-p_{f1}s^2 - p_{f2} \cos(2\phi) s^2) \quad (19)$$

Therefore, the length of the fibrillar structure along ($L_{f\parallel}$) and perpendicular to ($L_{f\perp}$) loading direction should be

$$L_{f\parallel} = \sqrt{\frac{p_{f1} + p_{f2}}{\pi}} \quad (20)$$

$$L_{f\perp} = \sqrt{\frac{p_{f1} - p_{f2}}{\pi}} \quad (21)$$

The results are given in **Figure 10**. It can be found that $L_{f\parallel}$ increases from 365 nm to 497 nm and $L_{f\perp}$ keeps at 102 nm.

If misorientation of the fibrillar structure is taken into account, then the decrease of $B_{obs}(s)$ with increasing s is a function of the analytical shape of the orientation distribution as

$$B_{obs}(s) = B_{\phi} + \frac{1}{s \cdot \langle L'_f \rangle} \quad (22)$$

B_{ϕ} is the orientation parameter. L'_f as a function of creep time is also presented in **Figure 10**. One can see that L'_f shows a similar trend as $L_{f\parallel}$ but it is slightly smaller than $L_{f\parallel}$. L'_f is 283 nm once it is formed, and then it increases to 372 nm finally.

It should be mentioned that the polydispersity of the fibrillar structure is not considered in the Ruland's method, this can cause errors using this procedure.^[51] $L_{f\parallel}$, $L_{f\perp}$, and L'_f given in **Figure 10** are average value. In order to estimate the statistical certainty, $L_{f\parallel}$, and L'_f are fitted by a second order polynomial

$$y = a_1 x^2 + a_2 x + a_3 \quad (23)$$

The fitted lines for these approximations are added in **Figure 10**, the coefficients of determination for both curves are $R^2 = 0.987$. $L_{f\perp}$ is approximated by a straight line, the

standard deviation is 4.1. Generally, the formation of the fibrillar structure can be triggered by lamellae breaking and reorganization during yielding.^[4, 52] By comparing the length of the fibrillar structure (either $L_{f\parallel}$ or L'_f) with the long period of original lamellae (16 nm), it can be inferred that the formation of fibrillar structure needs the disaggregation of a group of lamellae connected by tie molecular chains.

Figure 10 The length of the fibrillar structure along ($L_{f\parallel}$) and perpendicular ($L_{f\perp}$) to the loading direction under the assumption that the fibrillar structure is perfectly oriented, and the length (L'_f) of the fibrillar structure after taking the misorientation into account as a function of creep time. The solid lines are a second order polynomial fitting for the experimental data for $L_{f\parallel}$ and L'_f as well as a linear fit for $L_{f\perp}$. Error bars for L'_f are added to demonstrate the quality of the estimation of this length.

4. Conclusions

In this study, the microstructural evolution during creep is investigated by *in-situ* synchrotron SAXS. Results reveal that the microstructural evolution in different creep stages differs from each other distinctly, especially in secondary and tertiary creep. During primary creep, strain grows nonlinearly to a value less than 15 % in a short time. In this stage, the long period along loading direction ($L_{\parallel}$) increases with time, whereas the long period perpendicular to loading direction ($L_{\perp}$) decreases slightly. The change of long period is caused by elastic deformation of molecular chains in the amorphous phase. During secondary creep, strain increases linearly

with time. Both $L_{\parallel}$ and $L_{\perp}$ exhibit the same tendency with strain. The growth rate of $L_{\parallel}$ is larger than that of $L_{\perp}$, which benefits from a higher polymer chains orientation along loading direction. During tertiary creep, strain grows dramatically within a limited time due to yielding. The reflections in 2D-SAXS pattern changes from light ellipse to a distinct ellipse firstly, and then grows into “two-spot” pattern. This significant transition indicates that the lamellae are tilted and rotated during yielding. After that, the lamellae are disaggregated and aligned mainly along the loading direction. After yielding, the lamellar orientation degree is about 0.45, and it increases to 0.5 with creep time. Additionally, the fibrillar structure can be induced by lamellae breaking and subsequent reorganization. The length of the fibrillar structure increases from 364 nm to 497 nm as creep time increases; and its width keeps at 102 nm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: creep, *in-situ* small angle X-ray scattering, isotactic-polypropylene, microstructure evolution

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