

# Micro-Macro Scale Relationship in Creep Deformation of Ultra High Molecular Weight Polyethylene

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**Abstract** Macroscopic and microscale creep deformations of UHMWPE were investigated by using *in situ* SAXS. A methodology for the measurement of the local creep deformation of inter-lamellar amorphous phase has been proposed. The local strain of inter-lamellar amorphous phase ( $\epsilon_a$ ) and macroscopic strain ( $\epsilon_{\text{macro}}$ ) were evaluated and they were compared to study the relationship between macroscopic and microscale creep deformation of UHMWPE. Both of them exhibit two deformation regions against creep time. The entanglements show a strong impact on both the macroscopic and local inter-lamellar amorphous phase creep behavior and they can be well correlated to the molecular weight between two entanglements estimated from strain-hardening modulus. Compared to the macroscopic creep deformation, local inter-lamellar amorphous layers have a smaller creep deformation. From the local creep measurement, the apparent modulus of inter-lamellar amorphous phase can also be estimated ( $200 < M_a < 500$  MPa). These values are much higher than the Young's modulus of bulk amorphous PE, which can be well explained by the confinement of the lamellar stacks and the enhancement of the amorphous phase with the relatively high concentration of entanglements. This study provides a useful means and quantitative data for achieving the scale transition between the micro and the macro structural levels for the study of visco-elastic deformation.

**Keywords** Ultra-high molecular weight polyethylene; Creep; Small angle X-ray scattering; Microscale

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## INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) possesses many unique properties, such as very low friction coefficient, high wear resistance, high impact strength, and excellent biocompatibility.<sup>[1–13]</sup> One of the most important applications of UHMWPE as a biomedical implant has been in acetabular cup components of total hip replacements.<sup>[10,14]</sup> However, the use of UHMWPE generally associates with problems, such as creep deformation, since the polymer is a viscoelastic material and has lower elastic modulus compared to those of metal implants and cortical bones. These problems significantly limit the long-term application of UHMWPE *in vivo*.

The creep behavior of UHMWPE has been studied in numerous literatures, and many methods have been reported to investigate the creep resistance of UHMWPE.<sup>[1,2,9,15,16]</sup> UHMWPE is a typical semi-crystalline polymer consisting of crystalline lamellae and amorphous phase, which generally displays a complex structural hierarchy from microscale to macroscopic level.<sup>[17,18]</sup> The complex connection structure

between the crystal lamella and the amorphous phase and their significantly different deformation ability make it difficult to predict the creep behavior of semi-crystalline polymers by using the principle of time-temperature equivalence which can be well used to predict the long-term creep behavior of amorphous polymers.

In a previous study, a creep deformation model of polyethylene has been proposed.<sup>[19]</sup> In this model, the entanglement of amorphous molecular chains and the content of tie chains are the two most important factors affecting the creep behavior of polyethylene. In the initial stage of creep, the amorphous molecules are disentangled, and the creep deformation mainly comes from the movements of the amorphous molecules. Then, the tie chains are stretched, leading to the out of chains from crystals or break of the crystalline lamella. However, considering the complex hierarchical structure of the semi-crystalline polymer, the properties of amorphous phase are heterogeneous. Recently, the apparent Young's modulus of amorphous morphology between crystalline lamellae has been evaluated as 200–300 MPa at room temperature which is much higher than the Young's modulus of rubberized polyethylene.<sup>[20,21]</sup> The wide distribution of the mechanical properties of amorphous phase makes it difficult to study the local deformation of the samples during the creep experiment.

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The local deformation of polyethylene is correlated to the local stress which is heterogeneously distributed, and the stress distribution is strongly correlated to the orientation of the crystalline lamellae. Recently, we have used *in situ* X-ray scattering method for measuring the local stress and strain during the deformation of polyethylene and the results prove that the local stress of parallel oriented lamellae is higher than the macroscopic stress, which provides evidence for the heterogeneous stress distribution in PE.<sup>[20,22–25]</sup> However, quantitative measurement of micro stress distribution is still very difficult. Ivan'kova *et al.*<sup>[26]</sup> studied the creep behavior of UHMWPE films with different orientations in the creep process by *in situ* WAXS experiment. In this work the local creep behavior of oriented lamellae in the tensile direction has been estimated by the displacement of (002) crystal plane and the results show that the local stress in the lamella during the creep process is remarkably correlated to the degree of orientation. Zhou and Wilkes<sup>[27]</sup> also have studied the macroscopic creep behavior of polyethylene with different lamellar orientations and the results show that the 45° oriented sample has the largest instantaneous macroscopic elastic deformation, followed by the 0° oriented sample (the normal direction of the crystalline lamella is parallel to the tensile direction), and then the 90° oriented sample (the normal direction of the crystalline lamella is perpendicular to the tensile direction). However, the local creep behavior of single oriented polyethylene, such as the deformation behavior of inter-lamellar amorphous phase under constant external force, is still hard to be measured.

In this work, macroscopic and microscale creep deformations of UHMWPE were investigated by using *in situ* SAXS. A methodology for the measurement of local creep deformation of inter-lamellar amorphous phase has been proposed. The relationship between local strain and macro strain has been studied. Through this relation, the micro strain and macro strain can be correlated and the viscous-elastic properties of inter-lamellar amorphous phase can be obtained. This study provides a useful means and quantitative data for achieving the scale transition between the micro and the macro structural levels for the study of viscos-elastic deformation of semi-crystalline polymers.

## EXPERIMENTAL

### Materials and Sample Preparation

Two ultra high molecule weight polyethylene powders (UPE5 and UPE9 with molecule weight  $\sim 5 \times 10^6$  and  $\sim 9 \times 10^6$  g/mol, respectively, deduced from viscosity measurements) were purchased from Sigma-Aldrich and the powders were used as

received. The polymer powders were compression-molded into 0.5-mm-thick sheets at 180 °C and then quenched into cold water (the average cooling rate was  $\sim 30$  °C/s) or slowly cooled to room temperature (the average cooling rate was  $\sim 1$  °C/s). These samples were labeled “quenched” and “slow cooled”, respectively. Thermal annealing was performed for the quenched samples in order to generate one additional crystalline microstructure for each of the two polymers. The samples hereafter designated as “annealed” were prepared by heat-treatment of quenched sheets for 10 h in a thermostatic oil bath at 110 °C for 10 h. Totally, 6 samples with different microstructures were prepared (Table 1).

### Differential Scanning Calorimetry (DSC)

A DSC1 Star<sup>e</sup> System (Mettler Toledo Instruments, Swiss) was used for thermal analysis. The heating rate was set at 10 °C/min. The crystalline weight fraction,  $X_c$ , was computed from the melting enthalpy of the samples  $\Delta H_m$  ( $X_c = \Delta H_m / \Delta H_m^0$ ), where  $\Delta H_m^0$  is 290 J/g for the heat fusion of fully crystalline PE.<sup>[28]</sup> The calculated crystallinity values have been listed in Table 1.

### Tensile Test

Stress-strain curves were measured using a homemade stretching stage equipped with a 5 kN load cell and a heating chamber. The dumbbell samples having 6.5 mm in gauge length and 4 mm in width were stretched at a head speed of 0.01 mm/s. The symmetric displacement of the two clamps allowed probing the same zone of the sample during the tests.

True strains were determined using photographs of the deformed samples with respect to the undeformed ones. The Hencky measure of strain  $\epsilon_H$  is used as the true strain, which is defined as<sup>[29,30]</sup>

$$\epsilon_H = 2 \ln \frac{b_0}{b} \quad (1)$$

where  $b_0$  and  $b$  are the widths of undeformed and deformed areas, respectively.

### Small-angle X-ray Scattering (SAXS) Characterization

SAXS experiments were performed on a Xeuss system of Xenocs France equipped with a semiconductor detector (Pilatus 100 K, DECTRIS, Swiss) attached to a multilayer focused Cu K $\alpha$  X-ray source (GeniX3D Cu ULD, Xenocs SA, France), generated at 50 kV and 0.6 mA. The wavelength of the X-ray radiation is 0.154 nm. The sample-to-detector distance was set at 1200 mm for SAXS. Each pattern was recorded with an exposure time of 1 min. The data correction and background subtraction were performed after recording.<sup>[31,32]</sup>

The intensity profiles were obtained by integration of the 2D patterns. The average long period of the lamellar stacking,  $L_p$ , was determined from the Bragg's relation:

**Table 1** Structural characteristics of the samples.

| UHMWPE | $M_w$ (g/mol)        | Sample | Thermal history | $X_c$ (%) | $L_p$ (nm) | $L_c$ (nm) | $L_a$ (nm) | $M_e$ (g/mol) |
|--------|----------------------|--------|-----------------|-----------|------------|------------|------------|---------------|
| UPE5   | $\sim 5 \times 10^6$ | UPE5Q  | Quenched        | 46        | 31.6       | 13.3       | 18.3       | 956           |
|        |                      | UPE5A  | Annealed        | 50        | 39.8       | 18.3       | 21.5       | 836           |
|        |                      | UPE5S  | Slow cooled     | 53        | 45.9       | 22.4       | 23.5       | 715           |
| UPE9   | $\sim 9 \times 10^6$ | UPE9Q  | Quenched        | 40        | 36.1       | 13         | 23.1       | 917           |
|        |                      | UPE9A  | Annealed        | 51        | 42.2       | 19.8       | 22.4       | 740           |
|        |                      | UPE9S  | Slow cooled     | 51        | 50.7       | 23.8       | 26.9       | 511           |

$X_c$ : crystallinity;  $L_p$ : long period;  $L_c$ : thickness of the crystalline lamellae;  $L_a$ : thickness of the inter-lamellar amorphous phase;  $M_e$ : average molecular weight between entanglements.

$$L_p = 2\pi/q_{\max} \quad (2)$$

where  $q_{\max}$  is the scattering vector at the peak intensity. The calculated values of  $L_p$  for each sample without deformation are listed in Table 1.

The crystalline thickness,  $L_c$ , of the samples was computed from Eq. (3):<sup>[33,34]</sup>

$$L_c = L_p X_c \rho_c / \rho_a \quad (3)$$

with  $\frac{1}{\rho} = \frac{X_c}{\rho_c} + \frac{1-X_c}{\rho_a}$ , where  $L_p$  is long period,  $\rho_c$  is the density of the crystalline phase (1.003 g/cm<sup>3</sup>) and  $\rho_a$  is the density of amorphous phase (0.865 g/cm<sup>3</sup>).<sup>[20,22]</sup>

*In situ* small angle X-ray scattering (SAXS) experiments were carried out by using the same SAXS system equipped with a homemade stretching stage. The tensile machine symmetrically stretched the samples, ensuring that all data were recorded from the same location on the sample during deformation. The dumbbell-shaped samples were tested with gauge length of 10 mm, width of 4 mm and thickness of ~0.5 mm. The creep was carried out at a constant stretch force of 30 N. The constant force was loaded within ~1 s and then the loading force was kept in a constant value. Each SAXS pattern was recorded within 30 s including exposure of 25 s and recording time of 5 s. The data correction and background subtraction were performed according to standard procedure.

## RESULTS AND DISCUSSION

The microstructure of the samples has been characterized before mechanical tests. The microstructure parameters include the crystalline and amorphous lamella thicknesses,  $L_c$  and  $L_a$ , the crystallinity,  $X_c$ , and long period of lamellar structure,  $L_p$ , have been listed in Table 1. The crystallinity and lamellar thickness were found to be lowest for the quenched samples and the highest for the slow cooled samples. The annealing procedure was successfully applied to obtain intermediate levels of crystallinity and lamellar thicknesses for the two materials. The crystallinity of UPE5 is higher than that of UPE9, whereas  $L_p$  of UPE5 is smaller than that of UPE9 for the samples with the same thermal history. This observation can be ascribed to the high molecular weight of UPE9, resulting in the relatively high concentration of entanglements and large  $L_p$ .

In Fig. 1, true stress is plotted against the true strain for a series of UPE5 samples. A typical tensile deformation for semi-crystalline polymers is observed: an initial elastic region followed by a yield stress and strain hardening occurs. Increasing the crystallinity results in an increase in yield stress. Apparently, the crystalline domains contribute more to the yield stress than the amorphous part, resulting in a larger total yield stress of the material.

From the true stress-true strain curves, the strain hardening modulus can be determined at large strains. According to a neo-Hookean description, which was found to be valid for most polymers, at large strains the stress is a function of extension ratio  $\lambda$ :<sup>[35–37]</sup>

$$\sigma_{\text{true}} = Y + G_p \left( \lambda^2 - \frac{1}{\lambda} \right) \quad (4)$$

where  $\sigma_{\text{true}}$  is the true stress,  $Y$  is the extrapolated yield stress,  $G_p$  is the strain hardening modulus and  $\lambda$  is the extension ratio ( $\lambda = \text{extended length} / \text{original length } l_0$ ). Considering the

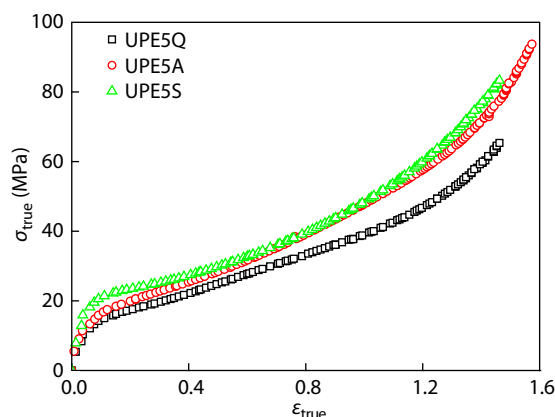


Fig. 1 True stress-strain curves of UPE5 samples.

Gaussian background of the neo-Hookean behavior, the strain hardening modulus is related to the entanglement (network) density, which was experimentally proven to be valid for thermoplastics.<sup>[38]</sup> According to the conventional theory of rubber elasticity,

$$G_p = \rho \frac{RT}{M_e} \quad (5)$$

where  $\rho$  is density,  $R$  is gas constant,  $T$  is temperature and  $M_e$  is average molecular mass between entanglements. From Eq. (5)  $M_e$  for all samples have been evaluated and listed in Table 1. One thing should be noted that  $M_e$  evaluated from strain hardening modulus only correlates to the entanglements of the amorphous phase although crystalline lamellae behave as a physical cross-link. It will be seen that  $M_e$  is in the range of 500–1000 and remarkably depends on the thermal history, which is in accordance to the previous observation of polyethylene.<sup>[35]</sup> The quenched sample is close to the molten polyethylene in an equilibrium state ( $M_e \sim 1240$ ),<sup>[38]</sup> where the entanglements in the melt can be preserved during the fast cooling process. For annealed and slow cooled samples, entanglements have to be excluded into the amorphous phase during crystallization process and the ultra long chains of UHMWPE prefer to form tie chains which are generally in favor of the entanglement.

Both crystals and entanglements affect the macroscopic creep behavior of UHMWPE. The variation of the compliance of the samples against creep time has been plotted in Figs. 2(a) and 2(b). Typical two stages including an initial fast creep and a stable secondary slow creep can be seen.<sup>[39]</sup> Similarly to the tensile deformation, compliance shows remarkable dependence on the thermal history and crystalline structure of the samples. Compliance at the initial creep ( $t=0$  s) reflects the relative stiffness of the samples during the instantaneous loading, mainly determined by the stiffness of the crystalline networks. Generally, higher crystallinity is beneficial to the interlock of the crystalline lamellae and consequently enhances the strength of the crystalline networks. Thus, it will be seen that compliance at the initial creep ( $t=0$  s) linearly decreases with increasing crystallinity (Fig. 3c).

In the first stage, the compliance linearly increased with the increasing creep time (Figs. 2a and 2b) within a very short period ( $t < 5$  s). The primary creep rate (increase rate of compliance in the first stage) exhibits a positive correlation to  $M_e$  as

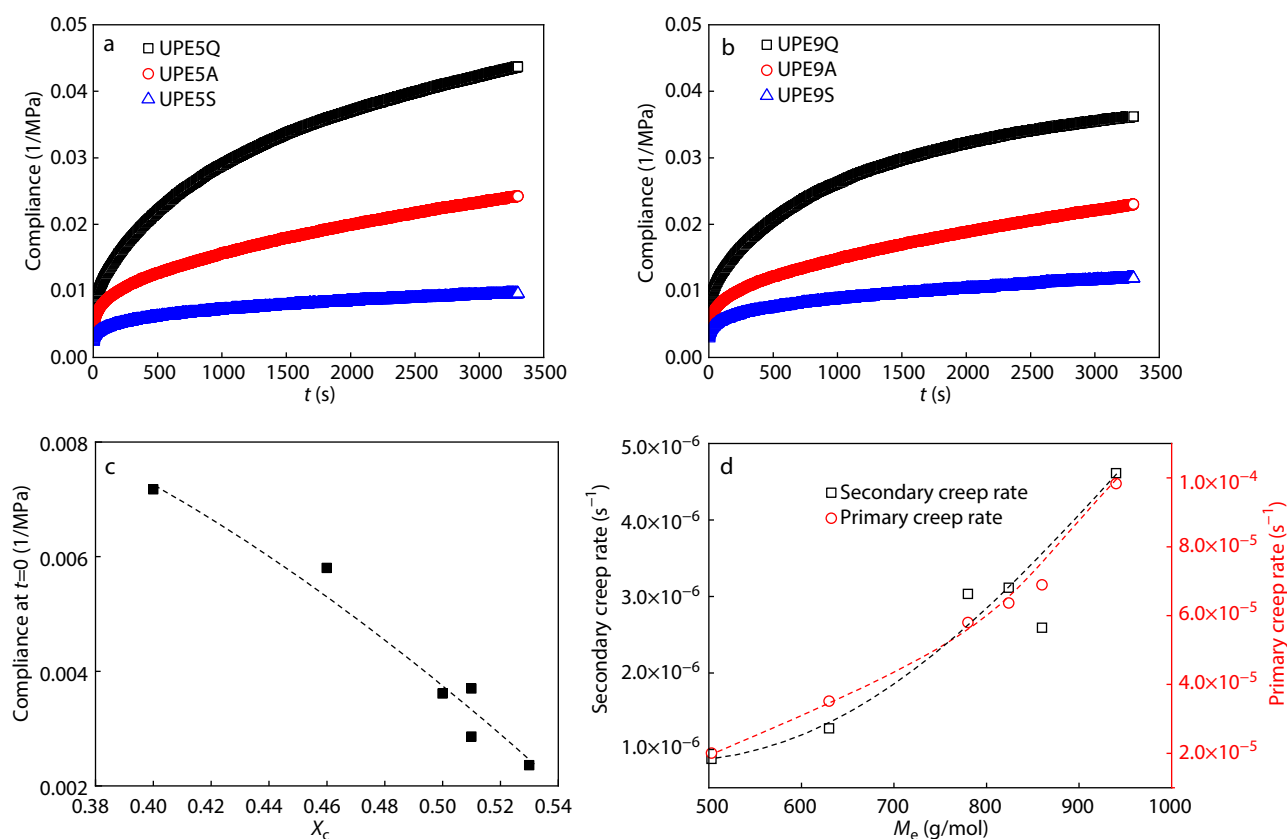


**Fig. 2** Compliance plots against creep time for samples of (a) UPE5 and (b) UPE9. Creep tests were performed under a constant force of 30 N at room temperature. (c) Compliance value of elastic instantaneous deformation ( $t=0$  s) plots against crystallinity. (d) Primary and secondary macroscopic creep rates evaluated from compliance curves in function of  $M_e$ .

shown in Fig. 2(d). This result is in accordance to a previous report<sup>[40]</sup> that the rates of compliance increase were similar for different amorphous polymers with similar molecular weights. It is known that polymers with high molecular weight generally create more entanglements. The high concentration of entanglement may restrict the conformation rearrangements upon loading and enhance the stiffness of the entanglement network, which remarkably affect the viscous movement of the local chains under a constant force. In the second stage, the compliance also shows linear relation with the creep time (Figs. 2a and 2b) and it keeps constant within a relatively long time. However, compared to the first stage, the secondary creep rate significantly decreases (Fig. 2d). In this stage, the amorphous phase chains have been stretched and the deformation may from the disentanglements of the chains, and thus the stronger entanglement network (smaller  $M_e$ ) results in the lower creep rate (Fig. 2d).

The high modulus contrast between the crystal and the rubbery amorphous phase is likely to have a strong impact on the macroscopic behavior of various materials depending on their microstructure. For the creep deformation, it is valuable to investigate the role of inter-lamellar amorphous phase due to its remarkable contribution to the viscous deformation during the creep deformation of PEs. However, due to its structural confinement at a nanometric scale between stiff crystalline lamellae, the inter-lamellar amorphous phase may

display different intrinsic properties.

In order to evaluate the local creep behavior of inter-lamellar amorphous phase, a model based on uniaxial deformation of lamellae measured *via in situ* SAXS experiments has been proposed. This model of local mechanical behavior of the inter-lamellar amorphous phase is approached in the framework of a two-phase model disregarding the role of the interphase. In this work, it was mainly focused on the deformation of lamellae stacks that only undergo uniaxial deformation without shearing. From the azimuth integration of scattering pattern in equatorial region (Fig. 3a), the scattering signals of lamellar stacks along loading direction can be obtained.<sup>[20]</sup> It can be seen that long period increased with the creep time (scattering peaks move to small  $q$  region as shown in Fig. 3b).

It was assumed that the deformation of the crystal in this region can be ignored in the viscoelastic strain domain compared to the deformation of the amorphous phase considering that the crystal is strained along the chain axis. Indeed, the crystal stiffness in the chain direction is about 2 orders of magnitude higher than that of the amorphous phase in PE.<sup>[20]</sup> In this hypothesis, the local change of the amorphous phase thickness is  $\Delta L_a \approx \Delta L_p$ , where  $\Delta L_p$  is the long period variation as determined by *in situ* SAXS (Fig. 3b). Thus, the local strain ( $\epsilon_a$ ) at the scale of the inter-lamellar amorphous phase normal to the lamellar surface and parallel to the macroscopic

stress can be expressed as

$$\varepsilon_a = \Delta L_a / L_a \approx \Delta L_p / L_a \quad (6)$$

The  $\varepsilon_a$  and macroscopic strain  $\varepsilon_{\text{macro}}$  variations of UPE5Q and UPE5S are plotted in Figs. 4(a) and 4(b) as a function of the creep time. Similar to the macroscopic creep deformation, typical two deformation regions against creep time can be observed. In the first region ( $t < 100$  s), local strain roughly linearly increases with a fast increase rate, following a decrease

with increase rate in the second region. The local creep rate also exhibits a structure dependence that both primary and secondary creeps increase with increasing  $M_e$  (Fig. 4c). Additionally, it can be seen that both local strain and local creep rate are smaller than macroscopic creep. Indeed, the macroscopic strain is the accumulation of deformation of all components. In order to reach the average macroscopic deformation, there should be a component having a large strain. This

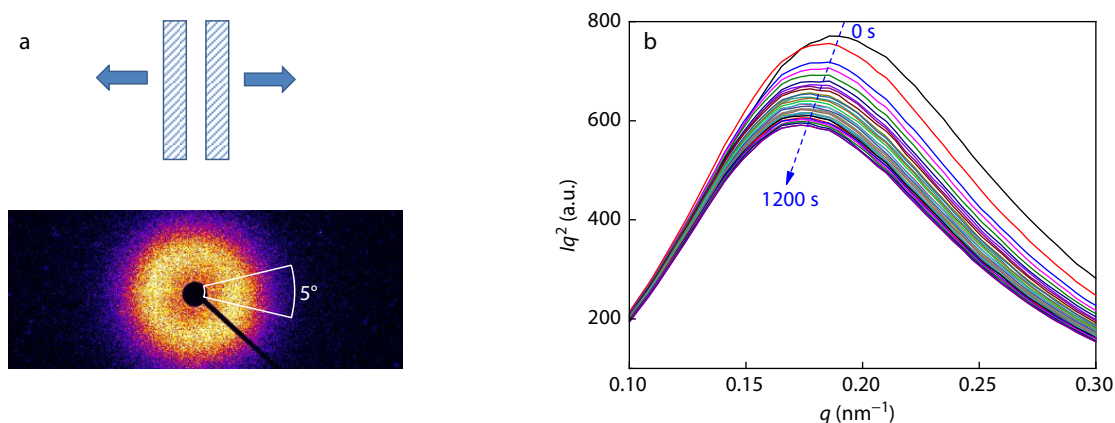


**Fig. 3** (a) Schematic of local deformation of crystalline lamella in load direction, and its corresponding scattering pattern; (b) Equatorial profile of SAXS patterns of UPE9Q (exposure time 10 s, time interval 30 s for each curve). Tests were performed under a constant force of 30 N.

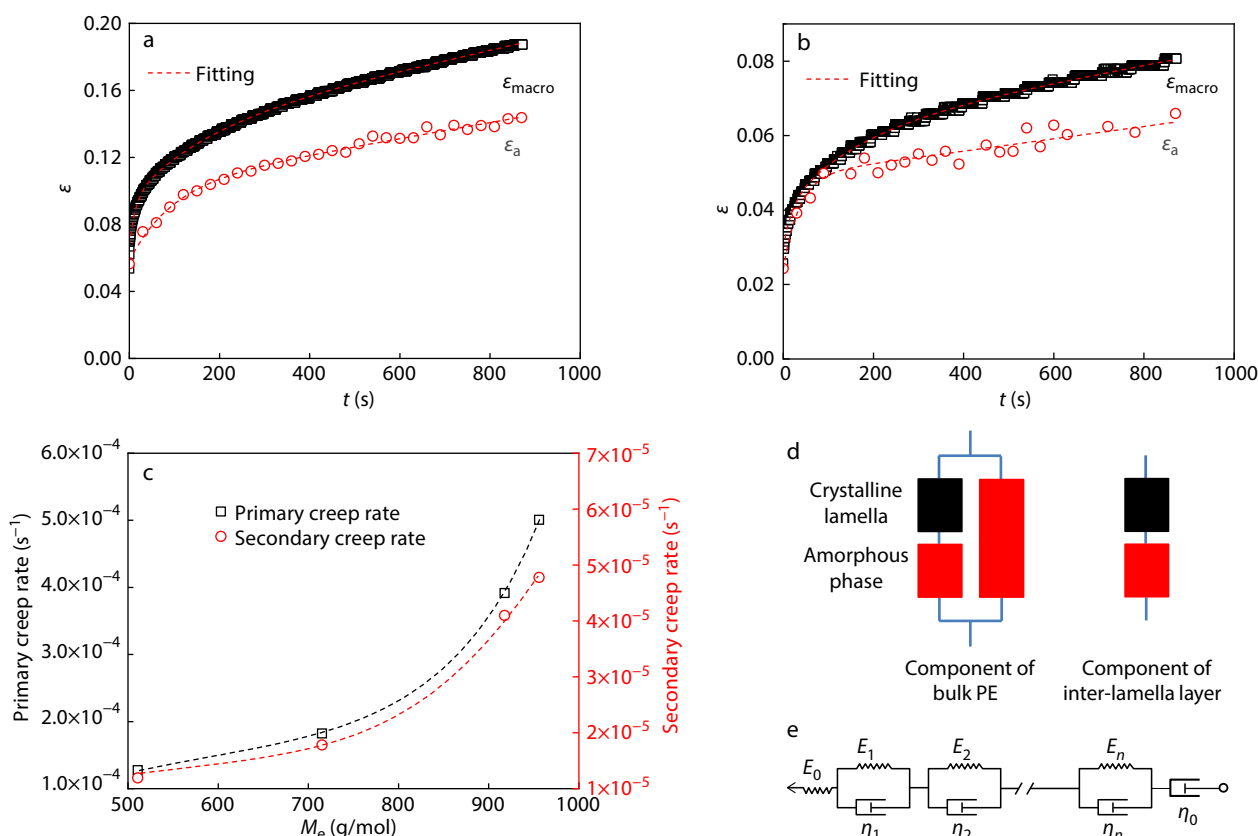


**Fig. 4** Macro and local creep strains of (a) UPE5Q and (b) UPE5S in function of creep time. The dash lines are the fitting curves with viscoelastic model. (c) Primary and secondary local creep rates of inter-lamellar amorphous phase evaluated from creep deformation curves in function of  $M_e$ . (d) Schematic of the component of bulk PE and inter-lamellar layers in loading direction. (e) Schematic of Maxwell-Kelvin-Voigt model used for the fitting of macroscopic and local creep deformation curves.

component is mainly from the amorphous phase out of the lamellar stacks as schematized in Fig. 4(d). Compared to inter-lamellar layer, this rubbery amorphous phase is more deformable and less entangled. This could be reasonable since that the inter-lamellar amorphous phase is well confined and may display strong modifications of its intrinsic properties. Therefore, from the local creep behavior of inter-lamellar amorphous phase, it can conclude that the inter-lamellar layer is stiffer than the bulk amorphous phase.

Generally, the viscoelastic behavior can be described by a series or parallel arrangement of dashpots and linear springs known as Maxwell and Voigt-Kelvin models, respectively.<sup>[41]</sup> In the present case, we used a model consisting of 2 Voigt-Kelvin units in series with a Maxwell model to fit the creep curves (Fig. 4e). The total strain during the creep is expressed as:<sup>[39]</sup>

$$\varepsilon(t) = \varepsilon_0 + \frac{t}{\eta_0} + \sum_{i=1}^n \varepsilon_i (1 - e^{-\frac{t}{\theta_i}}) \quad (7)$$

where  $\varepsilon_0$  is the strain at  $t=0$  and  $\eta_0$  is the polymer viscosity.  $\theta_i$  is the retardation time of the  $i^{\text{th}}$  parallel element.

The fitted curves derived from Eq. (7) are shown in Figs. 4(a) and 4(b) and the fitting parameters are summarized in Table 2.  $\varepsilon_0$  and  $\frac{t}{\eta_0}$ , representing instantaneous elastic deformation and the linear non-recoverable deformation, respectively, are two important parameters for the creep deformation. Fig. 5 plots  $\varepsilon_0$  and  $\eta_0$  against  $M_e$  and it can be seen that the  $\varepsilon_0$  increased whereas  $\eta_0$  decreased with increasing  $M_e$ , indicating that the entanglements remarkably affect the viscoelastic properties of UHMWPE. It should be noted that the macroscopic creep deformation needs 2 Voigt-Kelvin units to obtain a good fitting whereas only one Voigt-Kelvin

unit is enough to get good fitting for local inter-lamellar creep deformation, suggesting that except inter-lamellae other amorphous components contribute to the macroscopic deformation. Additionally, it can be seen that local strain is smaller than macroscopic strain (Figs. 4a and 4b), also suggesting that except the inter-lamellar amorphous phase, a soft amorphous phase exists in order to overcome the overall macroscopic deformation of the macroscopic sample. This soft phase may locate in the connect point of crystalline lamellae where the stress prefers to transform through.

Assuming that the local stress in the studied lamellar stacks ( $\sigma_a$ ) is similar to the macroscopic stress  $\sigma_{\text{macro}}$ , the elastic modulus of inter-lamellar amorphous phase can be estimated for the instantaneous elastic deformation. It should be noted that the local stress distribution is not homogeneous. However, previously, it has been proven that the local stress in equatorial lamellae of spherulites with orientation vertically to the loading direction is almost the same to the macroscopic stress for the low crystallinity sample (the crystallinity is smaller than 55%).<sup>[20,22]</sup> In this work, the crystallinity is relatively low (<53%), and the studied lamellae are comparable to the equatorial lamellae (similar loading condition). Thus, it is reasonable that the local stress is similar to the macroscopic stress. From the initial instantaneous strain, an apparent modulus of the inter-lamellar amorphous phase,  $M_a$ , can be defined from the equation

$$\sigma_{\text{macro}} \approx \sigma_a = M_a \varepsilon_a \quad (8)$$

This elastic modulus of the stretched inter-lamellar amorphous phase is called apparent modulus since it is actually a combination of tensile and bulk moduli, due to the stress triaxiality imposed on the amorphous layers by the structural confinement between the very large and stiff crys-

**Table 2** Fitting parameters of general Maxwell-Kelvin-Voigt model.

| Parameter       | UPE5Q macro creep | UPE5Q local creep | UPE9S macro creep | UPE9S local creep |
|-----------------|-------------------|-------------------|-------------------|-------------------|
| $\varepsilon_0$ | 0.07              | 0.06              | 0.03              | 0.02              |
| $\eta_0$        | 16700             | 20900             | 43800             | 60300             |
| $\varepsilon_1$ | 0.03              | 0.04              | 0.01              | 0.03              |
| $\theta_1$      | 13                | 93                | 19                | 36                |
| $\varepsilon_2$ | 0.04              | /                 | 0.02              | /                 |
| $\theta_2$      | 168               | /                 | 160               | /                 |

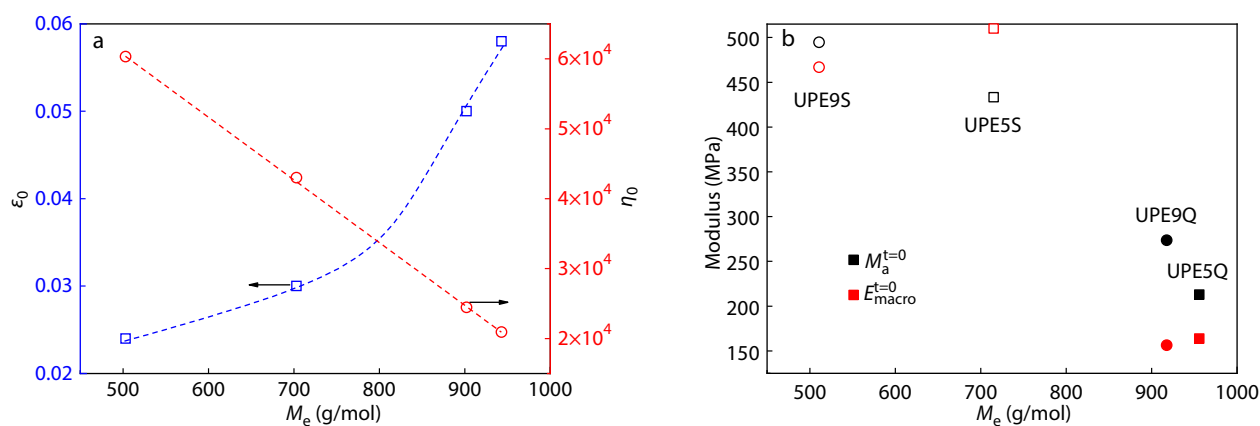


**Fig. 5** (a)  $\varepsilon_0$  and  $\eta_0$  plot against  $M_e$ ; (b) Apparent modulus of inter-lamellar amorphous phase  $M_a$  ( $t=0$ ) and macroscopic elastic modulus  $E_{\text{macro}}$  ( $t=0$ ) plot against  $M_e$  for UHMWPEs.

talline lamellae.<sup>[26]</sup> Thus the estimated modulus cannot be associated with the Young's modulus.

Fig. 5(b) shows the  $M_a$  and macroscopic modulus  $E_{\text{macro}}$  variations with  $M_e$  for UHMWPEs. It can be seen that both the macroscopic modulus and the apparent modulus of the inter-lamellar amorphous phase decreases with increasing  $M_e$  as expected that increasing the concentration of entanglements can enhance the stiffness of the amorphous phase. Additionally, it is noteworthy that  $200 < M_a < 500$  MPa can be obtained, which are similar to our previous reported values of PEs measured by local stress-strain curves. These findings are much higher than those reported in the literature for the Young's modulus of bulk amorphous PE that is in the range of 2–10 MPa.<sup>[20]</sup> This could be ascribed to the confinement of the lamellar stacks which are only under oedometric strain conditions and also the enhancement of the amorphous phase with the relatively high concentration of entanglements.<sup>[20]</sup>

From local creep results, one can get a conclusion that the inter-lamellar amorphous phase and the soft bulk amorphous phase exhibit significantly different contributions to the macroscopic creep deformation. The relatively high resistance of local creep deformation of inter-lamellar amorphous phase mainly originates from two aspects. First, the inter-lamellar layers have the higher concentration of entanglements. Indeed, during the crystallization process the entanglements are excluded into the inter-lamellar layer, which may increase the concentration of the entanglements. Additionally, the tie chains and inter loops formed during crystallization also prefer to increase the entanglements. Second, the structural confinement of the amorphous phase between large and stiff crystalline lamellae can enhance the stiffness of the inter-lamellar amorphous phase.

## CONCLUSIONS

A methodology for the measurement of local creep deformation of inter-lamellar amorphous phase *via in situ* SAXS has been proposed. The local strain of inter-lamellar amorphous phase ( $\epsilon_a$ ) and macroscopic strain ( $\epsilon_{\text{macro}}$ ) have been evaluated at the same time and both exhibit typical two deformation regions against creep time. Microstructures, especially the entanglements, have a strong impact on both the macroscopic and microscale creep behaviors. The creep deformation has been well correlated to the molecular weight between entanglements estimated from strain-hardening modulus which has been found to be the key parameter for the micro and macroscopic creep behaviors.

Compared to the macroscopic creep deformation, local creep deformation of inter-lamellar amorphous layers has a small creep deformation. The macroscopic creep deformation is mainly from inter-lamellar amorphous phase and soft bulk amorphous phase out of the inter-lamellae. From the local creep measurement, the apparent modulus of inter-lamellar amorphous phase can be estimated ( $200 < M_a < 500$  MPa). These values are much higher than the Young's modulus of bulk amorphous PE, which can be explained as the confinement of the lamellar stacks and also the enhancement of the amorphous phase with relatively high concentration of entanglements.

## Notes

The authors declare no competing financial interest.

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