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Comparative Investigation on Step-cycle Tensile Behaviors of Two Bimodal Pipe-grade Polyethylene with Different Slow Crack Growth Resistance

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Electronic Supplementary Information

Abstract In this work, step-cycle tensile behavior of two bimodal polyethylene (PE) materials, a PE100 grade pipe material, XS10, and a PE100-RC (Resistant Crack) grade pipe material, XSC50, was comparatively investigated. By decomposing the strain into a recoverable part and an unrecoverable part, it was found that the deformation recovery capability of XSC50 during stretching was larger than that of XS10. Structural evolution characterized by *in situ* synchrotron small angle X-ray scattering indicated that the fragmentation of initial crystals in XSC50 occurred at lower strain than in XS10. Considering that XSC50 had relatively small lamellar thickness and similar crystallinity to XS10, we speculated that the larger deformation recovery capability of XSC50 during stretching probably derived from stronger entangled amorphous region caused by larger density of tie molecules and entanglements, which were usually regarded to have a significant influence on the slow crack growth (SCG) resistance of PE materials. As expected, the experimental result of strain hardening modulus test suggested that the deformation recovery capability during stretching was positively correlated with the SCG resistance for XS10 and XSC50 used in this work. The step-cycle tensile test had the potential to be developed into a supplement for comparison of SCG resistance of PE materials.

Keywords Polyethylene; Step-cycle tensile test; Deformation recovery; Slow crack growth resistance

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INTRODUCTION

Polyethylene (PE) resins are widely used in the production of pipes for their excellent chemical corrosion resistance, low temperature toughness, abrasion resistance, processability, and low cost of installation.^[1–3] In the past decades, with the optimization of the composition and chain structure, the performance of PE pipe materials has been constantly improving. PE pipe materials are classified into such grades as PE40, PE63, PE80, and PE100, corresponding to 4.0, 6.3, 8.0, and 10.0 MPa of minimum required strength (MRS) on the bases of 50 years' service life.^[4,5] PE100 has become the mainstream of current applications because of significantly improved long-term performance, which is developed on the basis of dual cascaded reactor polymerization technique. After produced in the first reactor, the low molecular weight linear component is transferred to the second reactor, and a mixture of ethylene and a few α -olefin comonomers will be added for the second

polymerization procedure. The PE100 materials are actually composed of linear fraction with lower molecular weight and short chain branched (SCB) fraction with higher molecular weight.^[6–9] It is generally considered that the linear fraction contributes to stiffness and processability, and the SCB chains tend to improve the creep resistance and long-term performance of pipe materials.^[3,10–14] Because of a good balance between mechanical properties and processability, PE100 is widely applied to produce large trunk pipes for pressure gas and water distribution network.

Currently, trenchless pipe laying technology has been widely used because of short occupation time and small damage to the surface of road. During trenchless installation, the friction of sand and stones would inevitably cause scratches and cracks on the outer surface of pipes. It is commonly accepted that the existence of local heterogeneities, such as scratches and cracks, would bring about stress concentration. When the local stress around these heterogeneities exceeds the yield stress, extension of the cracks would happen and is followed by rupture of pipes.^[11,15,16] Bhattacharya *et al.* reported that, at the tip zone of existing cracks, PE was highly stretched to form craze fibrils, and then the crack propaga-

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tion led to fibril formation and material creep until the craze fibril failure occurred, which was followed by rapid crack growth and final failure of PE pipes.^[17–19] These brittle mechanical failure that appears when pipes are subjected to a stress below the yield stress is named as slow crack growth (SCG). The occurrence of SCG will severely reduce the long-term service lives of PE pipes. Therefore, higher SCG resistance of PE pipe materials is widely required in actual applications. To solve this problem, PE100 grade materials with improved SCG resistance, which is named as PE100-RC (Resistant Crack), have been developed by optimizing composition and structure on the basis of PE100.^[20–23] Up to now, both PE100 and PE100-RC are widely used in various applications.

Given the importance of developing high performance pipe materials and understanding the physical mechanism of the SCG resistance, many researchers have devoted to the investigation of relationship between deformation behavior and SCG resistance of PE pipe materials.^[23–27] Connell and Capaccio *et al.* tried to characterize SCG resistance of PE by creep test and reported that creep of craze fibrils was the rate-determining factor of SCG in PE pipe materials.^[23–25] Brown *et al.* reported that the extension of craze fibrils was determined by the disentanglement process of tie molecules, thus the density of tie molecules was a decisive factor to SCG resistance.^[28–30] Kurelec and Teeuwen *et al.* developed the strain hardening modulus test, which could be used for convenient characterization of the SCG resistance of PE pipe materials *via* uniaxial stretching at 80 °C.^[26] PE pipe materials with stronger SCG resistance had a higher strain hardening modulus during stretching, corresponding to large density of tie molecules and entanglements in amorphous region. The strain hardening modulus test has already been standardized as ISO 18488:2015 because of its effectiveness in characterizing the difference of SCG resistance between various PE pipe materials.^[31–34] These excellent studies not only provided alternative methods for evaluating SCG resistance, but also demonstrated that the deformation of PE during crack propagation is highly correlated with its tensile behavior. Considering the similar chain structures and different SCG resistances between PE100 and PE100-RC, comparatively investigating the tensile behavior and deformation process of these materials would be helpful for deepening the understanding of the physical mechanism of SCG resistance of PE materials.

In recent years, Strobl and Men *et al.* have performed systematically investigation on the deformation mechanism of semi-crystalline polymers.^[11,35–38] They used the step-cycle tensile test to divide the tensile strain of PE and ethylene-octene copolymers into an elastic (recoverable) part and a plastic (unrecoverable) part, which reflected the deformation recovery capability of samples. As is known, the deformation during stretching is implemented by distortion of crystalline rigid network and entangled amorphous phase. The deformation recovery capability is mainly provided by the amorphous region, while the crystals restrain the deformation of amorphous region before reaching the maximum stress that could be afforded and fix tie molecules. When the stress is increased to overcome the stability of the lamellas, the crystal region would slip and break, providing a large amount of plastic de-

formation.^[39] For the amorphous region, molecular chain entanglements and tie molecules inhibit the slip of molecular chains and thus become the key structure for deformation recovery capability. Meanwhile, the density of entanglements and tie molecules in amorphous region are also important structural bases for SCG resistance of PE materials. Therefore, we speculate that the difference in deformation recovery capability during stretching probably has the potential to be used for comparative evaluation of density of tie molecules and entanglements and accordingly reflects the SCG resistance of PE materials.

In this work, step-cycle tensile behavior and SCG resistance of a PE100 grade pipe material (XS10) and a PE100-RC grade pipe material (XSC50) with similar structures produced by same polymerization technique were comparatively investigated. It was found that the PE100-RC pipe with better SCG resistance had stronger deformation recovery capability during stretching. Structure evolution performed by the *in situ* synchrotron SAXS technique indicated that the fracture of crystalline lamellas occurred at a lower strain in XSC50 than in XS10. Stronger deformation recovery capability of XSC50 was attributed to a larger density of tie molecules and entanglements in amorphous region, and lower strain of crystalline fragmentation was due to a combination of thinner lamellas and larger modulus of amorphous region. These results suggested that, for the PE pipe materials with no significant difference in crystallinity used in this work, the SCG resistance had a positive correlation with the deformation recovery capability during stretching. The step-cycle tensile test had the potential to be developed into a supplement for characterization of SCG resistance comparison.

EXPERIMENTAL

Materials

Two commercial products of Total S.A. were employed in this work, *i.e.*, a PE100, XS10 and a PE100-RC, XSC50. Their molecular weights and polydispersity index (PDI) measured by gel permeation chromatography (GPC) are listed in Table 1. Comonomer of XS10 and XSC50 was 1-hexene, and the short chain branching degrees were about 3.2 branches/1000 C for XS10 and 4.0 branches/1000C for XSC50 determined by ¹³C-nuclear magnetic resonance (NMR) spectroscopy at the reference of Seger's work.^[40]

Table 1 Molecular weight and PDI of the PE samples.

Sample	Grade	M_n (kg/mol)	M_w (kg/mol)	PDI
XS10	PE100	20.1	222.1	11.0
XSC50	PE100-RC	12.7	233.0	18.3

Sample Preparation and Characterization

Differential scanning calorimetry (DSC) was employed to evaluate the melting and crystallization behaviour of XS10 and XSC50. The experiment was performed on a TA Q2000 apparatus (TA Instruments, USA). Each sample of about 6.0 mg weight was sealed in aluminium pans and the tests were carried out in nitrogen atmosphere. Before recording the corresponding endothermic curves during melting and crystallization, samples were firstly heated from 25 °C to 200 °C at

10 °C/min, kept for 5 min, and then cooled to 25 °C at the same temperature ramping rate to obtain a uniform “standard” initial state. The measurements were carried out by heating from 25 °C to 200 °C and then cooling from 200 °C to 25 °C at 10 °C/min.

Successive self-nucleation and annealing (SSA) thermal fractionation was used to investigate the distribution of crystalline lamellar thickness. The experimental procedures were as follows. After creating the same initial “standard” thermal history, samples were heated to a selected self-nucleating temperature (T_s) at 10 °C/min and held for 5 min, which was followed by cooling to 25 °C at 10 °C/min. Then, this process of heating, isothermal, and cooling was repeated several times, which was controlled by changing the isothermal temperature range from 130 °C to 90 °C with an interval of 5 °C and the annealing time of 5 min. Subsequently, samples were heated from 25 °C to 200 °C at 10 °C/min to obtain the heating enthalpy curve.

The deformation recovery capability of the samples during stretching was measured by step-cycle tensile test. The experiment was carried out on an Instron 5966 universal testing machine (Instron, USA). Specimens used for step-cycle tensile test were obtained by molding at a pressure of 5 MPa for 5 min at 180 °C. In order to avoid the interference of pre-orientation caused by the pressure cooling process, sheets were cooled to room temperature without pressure. The thickness of specimen sheets was controlled to about 1.0 mm, and the dog-bone specimens required for the tensile test were punched from sheets with a cutter. Width of the parallel section was 4.0 mm and the length was 20.0 mm. In order to unify the experimental conditions with the strain hardening modulus test for comparison, all specimens were tested under 80 °C after annealing at the same temperature for 30 min. The temperature of 80 °C was higher than the α -relaxation temperature of PE, which means that the sliding of molecular chain in crystal was activated.^[41–43] At this temperature, the stability of lamellas was weakened, and the mobility of entangled molecular chains in amorphous region was significantly enhanced. In this case, the anchoring effect of the short-chain branch on tie molecules was more prominent. Additionally, step-cycle tensile test at 25 °C was also performed. The testing procedure was as follows. Specimens were first subjected to a strain of 0.25 at 10 mm/min, and the motion of crosshead was immediately reversed to zero stress. The specimens were stretched to a strain of 0.5, which was 0.25 higher than the last stretching step, and the motion was reversed as above. Samples were extended step by step until the strain of 5.00, and the stress-strain curve and strain at zero stress in each contracting step were recorded. The tests for each sample were repeated at least three times.

In situ synchrotron small-angle X-ray scattering (SAXS) measurement was applied to monitor the structure evolution during step-cycle tensile test. The experiment was performed on a TST350 temperature controlled tensile testing stage (Linkam, UK) at 80 °C and 10 mm/min. The size of specimen was 10.0 mm $\times$ 4.0 mm $\times$ 1.0 mm. These experiments were performed at the beamline BL16B of Shanghai Synchrotron Radiation Facility (SSRF). Wavelength of the X-ray was 0.124 nm and a Mar165 CCD detector (2048 $\times$ 2048 pixels with pixel size of 80 μ m) was employed to collect the 2D SAXS patterns.

The exposure time was 20 s with an additional 6 s for data recording and saving, and the distance between sample and detector was 1824 mm. 2D SAXS patterns were recorded at the strain where tensile direction changes. The 2D scattering patterns were analysed with xPolar software from Precision-Works NY, Inc., while the air background was subtracted. 2D SAXS patterns were integrated along stretching direction to obtain the 1D scattering profile as a function of $q = 4\pi\sin\theta/\lambda$, where q is the module of scattering vector, and λ is the wavelength of X-ray. The stretching procedure in the *in situ* SAXS test was slightly different from the step-cycle tensile test. In the strain range of 0–1.5, the strain increase per step was 0.05; after the strain of 1.5, the increase was 0.25.

Strain hardening modulus test was applied to characterize the SCG resistance of samples according to ISO 18488:2015. The Instron 5966 universal testing machine was also employed for the experiment. Specimens used for strain hardening test were produced according to ISO 18488:2015 with a thickness of 1.0 mm and a width of 4.0 mm for parallel segment. Specimens were thermostated at 80 °C for 30 min before testing. The uniaxial stretching was carried out at 80 °C with the cross-head speed of 20 mm/min.^[33] σ - λ curves recorded during stretching were defined by the Standard as follows: $\lambda = l/l_0 = 1 + \Delta l/l_0$, where λ is the draw ratio, l is the specimen length, l_0 is the gauge length, and Δl is the increase in the specimen length between the gauge marks. $\sigma = F/A$, where F is the measured force, and A is the initial cross section of the specimen. The Neo-Hookean constitutive model is used to fit the $\langle G_p \rangle$ data from σ - λ curves according to the Standard:

$$\langle G_p \rangle = \frac{1}{N} \sum_{i=1}^N \frac{\sigma_{i+1} - \sigma_i}{\lambda_{i+1} - \lambda_i} = \left[\frac{\left(12^2 - \frac{1}{12}\right) - \left(8^2 - \frac{1}{8}\right)}{12 - 8} \right] \times G_p \approx 20 \times G_p \quad (1)$$

where G_p is calculated from $\sigma_{\text{true}} = G_p \times (\lambda^2 - 1/\lambda) + C$ at the range between $\lambda = 8$ and $\lambda = 12$, and $\langle G_p \rangle$ is the defined strain hardening modulus.

RESULTS AND DISCUSSION

Characterization of PE Samples

The melting and crystallization behaviors of XS10 and XSC50 were evaluated by DSC. Endothermic curves of samples during heating and cooling at 10 °C/min are shown in Fig. 1. The melting temperatures for XS10 and XSC50 were 130.0 and 129.0 °C, while the crystallization temperatures were 118.1 and 117.8 °C, respectively. The Thomson-Gibbs equation was used to establish the relationship between melting temperatures and mean lamellar thickness:^[44]

$$l_c = \frac{2\sigma T_m^0}{\Delta H_v (T_m^0 - T_m)} \quad (2)$$

where l_c is the lamellar thickness, σ is the lamellar surface free energy, ΔH_v is the enthalpy of fusion for infinitely thick lamella, T_m is the melting temperature, and T_m^0 is the equilibrium melting temperature of an infinitely thick lamella. For linear polyethylene, ΔH_v is 288×10^6 J/m³, σ is 70×10^{-3} J/m², T_m^0 is about 418 K, and the derived heat to the melting enthalpy of hypothetical 100% crystalline polyethylene is 293 J/g. Mean

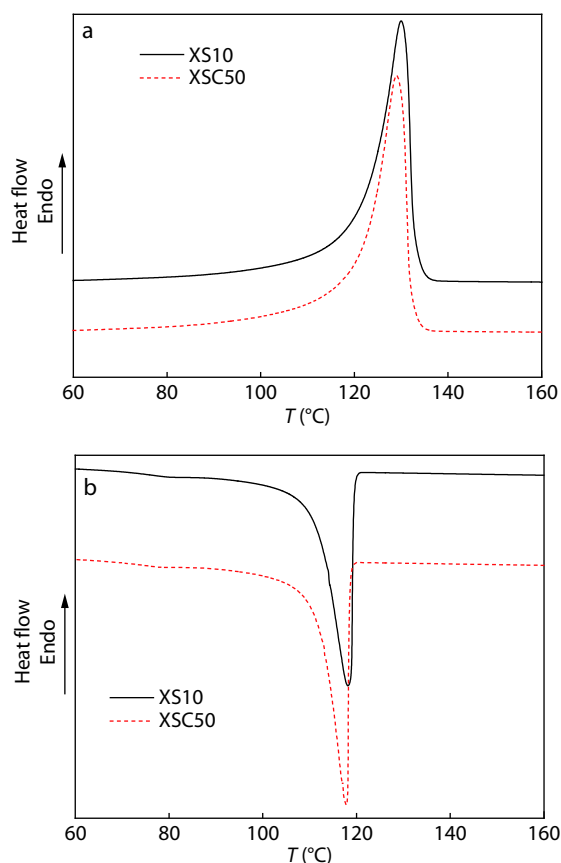


Fig. 1 DSC heating (a) and cooling (b) curves of XS10 and XSC50 samples.

thicknesses of crystalline lamellas of XS10 and XSC50 were calculated, which were 13.7 nm for XS10 and 12.8 nm for XSC50. In addition, the crystallinity calculated by melting enthalpy was 63.2% for XS10 and 62.0% for XSC50. Those results indicated that the crystalline lamellas of XSC50 were little thinner than that of XS10, although the crystallinities of both samples were similar.

SSA thermal fractionation was employed for further investigation. DSC heating enthalpy curves of XS10 and XSC50 after SSA thermal fractionation are shown in Fig. 2. Eight melting peaks were labeled as Fractions 1–8 from high to low by temperature. Using Thompson-Gibbs equation, lamellar thickness distribution of XS10 and XSC50 was obtained. Gaussian function was used to fit the heating enthalpy curves, and the lamellar thickness and integral area ratio of every fraction are listed in Table 2. The average lamellar thickness of Fraction 1 was 15.1 nm for XS10 and 14.4 nm for XSC50, while those of Fractions 2–8 had no significant difference. Integral area ratios reflected that the content of Fraction 1 was 59.1% for XS10 and 54.7% for XSC50, and contents of Fractions 2–4 were clearly larger in XSC50 than in XS10. This result indicated that the majority of lamellas in XSC50 were thinner than that in XS10, which were probably caused by the larger short chain branching degree of XSC50. According to the result of ^{13}C -NMR, the larger short chain branching degree of XSC50 was due to a higher content of 1-hexene comonomer.

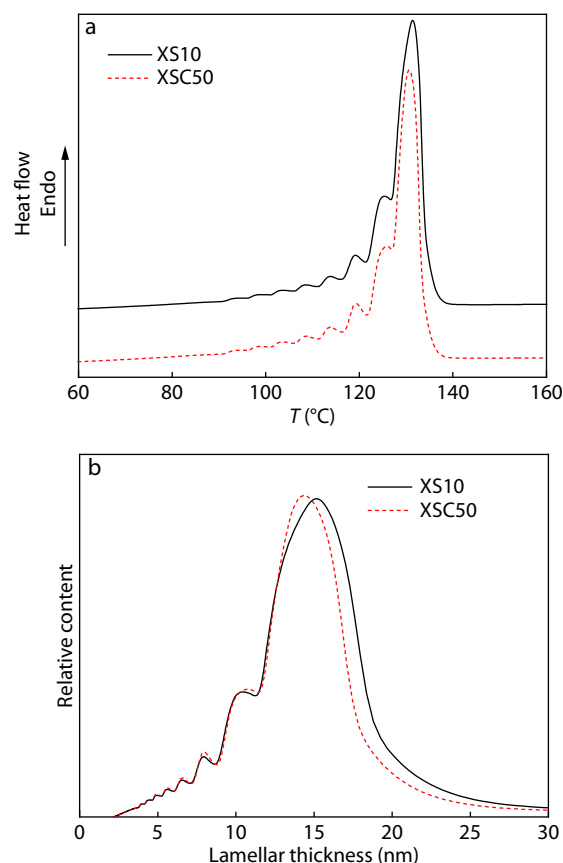


Fig. 2 DSC melting curves (a) and lamellar thickness distribution (b) of PE samples after SSA thermal fractionation.

Table 2 Melting temperature, lamellar thickness, and integral area ratio of each fraction.

Fraction ^a	XS10			XSC50		
	T_m^b (°C)	l_c^c (nm)	AR ^d (%)	T_m^b (°C)	l_c^c (nm)	AR ^d (%)
1	131.4	15.1	59.1	130.7	14.4	54.7
2	124.8	10.1	19.4	125.1	10.3	20.9
3	119.2	7.9	7.5	119.3	8.0	8.4
4	114.0	6.6	5.2	114.0	6.6	5.8
5	108.6	5.6	3.6	108.5	5.6	3.9
6	103.5	4.9	2.4	103.4	4.9	2.7
7	98.5	4.4	1.7	98.5	4.4	1.9
8	93.6	4.0	1.2	93.5	4.0	1.4

^a Fractions are arranged in descending order of melting temperature; ^b T_m is the temperature at the peak maximum of fractions on the enthalpy curve; ^c l_c is the mean lamellar thickness of fractions calculated by Thompson-Gibbs equation; ^d AR is the integral area ratio of fractions, which could reflect the relative content of fractions.

Step-cycle Tensile Behavior

The stress-strain curves of XS10 and XSC50 samples during step-cycle tensile test are illustrated in Fig. 3, and the elastic modulus, yield strength, and yield strain of XS10 and XSC50 are summarized in Table 3. It is obvious that the elastic modulus and yield strength of XSC50 were smaller than those of XS10, and the yield strain of XSC50 was slightly larger than that of XS10. This result indicated that the rigidity of XSC50 during stretching was weaker than that of XS10. Considering the reduction of difference in stress between XS10 and XSC50, weaker rigidity of XSC50 was due to the less stability of initial

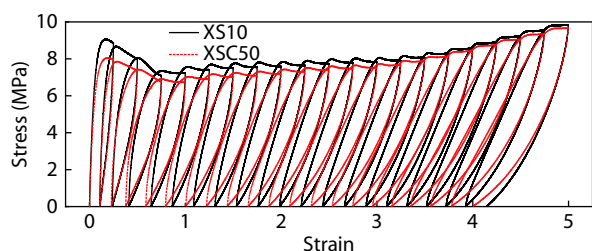


Fig. 3 Stress-strain curves of the samples derived from the step-cycle tensile test at 80 °C.

Table 3 Elastic modulus, yield strength, and yield strain of XS10 and XSC50 from the step-cycle tensile test at 80 °C.

Sample	Elastic modulus (MPa)	Yield strength (MPa)	Yield strain
XS10	236.3 ± 6.5	8.93 ± 0.12	0.167 ± 0.005
XSC50	189.7 ± 9.3	8.02 ± 0.06	0.187 ± 0.003

crystals, which was derived from smaller thickness of lamellas.

Deformation recovery capability of XS10 and XSC50 was represented by the elastic ratio of strain, ϵ_e/ϵ , and is shown in Fig. 4. It is obvious that the elastic ratio of strain of XS10 and XSC50 monotonically decreased with the increase of strain. The reduction of elastic ratio of strain mainly occurred in the strain range of 0.50–3.50, which is covered by deformation after yield point and extension of the neck. This sharp drop of deformation recovery capability is mainly related to the plastic deformation growth caused by slip and fracture of the initial crystal structure. When strain hardening began at the strain of about 3.50, neck expansion ended and the deformation of PE was dominated by the disentanglement of tie molecules and amorphous entanglements, which inhibited the increase of plastic deformation, and thus the deformation recovery capability remained stable. The deformation recovery capability of XSC50 was larger than that of XS10 during stretching. According to the work of Strobl *et al.*,^[11] the deformation recovery capability of a semi-crystalline polymer material is highly correlated with a network composed of crystals, tie molecules, and entanglements in amorphous region. This network has a memory effect on the initial shape of the material. When subjected to an external force, the entangled network and the relaxed tie molecules would be extended in the deformed amorphous region, thereby storing energy. When the external force is removed, the energy would be released, thereby achieving a recovery of the deformation. The experimental result of step-cycle tensile test showed that the elastic network of XSC50 was stronger than that of XS10 during stretching.

As mentioned above, the crystalline lamellar thickness of XSC50 was slightly smaller than that of XS10, which reduced the resistance to the slip of tie molecules and lamellas. Meanwhile, similar crystallinity of XS10 and XSC50 indicated that the difference in deformation recovery capability was not contributed by the content of amorphous region. At 80 °C, the molecular disentanglement and slip of tie molecules were significantly promoted, which enhanced the fixing effect from short chain branches on tie molecules. Therefore, we believed that the stronger deformation recovery capability of XSC50 during stretching was primarily attributed to the relat-

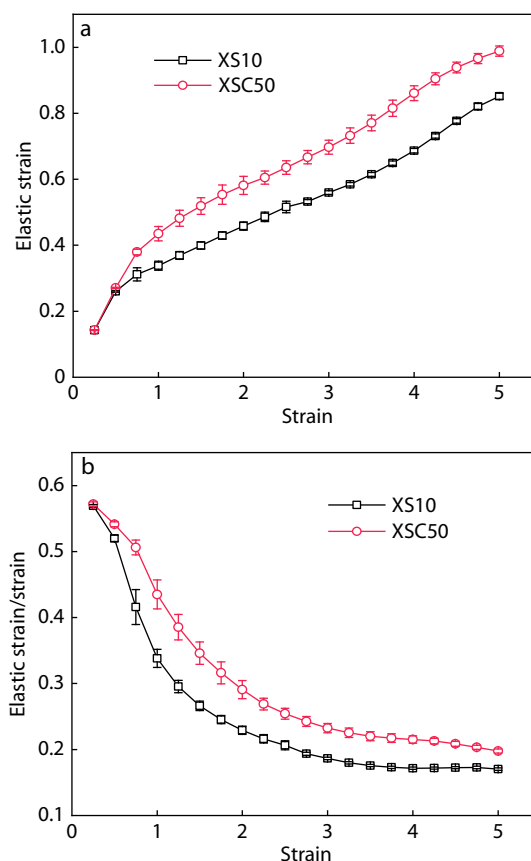


Fig. 4 Strain dependence of elastic strain (a) and elastic ratio (b) of XS10 and XSC50 derived from the step-cycle tensile test at 80 °C.

ively large density of tie molecules and entanglements. Experimental results of structural characterization indicated that XSC50 had more 1-hexene comonomer and larger molecular weight than XS10. The increase of comonomer content and molecular weight promoted the long molecular chain to pass through more crystalline lamellas to improve the density of tie molecules. Additionally, short chain branches could act as an "anchor" to fix tie molecules and to inhibit the slip of tie molecules.

Structural Evolution during Step-cycle Tensile Test

In order to explore the correlation among microstructural evolution and apparent properties of both samples, *in situ* SAXS measurement was performed during step-cycle tensile tests at 80 °C. 2D SAXS patterns recorded at the maximum strain and zero-stress point in each stretch-unload cycle are shown in Fig. 5.

From the scattering patterns, the crystalline structure evolution of XS10 and XSC50 along the stretching direction is well exhibited. It is obvious that the SAXS patterns converted from an isotropic signal to a signal that is highly oriented in the stretching direction. It is worth noting that compared with the case of XS10, the patterns of XSC50 changed at lower strain. For example, the patterns of $\epsilon = 0.4$ –0.8 for XS10 were quite similar in orientation to the corresponding patterns of $\epsilon = 0.3$ –0.7 for XSC50.

For further investigation, the 2D SAXS patterns were integrated along stretching direction to obtain the $I(q)$ - q curves.

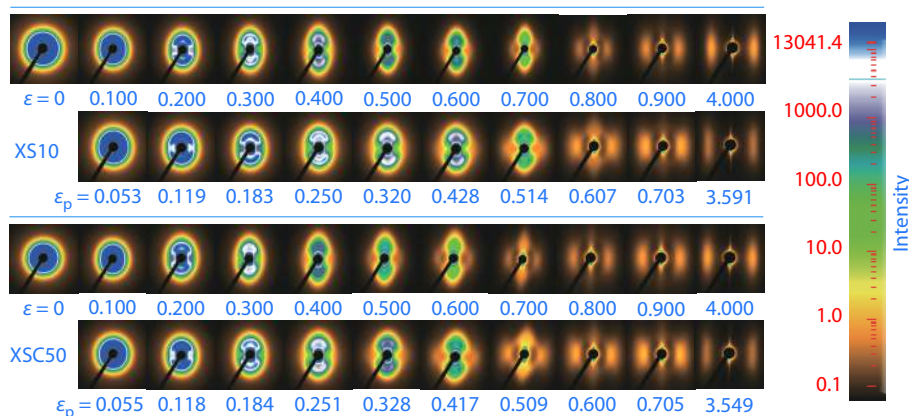


Fig. 5 Selected 2D SAXS patterns of XS10 (top) and XSC50 (bottom) at different strains during step-cycle tensile test at the 80 °C. Upper patterns correspond to the stretched states at the maximum strain in each cycle, whereas the lower ones directly below show the unloaded states from the upper ones. Stretching direction: horizontal.

Periodic lamellar structures of PE exhibited local maxima at $l(q)$ - q curves and the value of long period (d_{ac}) could be calculated by the Bragg equation: $d_{ac} = 2\pi/q_{max}$, where long period (d_{ac}) was considered as the average thickness of a crystalline lamella together with an interlamellar amorphous layer. Because the q_{max} value was so close to beam stop that the signal was covered by background in original $l(q)$ - q curves, the Lorentz correction was applied to obtain $l(q)q^2$ - q curves for analysis. It has been reported that the Lorentz correction of SAXS data for highly stretched samples has no significant effect on difference between samples, and still can be used for qualitative analysis.^[45,46] In order to analyze the structural evolution during stretching, the mean thickness of amorphous region and the crystalline phase measured along tensile direction were evaluated from the one-dimensional electron density correlation function $K(z)$:^[37]

$$K(z) = \frac{\int_0^\infty l(q)q^2 \cos(qz) dq}{\int_0^\infty l(q)q^2 dq} \quad (3)$$

where the strain dependency of long period (d_{ac}), thickness of crystalline lamellas (d_c), and thickness of amorphous region (d_a) are shown in Fig. 6.

Fig. 6 shows that the change of long period during step-cycle tensile test was mainly contributed by the change of crystal region, and the size of amorphous region was too small to affect the evolution of long period significantly. In the strain range of about 0.00–0.20, the long period, thickness of crystal phase, and thickness of amorphous regions increased with elongation. At the beginning of tensile test, amorphous regions were elongated, and the crystalline lamellas were slightly twisted and rearranged in the stretching direction under applied external force. When tensile process reached the yield strain of about 0.20, the size of amorphous regions along stretching direction decreased rapidly. At the yield point, stress overcame the stability of initial crystals, and the resultant massive slip and twist aggravated plastic deformation seriously. The plastic deformation of the crystal relaxed the stress afforded by the amorphous region, so the size of the amorphous region along stretching direction was reduced. Meanwhile, crystal regions were still exten-

ded because of slip and twist, but the fracture and separation of lamellas began to decrease the thickness of crystalline lamellas gradually. When the strain reached about 0.30–0.40, severe fracture of crystals dominated the deformation process, resulting in a rapid decline in long period. At the strain of 0.80–0.90, the long period, the thickness of crystalline phase, and the thickness of amorphous region simultaneously reached their minimum values, indicating that the initial crystal structure was destroyed to the utmost extent. Subsequently, in the strain range of about 0.90–1.20, the size of both crystal and amorphous region showed an increase because of the recrystallization of PE molecular chain and the orientation of crystalline blocks along stretching direction. The absorption of molecular chains during recrystallization improved the stress afforded by amorphous region, leading to increasing thickness along the stretching direction. The decrease in the long period at about 1.20–1.50 strain was probably caused by the rupture of the oriented crystal at a further elongation, and the molecules were further oriented to form fibers. Thereafter, the deformation was dominated by disentanglement of tie molecules and entanglements, so that the crystal size remained stable while the amorphous region size increased along stretching direction.

The sharp drop in long period of XSC50 occurred at a lower strain than that of XS10. This phenomenon was consistent with the 2D SAXS patterns. The strain required for the fragmentation of crystals was related to the modulus of amorphous network and the stability of crystalline blocks.^[38] Experimental result of SSA fractionation indicated that crystalline lamellas of XSC50 were slightly thinner than those of XS10, which meant the critical stress of lamellar fracture of XSC50 was lower than that of XS10. Earlier fragmentation was due to a combination of weaker crystalline lamellas and larger density of tie molecules and entanglements of XSC50 caused by the higher content of 1-hexene comonomer and larger molecular weight.

Correlation between Results of Step-cycle Tensile Test and SCG Resistance

As mentioned above, XSC50 with stronger SCG resistance had a larger deformation recovery capability during stretching than

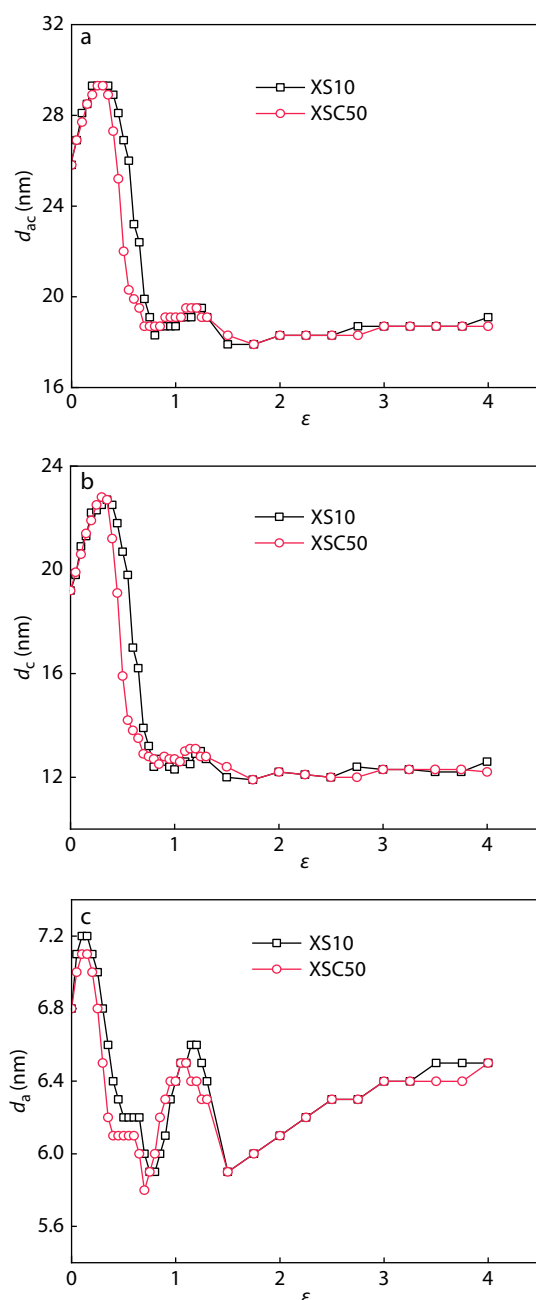


Fig. 6 Strain dependency of long period (d_{ac}) (a), thickness of crystal region (d_c) (b), and amorphous region (d_a) (c) of XS10 and XSC50 along tensile direction at stretched state during step-cycle tensile test at 80 °C.

XS10 did. Considering the significant effect of density of tie molecules and entanglements on SCG resistance and deformation recovery capability, the structural bases of the two performances were similar. Therefore, the deformation recovery capability could partially reflect the difference in SCG resistance. Currently, the evaluation methods for characterization of SCG resistance are mainly based on environmental stress crack resistance (ESCR) test, such as Notched Pipe Test (NPT), Full Notch Creep Test (FNCT), and Pennsylvania Edge Notch Tensile (PENT) Test.^[47–50] These methods focus on accelerating the

occurrence of slow crack growth of PE pipe material by regulating the test environment, and the SCG resistance is confirmed by failure time and growth rate of cracks. However, these traditional methods have abundant cost both in time and experimental instruments, such as dedicated sample preparation machine and thermostatic surfactant solution environmental chamber. The experimental process of these methods could take up to one year for the characterization of currently used PE100 and PE100-RC. Kurelec and Teeuwen reported the correlation between strain hardening modulus in uniaxial stretching and SCG resistance of PE materials.^[26] After compared with the result of traditional ESCR test methods, the measurement of strain hardening modulus was found to be able to characterize the SCG resistance of PE pipe materials. Up to now, the strain hardening modulus test has been developed to an ISO standard and widely used in industry because of its accuracy and convenience.^[33] We herein use this method to contrastively investigate the SCG resistance of XS10 and XSC50 in this work. The strain hardening modulus was 30.8 ± 0.1 MPa for XS10 and 33.4 ± 0.2 MPa for XSC50, which means that the XSC50 material with stronger deformation recovery capability had better SCG resistance. This result indicates that the deformation recovery capability of XS10 and XSC50 had a positive correlation. Although further investigation is needed, step-cycle tensile test probably has the potential to be developed into a supplement method for SCG resistance characterization of PE pipe materials.

CONCLUSIONS

In this work, step-cycle tensile behavior and SCG resistance of XS10, a PE100 grade pipe material, and XSC50, a PE100-RC grade material with similar polymerization technique were investigated. It was found that XSC50 with better SCG resistance had stronger deformation recovery capability than XS10 during stretching. Structure evolution performed by the *in situ* synchrotron SAXS technique indicated that the fragmentation of crystals occurred at a lower strain in XSC50 than in XS10. Considering the similar crystallinity and smaller mean lamellar thickness of XSC50, its stronger deformation recovery capability was attributed to higher density of tie molecules and entanglements, which inhibited the plastic deformation of molecular chains in amorphous region. Smaller critical strain of XSC50, where the stability of crystalline lamellas was overcome by stress, was due to thinner lamellas with lower stability and higher modulus of amorphous region provided by higher density of tie molecules and entanglements in amorphous region. These results suggested that the SCG resistance showed a positive correlation with the deformation recovery capability during stretching of PE materials with similar crystallinity. Both SCG resistance and deformation recovery capability depend on the density of tie molecules and entanglements in amorphous region, so the structural bases of the two apparent performances have an obvious similarity. Additionally, the deformation recovery capability obtained from step-cycle tensile test showed a good correspondence with the strain hardening modulus test, which probably means that the step-cycle tensile test has the potential to be developed into a supplement for characterization of SCG resistance comparison.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2364-3>.

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