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Molecular Mobility in the Amorphous Phase Determines the Critical Strain of Fibrillation in the Tensile Stretching of Polyethylene

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Abstract The microstructural development of bimodal high density polyethylene subjected to tensile deformation was investigated as a function of strain after annealing at different temperatures by means of a scanning synchrotron small angle X-ray scattering (SAXS) technique. Two different deformation mechanisms were activated in sequence upon tensile deformation: intralamellar slipping of crystalline blocks dominates the deformation behavior at small deformations whereas a stress-induced crystalline block fragmentation and recrystallization process occurs at a critical strain yielding new crystallites with the molecular chains preferentially oriented along the drawing direction. The critical strain associated with the lamellar-to-fibrillar transition was found to be ca. 0.9 in bimodal sample, which is significantly larger than that observed for unimodal high-density polyethylene (0.4). This observation is primarily due to the fact that the bimodal sample possesses a greater mobility of the amorphous phase and thereby a reduced modulus of the entangled amorphous network. The conclusion of the mobility of the amorphous phase as a determining factor for the critical strain was further proven by the ¹H-NMR T_2 relaxation time. All these findings contribute to our understanding of the excellent slow crack growth resistance of bimodal polyethylene for pipe application.

Keywords SAXS; Bimodal high density polyethylene; Molecular mobility

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INTRODUCTION

Polyethylene (PE) has triggered considerable research interest in the fields of pipe applications due to its well-balanced mechanical performance including high stiffness and excellent environmental stress cracking resistance. To a large extent, the mechanical properties of PE are dependent on microstructure and morphology.^[1,2] Polyethylene, like many other crystallizable polymers, crystallizes into periodically stacked crystalline lamellae together with entangled amorphous polymeric chains in between when being cooled down from the melt.^[3] The interpenetrated hard crystalline phase offers desirable attributes such as stiffness, strength, barrier to gas transport, and dimensional stability. On the other hand, the soft amorphous domain imparts such attributes as toughness and resistance to slow crack growth.^[4,5] As a consequence of tensile deformation, the original lamellar superstructure of PE is transformed into a fibrillar one where polymeric chains are preferentially oriented along the extensional direction.^[6] Being composed of interlocked lamellae and entangled amorphous phase, semicrystalline polymers always exhibit a complex deformation behavior

under uniaxial stretching. On a microscopic level, an especially effective means to gain more insight into the molecular mechanisms and laws controlling deformation is to study the microstructural changes during mechanical treatments of the polymeric material.^[7–11] To explain the intrinsic nature of lamellar-to-fibrillar transition, two different mechanisms have been put forward in the tensile stretching of crystalline polymers, including interlamellar and intralamellar block slips,^[6,12,13] as well as stress-induced melting and recrystallization process.^[14–16] Experimental evidence for both the slip mechanism^[12,17] and the melting-recrystallization scheme^[18,19] have been extensively reported in the previous investigations.

In recent years, many studies on the deformation behavior of semicrystalline polymers based on “true stress-strain” curves revealed that a combination of these two deformation mechanisms discussed above is activated in the process of tensile deformation.^[10,20] Upon stretching, block slippage within the crystalline lamellae takes place first, followed by the stress-induced fragmentation and recrystallization of the freed polymeric chains at a critical strain. It was also found that this critical strain depends on the interplay between the entanglement state of the amorphous phase and the stability of the crystalline blocks.^[5] Furthermore, tie molecules, which connect adjoining lamellae, play a lesser important role in de-

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termining the value of the critical strain with respect to the amorphous phase as a whole.^[5] In the case of PE, a critical true strain of about 0.6 for the onset of fibril formation was obtained irrespective of crystallinity, deformation temperature, strain rate, and lamellar thickness.^[20] However, for PE copolymer this critical strain was found to increase with increasing comonomer content^[21] and stretching temperature,^[22] and a three phase model should be taken into account in such cases.

In many practical applications, an apparently brittle failure mode, typically referred to as slow crack growth (SCG), occurs at a pressure lower than corresponding yield stress through the initiation and growth of a craze being followed by rupture of the craze fibrils, and therefore limits the service lifetime of the conventional PE pipes. With the progress of industrial technique, bimodal PEs have been produced that exhibit excellent SCG resistance, which are composed of linear short chains and long chains with short side chain branches. Despite more than two decades of commercial practice using preferential placement of short chain branches (SCB) along the longer molecules of high density polyethylene (HDPE), a molecularly based understanding for this resistance is not clear yet.^[23,24] As pointed out in the previous publications, the lifetime of pipe materials was often considered as being determined by the density of tie molecules.^[25–27] Increasing the concentration of interlamellar tie chains would promote toughness and resistance to crack growth fracture. This conclusion, however, cannot explain the excellent durability of the bimodal grade HDPE for pipe application. An important finding that has been reported is that materials which possess better SCG resistance always show longer and thicker craze fibrils before they break down.^[26] This morphological feature can be linked to the mobility of the amorphous phase.^[28]

It is well accepted that the structural rearrangement occurring during annealing corresponds to a process of defect clustering, leading to an improvement in the crystalline-amorphous ordering and the thickening of both crystallites and amorphous layers.^[3,29] In real-life applications, one often meets situations where a polymeric product is used under varying temperature conditions. In such a case, knowledge about the dependence of microstructure on the extension ratio upon annealing is of significant importance. In this work, we report the structural development of bimodal HDPE as a function of strain and annealing temperature *via* scanning synchrotron SAXS measurements. The value of the critical strain associated with the beginning of fibril formation is found to be *ca.* 0.9, which is significantly larger than that observed for unimodal HDPE (0.4).^[18] This behavior is due to the bimodal sample with a more mobile amorphous phase and thus a reduced modulus of the entangled amorphous network.

EXPERIMENTAL

The bimodal HDPE, which was composed of linear short chains and high molecular weight chains with 3.1 C₄H₉-branches per 1000 backbone carbons, was supplied by BASSELL Polyolefine, Frankfurt, Germany. The molecular weights of the material were $M_w = 4.4 \times 10^5$ g/mol and $M_n = 1.0 \times 10^4$ g/mol. As a

comparison, the unimodal HDPE, which consisted of linear long chains and short chains with 2 C₄H₉-branches per 1000 backbone carbons, had molar masses of $M_w = 3.24 \times 10^5$ g/mol and $M_n = 2.3 \times 10^4$ g/mol. The short side chain branches were randomly distributed in the main chain for both polyethylene systems. The bimodal material was first compression molded at 180 °C and held at this temperature for 5 min to complete the polymer chain relaxation. A fast crystallization process was induced by rapidly quenching the melt into ice water yielding a plate of 2 mm thickness. Samples prepared in this way were tensile deformed without stress-whitening at room temperature. However, such a stress-whitening phenomenon normally occurs for HDPE samples produced by slowly cooling down from the molten state when being stretched at room temperature. Stress-whitening implies the occurrence of cavitation in the samples during tensile elongation, which will overlap the scattering signal of lamellar structure as a result of much enhanced electron density difference between the cavities and surrounding polymeric matrix.^[30] Rectangular strips of 20 mm (width) × 70 mm (length) used for tensile measurements were cut from the plates. The as-received samples were stretched with a constant crosshead speed of 10 mm/min at room temperature until neck propagation over a large portion of the sample. The deformed samples were then annealed at selected temperatures of 23, 80, 100, and 120 °C for 24 h by fixing their two ends in metal frames in a vacuum oven in order to avoid macroscopic shrinkage. The true strains of the stretched samples along the neck shoulder were obtained from the following equation

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

where b_0 and b denote the initial width of samples and the width of tensile stretched samples at a specific spot, respectively. Application of this expression to the measure of deformation requires the assumption of a constant volume during extension. This prerequisite is fulfilled in the present case where no cavity scattering is observed.

Synchrotron scanning SAXS measurements were performed at the beamline BW4 at HASYLAB, DESY, Hamburg, Germany with a wavelength of X-ray radiation of 0.13808 nm. The size of the incident X-ray beam at the sample position was 0.4 mm × 0.4 mm. The pre-stretched sample was mounted on a two-dimensional mobile stage at the beamline at a sample-to-detector distance of 6432 mm. The primary X-ray beam first illuminated at the middle of the deformed sample bar, and the sample was then moved step by step in such a manner that the X-ray radiation scanned over the stretched sample from a deformation ratio of *ca.* 0.07 up to 1.45 at a step length of 0.5 mm. Simultaneously, SAXS pattern was recorded at each step within an acquisition time of 120 s. The effective scattering vector q ($q = (4\pi \sin \theta) / \lambda$, where 2θ is the scattering angle and λ the wavelength of X-ray beam) range in this work was 0.04–0.54 nm^{−1}. The SAXS data were calibrated for background scattering and normalized with respect to the primary beam intensity *via* considering sample adsorption.

In order to characterize the molecular mobility in crystalline lamellae and amorphous phase of polyethylene, proton

NMR relaxation measurements were performed for static samples on a Bruker Minispec MQ-20 (series F) relaxometer. The relaxometer was operated at a proton resonance frequency of 19.65 MHz, and the dead time of the receiver was 9 μ s. The lengths of a radio-frequency 90°- and 180°- pulses were about 2.8 and 5.6 μ s, respectively. Samples were placed in the most homogeneous part of the radio-frequency field of the relaxometer. The free induction decay (FID) was recorded at 70 °C after approximate 5 min for temperature stabilization within sample volume using single pulse excitation (SPE): 90°_x – dead time – [acquisition of amplitude $A(t)$ of FID as a function of time t].

RESULTS AND DISCUSSION

The textural variations on the lamellar length scales during deformation were characterized by means of SAXS. Selected SAXS patterns of bimodal HDPE samples annealed at different temperatures are presented as a function of imposed strain in Fig. 1. The value of the long spacing (d_{ac}) can be calculated from the position of scattering maximum q_{max} using the Bragg equation:

$$d_{ac} = \frac{2\pi}{q_{max}} \quad (2)$$

The long spacing d_{ac} is defined as the average thickness of crystalline lamellae together with entangled amorphous regions measured along the lamellar normal. Because isolated inter- and intra-lamellar slip processes set in already before the yield point, the un-necked region of the samples also displayed several percents of permanent macroscopic deformation.^[31] In the present study, this is indeed the case as indicated by the slight anisotropy of the scattering patterns at the un-necked region in Fig. 1. With increasing stretching ratio, the SAXS patterns become more anisotropic, and finally a pat-

tern with two straight streaks perpendicular to the direction of drawing at large strains develops, indicating a quasi-periodic density fluctuation along the highly oriented fibrils. This newly developed structural element can be confirmed by the equatorial scattering streak close to the beam-stop at high elongations. Additionally, in the course of the lamellar-to-fibrillar transition several structural differences can be identified between the bimodal and unimodal samples upon closer inspection of the SAXS data.

In the case of the stretched sample annealed at 23 °C, the original scattering intensity in the meridional direction (*i.e.*, along the stretching direction) becomes gradually weaker upon increasing strain, reflecting a loss of the positional correlation between the crystalline lamellae with their normal parallel to the stretching direction. When the strain reaches a critical value of about 0.9, a new scattering peak appears in the meridian at a larger q value corresponding to a reduction of the long spacing of the periodically stacked lamellae. This finding is well consistent with the previously proposed argument of stress-induced fragmentation and recrystallization during deformation. Since the deformation was performed at a relatively low temperature (*i.e.*, 23 °C) with respect to the typical crystallization temperature of HDPE, the recrystallization process produces new lamellae that are thinner than the original ones as a result of the high undercooling.^[32] For the original lamellar crystallites, two main features can be elucidated from the SAXS diagrams. First, the normalized scattering intensity decreases significantly with increasing deformation ratio, implying that the original lamellar stacks are destroyed gradually in the course of deformation. Second, it is quite evident that a four-point diagram occurs at small deformations (*e.g.*, $\varepsilon_H = 0.48$), suggesting a tilting of the oriented lamellar crystallites due to intra-lamellar slips. On the other hand, the effect of annealing on the SAXS patterns and thus

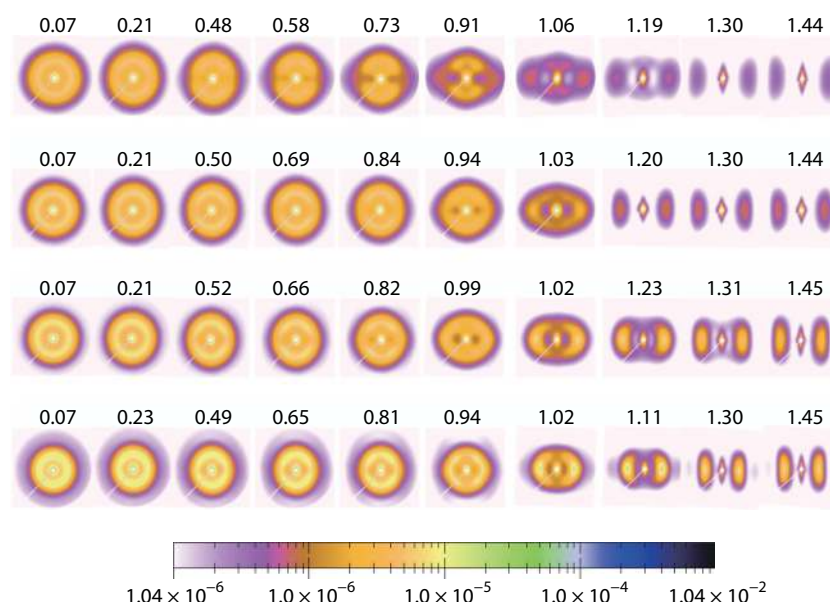


Fig. 1 Selected small angle X-ray scattering patterns of uniaxially drawn bimodal HDPE followed by annealing at 23, 80, 100, and 120 °C (from top to bottom) taken at different imposed strains as indicated on the graph. Stretching direction is horizontal.

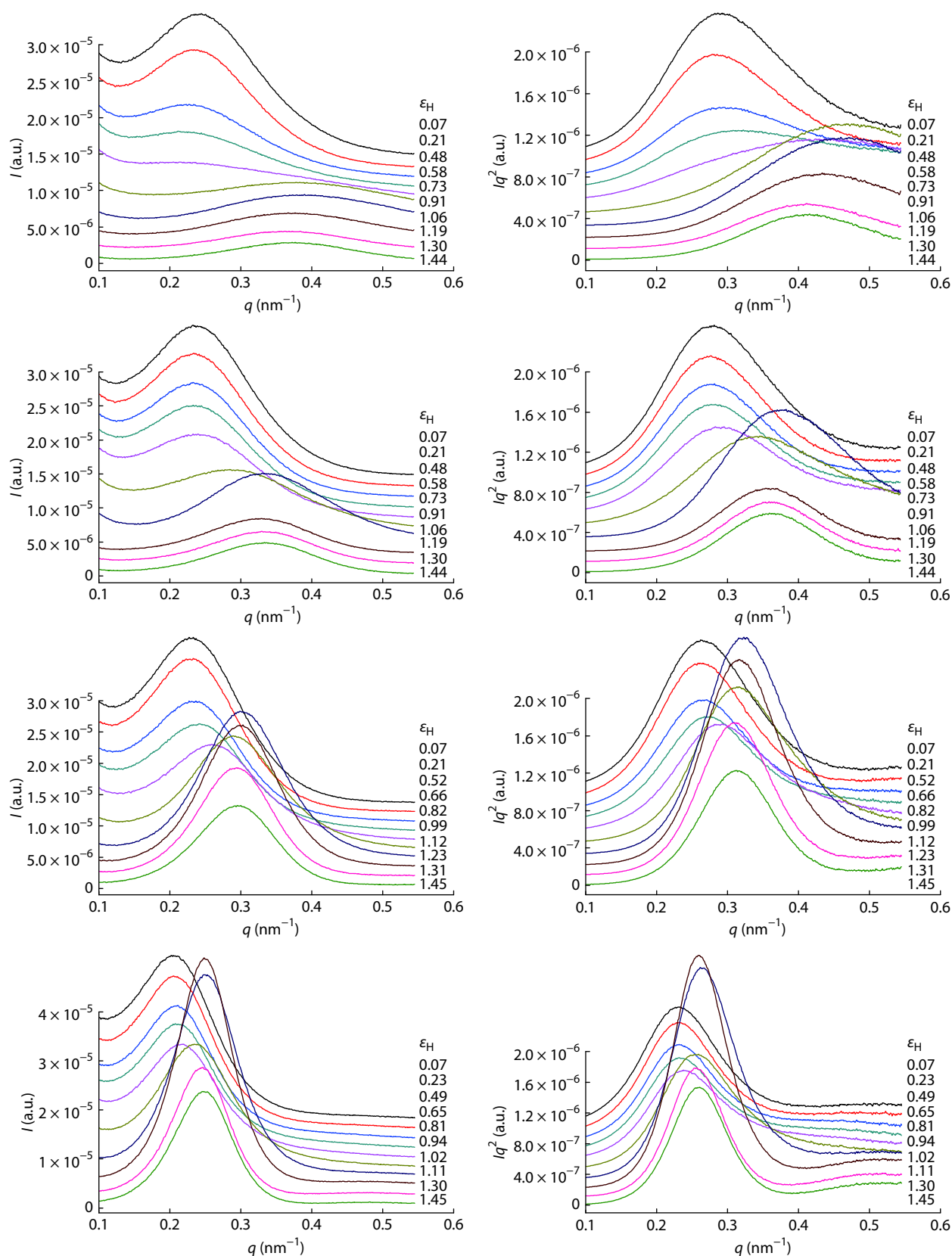


Fig. 2 SAXS: one-dimensional scattering intensity distribution profiles without Lorentz correction (left) and with Lorentz correction (right) taken along the stretching direction at different deformations for bimodal samples annealed at 23, 80, 100, and 120 °C (from top to bottom). Peak positions are used to calculate the long spacing (d_{ac}).

the lamellar structure of bimodal samples is also extracted from the data in Fig. 1. First, one notes an overall increase in the scattering intensity after annealing at chosen temperatures, which means an improvement of the ordering between crystalline and amorphous regions resulting from structural reorganization. Second, the position of the scattering maximum moves to a smaller q value after annealing, which is indicative of an increase in the crystalline lamellar long spacing. Finally, no qualitative difference of the shape of SAXS patterns is observed with respect to the annealing temperature, even at moderate deformations (e.g., a strain of around 0.9) where the stress-induced fragmentation and recrystallization just set in. This observation is distinctly different from the results of unimodal HDPE.^[8] It was found that in the case of a deformed HDPE with unimodal molecular weight distribution, at moderate strains the newly formed lamellae serve as nuclei, and the original lamellae melt and recrystallize onto them forming thicker lamellar crystals with the normal along the stretching direction upon annealing at temperatures lower than 100 °C. The discrepancy can be explained by a lesser degree of internal deformation acting upon the lamellae of bimodal HDPE as compared to the unimodal sample.

In order to illustrate the variations of lamellar long spacing with deformation ratio and annealing temperature, one-dimensional scattering intensity distributions along the drawing direction with and without Lorentz correction are separately presented in Fig. 2. The long spacing values for samples after deformation and annealing were obtained using Eq. (2) for both data sets, and are shown in Fig. 3. It should be noted that both recipes for SAXS data processing are strictly applicable to two extreme cases, namely, Lorentz correction for samples without deformation and no Lorentz correction for samples with highly oriented crystalline lamellae. So far there is no general method to deal with the data between the above two extremes due to nonuniform distribution of scattering intensity in reciprocal space. The data demonstrate that the type of data treatment (Lorentz correction versus no correction) is of lesser importance relative to a semiquantitative discussion of the characteristic change of the long spacing with strain. For the sample annealed at room temperature, a considerable reduction in long spacing from ca. 22 nm before necking to around 15 nm in the necked zone is observed. This behavior is assumed to be due to the fragmentation and recrystallization process, *i.e.*, the lamellar stacks established after stretching form by taking up the polymer chain segments freed from destabilized original crystalline lamellae that have been destroyed during deformation. The transitional strain locates between 0.6 and 0.9, which is larger than that obtained for unimodal sample.^[8] As the annealing temperature is elevated, the long spacing follows essentially a similar trend through the transitional strain zone where the long spacing decreases dramatically and then remains almost unchanged in the late stages of deformation.

Another important issue to be discussed is the main reason for the large discrepancy between the critical strains derived from bimodal and unimodal HDPE samples. It has been shown that the interaction between the state of the amorphous phase and the intrinsic stability of crystal blocks deter-

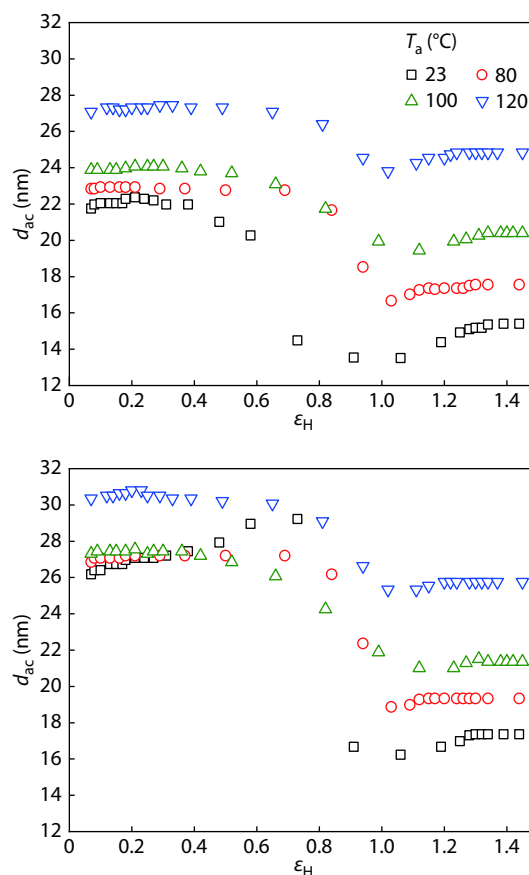


Fig. 3 Evolution of the long spacing d_{ac} along the stretching direction measured as a function of strain at different annealing temperatures. Data in the top plot of figure are obtained from Lorentz-corrected scattering profiles, and data in the bottom plot are derived from scattering curves without Lorentz correction.

mines the value of the critical strain at which the lamellar-to-fibrillar transition occurs.^[5] Since the equilibrium melting temperature can be chosen as a measure of the stability of crystal blocks,^[5] the mobility of the entangled amorphous network becomes a determining factor in the selected systems. The average thickness of lamellae and amorphous layers measured along the stretching direction can be calculated from the one-dimensional electron density correlation function $K(z)$ as follows:^[3]

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

where z is along the extensional direction. Multiplication of q^2 to $I(q)$ is performed in this expression due to the isotropic distribution of crystalline lamellae in the quenched samples before deformation.^[33] The resultant correlation functions for the two HDPE samples are presented in Fig. 4. The inset of Fig. 4 demonstrates how the amorphous layers thickness (d_a) and the long spacing (d_{ac}) are evaluated. Because the crystallinities as determined from differential scanning calorimetry measurements are 0.63 and 0.59 for bimodal and unimodal polyethylene samples, respectively, the small value in the

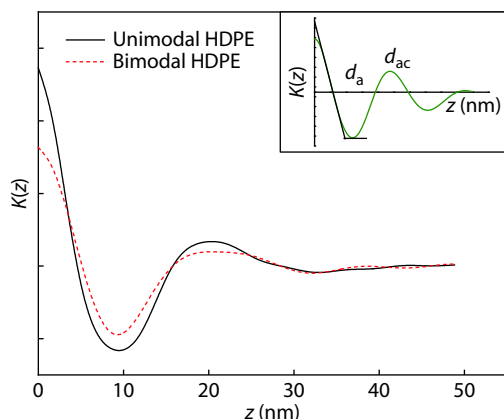


Fig. 4 One-dimensional correlation functions derived from the scattering intensity distributions for unimodal and bimodal HDPE samples before deformation. The long spacing (d_{ac}) and the average amorphous layers thickness (d_a) are obtained from the correlation function as illustrated in the inset of the figure.

correlation function can be safely assigned to the average thickness of amorphous phase. As it appears, the long spacing of bimodal material is *ca.* 20.7 nm, which is nearly equivalent to that of unimodal system (around 20.4 nm). The values of d_a for unimodal and bimodal samples are 5.5 and 7.4 nm, respectively. The much larger amorphous layer thickness of bimodal HDPE implies that the interlamellar amorphous phase is confined to a less extent, and therefore the bimodal system possesses a higher molecular mobility surrounding the crystallites when compared to the unimodal HDPE counterpart.

The molecular mobility of the interlamellar amorphous layers can be qualitatively characterized by solid state NMR^[34] and dielectric relaxation spectroscopy.^[35] We chose low-field ^1H -NMR T_2 relaxometry in this work, and Fig. 5 gives the variation of ^1H -NMR T_2 relaxation decay for bimodal and unimodal HDPE samples. As reported in previous literatures,^[36,37] T_2 relaxation decay of semicrystalline polymers can be deconvoluted into three components with Abragamian function for crystalline phase and two exponential functions for amorphous

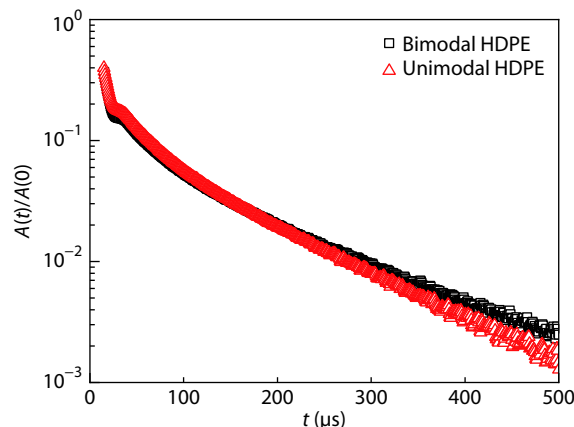


Fig. 5 Plots of normalized amplitude $A(t)/A(0)$ of FID as a function of time measured for bimodal and unimodal HDPE samples.

ous phase as follows:

$$A(t) = A(0)^{\text{short}} \exp\left[-\left(t/T_2^{\text{short}}\right)^2\right] \times [\sin(at)/at] + A(0)^{\text{int}} \exp[-t/T_2^{\text{int}}] + A(0)^{\text{long}} \exp[-t/T_2^{\text{long}}] \quad (4)$$

The value of a in the Abragamian function is set to be 0.155, and the three functions fit the T_2 relaxation decay very well for both samples as indicated in Fig. 6. The values of T_2^{short} , T_2^{int} , and T_2^{long} originating from crystalline lamellae, crystal-amorphous interface, and amorphous phase can be employed to compare distinction in the molecular mobility of the samples. The longer the T_2^{index} , the larger the frequency and/or the amplitude of molecular motions. It can be seen from Table 1 that the bimodal sample has a higher molecular mobility of chain segments in the amorphous phase as compared to its counterpart, which is in line with the SAXS data. This finding can be further proved by the magnitude of β -relaxation in DMA data.^[28,38] The physical origin of the mobile amorphous phase in bimodal sample can be attributed to the fact that preferential placement of SCB along the longer chains which cannot be incorporated into the crystallites during crystallization acts as an effective diluent of the entangle-

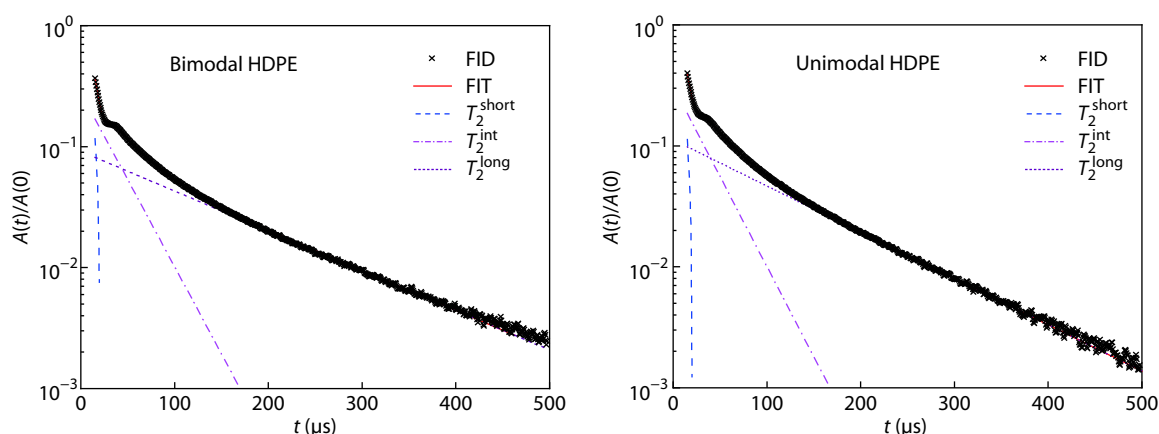


Fig. 6 ^1H -NMR T_2 relaxation decay measured for bimodal (left) and unimodal (right) HDPE samples. Abragamian and two exponential functions are used for the decay fit of both HDPE samples, and various types of dashed lines represent the respective relaxation components with short, intermediate, and long decay time.

Table 1 ^1H T_2 relaxation time for bimodal and unimodal HDPE samples.

Sample	T_2^{short} (μs)	T_2^{int} (μs)	T_2^{long} (μs)
Bimodal HDPE	15.778	30.157	132.258
Unimodal HDPE	15.662	29.153	113.618

ments compared with the molecular structure with the most SCB on the shorter chains in the distribution. Accordingly, the bimodal sample possesses a reduced modulus of the entangled amorphous network, and thus leading to a larger critical strain required to initiate the lamellar-to-fibrillar transition upon tensile stretching. This conclusion can be used to explain the observation that the bimodal HDPE exhibits an excellent slow crack growth resistance. The more mobile amorphous phase in the bimodal sample enhances the amount of material that can be sucked in by the craze fibrils and thus forms longer and less deformed craze fibrils. This morphological feature also implies a lower stress creep process. All these facts repress the propagation of the crack and prolong the time to failure.

CONCLUSIONS

In summary, our scanning synchrotron SAXS experiments support previous evidence for the deformation mechanism of semicrystalline polymers based on stress-induced fragmentation and recrystallization processes occurring at a critical strain imposed. Moreover, the effect of annealing on quenched samples deformed to different strains was investigated. It was found that the pronounced impact of annealing on the microstructure of a deformed bimodal HDPE cannot be observed at moderate strains where the fragmentation and recrystallization process was activated due to its lower extent of internal deformation. The critical strain associated with the onset of fibril formation is larger for bimodal HDPE ($\epsilon_H = 0.9$) than for unimodal one ($\epsilon_H = 0.4$), which can be understood as resulting from the higher mobility of the amorphous phase and the reduced modulus of the entangled amorphous network in bimodal sample. This enhanced mobility of the amorphous phase has its origin in primarily the preferential placement of SCB along the longer chains to function as an effective diluent of the entanglements as compared to the molecular structure with SCB preferentially located on the shorter chains.

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