

MAPPING THE DAMAGED ZONE AROUND THE CRACK TIP IN HIGH DENSITY POLYETHYLENE WITH SYNCHROTRON MICROFOCUS SMALL ANGLE X-RAY SCATTERING TECHNIQUE*

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Abstract The structural changes around a crack tip in a high density polyethylene were investigated by means of scanning synchrotron microfocus small-angle X-ray scattering technique. The scattering data confirm the process of craze structure development near a crack tip based on the evolution of voids. In addition, it was found that the main stress in the plastic zone near a crack tip exhibited a gradient distribution with respect to its strength and direction. The whole damaged area showed a strain distribution indicating a flow behavior toward the crack tip.

Keywords: High density polyethylene; Microfocus SAXS; Crack tip; Voids.

INTRODUCTION

High density polyethylene (HDPE) is the simplest polymer in terms of its chemical structure and is widely used for pipe applications such as water, gas and oil distribution. In real-life application, the fracture properties of HDPE limit its service life. Thus it is essential to investigate the fracture mechanism in HDPE pipe for providing possible routes for the improvement of the material.

Nowadays, it is assumed that the failure of HDPE pipe follows a mode of slow crack growth (SCG)^[1–5], which is caused by stress intensification in local areas induced by flaws in the polymeric products, such as catalyst residues, voids, *etc.* If one attempts to study the mechanism of SCG, it is important to fully understand the structural changes in the locally damaged area when a crack develops. Synchrotron microfocus small-angle X-ray scattering (SAXS) scanning provides such a microscopic spatial resolution.

To date, spatially resolved experiments using the SAXS technique have been conducted on several materials such as biological tissues like wood or bone^[6,7], poly(methyl methacrylate)-poly(methyl methacrylate) interfaces^[8], polystyrene^[9], poly(vinylidene fluoride) (PVDF)^[10] and polyamide 6 (PA6)^[11] amongst others. However, HDPE remains a special topic since the resultant scattering data of HDPE presented in the following sections reveal a different deformational behavior as compared to other semicrystalline polymers such as PA6

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and PVDF.

In the present work, we studied the microstructural evolution inside the damaged zone ahead of an induced crack on a bimodal HDPE which exhibits excellent crack-resistance. On the one hand the results confirmed the formation of a craze structure near a crack tip. On the other hand it was found that the plastic area showed a flow behavior toward the crack tip.

EXPERIMENTAL

Materials and Specimen Preparation

The HDPE sample used in this study was supplied by BASELL Polyolefine GmbH, Frankfurt, Germany. The molecular weights were $M_w = 3.7 \times 10^5$ and $M_n = 7.8 \times 10^3$. The material possesses a bimodal molar-mass distribution with linear short chains and long chains with short branches^[12]. Samples were prepared by compression-molding the pellets into sheets with a thickness of about 2 mm at 190°C for 5 min. Crystallization occurred during slowly cooling the plate in the press to room temperature. A rectangular strip of 20 mm × 70 mm was cut from the plate. Two opposite notches in the middle of the strip were introduced by a new blade, and filled subsequently by two triangle copper blocks with a vertex angle of 20°. The whitening phenomenon can be observed on both sides of the notches indicating the fact that cracks were introduced successfully.

Synchrotron SAXS Experiments

Synchrotron SAXS measurements were conducted at the synchrotron beamline BW4 at HASYLAB, DESY, Hamburg, Germany. The energy of the X-ray radiation was 8.979 keV, resulting in a wavelength of 0.13808 nm. The specimen with the two triangle copper blocks was mounted onto an x/y translational stage at the beamline. The scan was carried out using a step size of 50 μm in both directions, with a beam spot size of approximately 50 μm diameter, as shown in Fig. 1. The particular beamline setup enabled a resolvable range of $0.07 \text{ nm}^{-1} \leq q \leq 0.9 \text{ nm}^{-1}$, where q is scattering vector ($q = 4\pi\sin\theta/\lambda$, 2θ is scattering angle). SAXS patterns were collected at every step while scanning within 60 s. The SAXS data were calibrated for background scattering and normalized with respect to the primary beam intensity using Fit 2D software^[13].

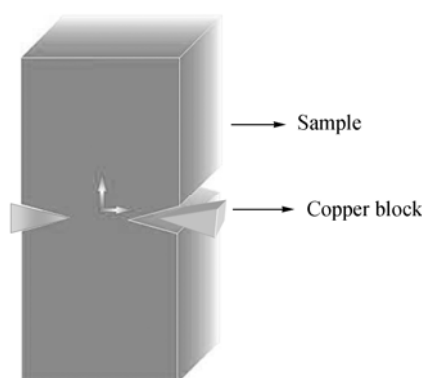


Fig. 1 Schematic illustration on sample preparation illustrating the way that two triangle copper blocks with a vertex angle of 20° were introduced into the sample to induce the formation of cracks.

RESULTS AND DISCUSSION

Figure 2 shows a composite image of the selected 2D-SAXS patterns recorded around the crack tip. There are in total nine rows of SAXS patterns given in Fig. 2, and the bottom one is defined as Row 1. The distances of every row away from Row 1 are indicated on the left of each row. Additionally, the undeformed SAXS pattern in Row 1 is defined as origin (0, 0), and the gaps between the selected patterns and (0, 0) point are marked below. In such a way, the map coordinates around the crack tip are established.

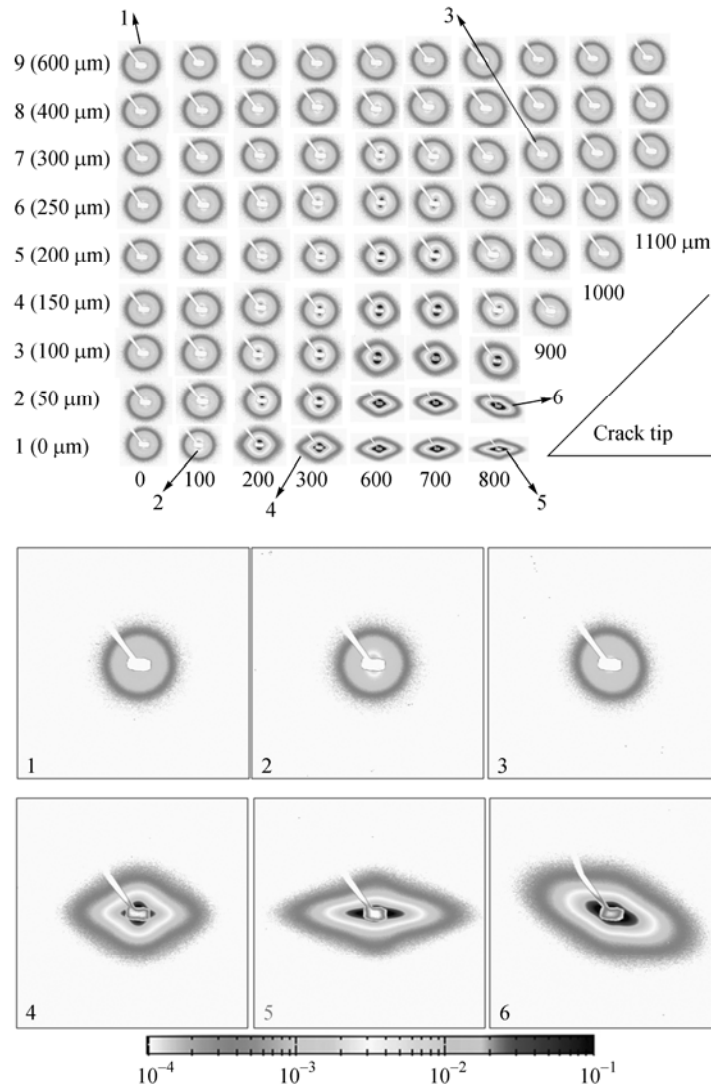


Fig. 2 Selected 2D-SAXS patterns for the plastic area around the crack tip

Each SAXS pattern corresponds to the morphology of the plastic zone under investigation at a beam size of 50 μm ; The patterns show isotropic scattering distributions (rings) in the undeformed area far away from the crack tip (1), isotropic and a second oriented signal along the vertical direction (2), oriented ellipses (3), cross streaks (4), and oriented streaks ahead of the crack tip (5, 6); Enlarged SAXS patterns for positions 1 to 6 are also presented at the bottom of the figure for the sake of clarity.

By examining the individual patterns, it was found that different deformational modes were realized at different positions. Therefore, the scanned area could be subdivided into several distinct domains defined by the shape of the scattering patterns: (i) the undeformed domain, far away from the crack tip, such as position 1; (ii) the outer plastic deformation area, for example positions 2 and 3; (iii) the most severely deformed zone close to the crack tip, as indicated by 4, 5 and 6. The patterns from position 1 to 6 are enlarged and characterized by the black and white as shown in the bottom of Fig. 2 for the sake of clarity.

Now take a closer look at these domains. In undeformed area (position 1), the SAXS patterns show isotropic scattering rings suggesting the random distribution of the lamellar stacks in HDPE. The Lorenz corrected^[14–16] one-dimensional scattering intensity distribution of the undeformed pattern $I(q)q^2$ versus q yields a value for the long spacing of 29 nm. The average thickness of the crystalline lamellae obtained by a rough

estimation according to the relationship, $d_c = d_{ac} \times \phi_c$, is 18 nm, where ϕ_c is the crystallinity obtained by differential scanning calorimetry with a value of 62%.

In the outer plastic deformation area (ii), an isotropic and a second oriented signal along the vertical direction appear in position 2, whereas position 3 exhibits oriented elliptical patterns. The features in position 2 indicate the intact crystalline lamellae as evidenced by the circular ring coupled with the occurrence of layer-like voids with their normal along the vertical. The elliptical pattern in position 3 is indicative of deformed lamellar stacks^[17]; according to the Bragg's law, the elongated long spacing corresponding to the minor axis of the elliptical pattern is 32 nm and the long spacing with respect to the relative major axis is 29 nm similar to that before deformation. One notices that the deformation mechanisms in position 2 and 3 are different. In the yielding process of crystalline polymers, there is always a competition between cavitation and plastic deformation of crystalline lamellae. If the stress level for cavitation is lower than the stress which can induce plastic deformation of crystalline lamellae, cavitation occurs first. On the contrary, if the crystals possess lower plastic resistance, they deform plastically before cavitation occurs. In the present experiment, the plastic deformation of crystalline lamellae requires high stress because of their large thickness with a value of 18 nm. Therefore it is not surprising that cavitation occurs before deformation of the lamellar stacks, just as the situation in position 2. However, a different deformational behavior appears in position 3 where the deformation of lamellar stacks is seen in the scattering data. This behavior is attributed to the "boundary effect" (at the edge of the crack tip), leading to less constraints imposed on the crystalline lamellae in the position 3 as compared to those in the middle of the sample. Consequently, the part of the sample in position 3 exhibits flow behavior free of voids when being stressed.

In the strongly deformed areas (positions 4, 5 and 6), it is notable that there are no circular scattering rings, but streaks with a high scattering intensity instead. At position 4, cross streaks appear, implying the occurrence of two populations of elongated voids including ones with their normal along the horizontal direction and another ones with their normal along the vertical direction. When considering areas close to the crack tip, such as position 5, only horizontal elliptical scattering patterns are observed. At position 6, the ellipse is tilted to an oblique angle of 20° with respect to the horizontal direction.

It is generally accepted that near a crack tip there is always a craze structure consisting of highly stretched fibrils and oriented voids in between. It is expected that voids play an important role during the formation of craze-like structures. Therefore, the question how the voids evolve near the crack tip in Row1 has evoked a great deal of interest. At first we tried to estimate the opening width of the voids using the Guinier approximation based upon the intensity distribution along the opening direction of the voids' scattering ($I = I_0 \exp(-q^2 R^2/3)$ ^[18–20]). However the resulting values are outside the range where the Guinier approximation applies ($qR < 1$). Therefore the evaluation of the opening width of the voids could not be performed. Subsequently, attention is paid to the evolution of the voids. At the origin (0, 0) where the sample is undeformed, there is only isotropic long spacing scattering. At the position (100, 0) one notices that a weak oriented streak along the vertical direction occurs indicative of the occurrence of a few elongated voids with their normal along the vertical direction. The number of voids and their size increase simultaneously when approaching the crack tip, as evidenced by the increased scattering intensity. A distinct feature with cross streaks shows up at position (300, 0) indicative of the occurrence of two populations of elongated voids consisting of one with their normal along the horizontal direction and the other one with their normal along the vertical direction. With decreasing distance away from the crack tip the scattering signal along the vertical direction gradually disappears. This behavior might be either due to the transition of the orientation of the voids with their normal from the vertical to the horizontal direction^[18, 21] or due to an opening size beyond the detection capability of the experimental setup — or both. It is evident that only elongated voids with their normal along the horizontal direction are present at the crack tip as identified by the scattering pattern at the position (800, 0). A model for the formation of craze-like structures is proposed in Fig. 3 on the basis of the evolution of voids in Row1, wherein the horizontal direction is the direction introduced by the notching of the sample. It is seen that at first only small voids with their normal perpendicular to the horizontal direction appear. Approaching to the notch tip, only

voids with their normal parallel with the horizontal direction occur. In between these two extremes, there is another population of voids with their normal along the horizontal direction occurring. This model is consistent with Capaccio's model of craze structure in polyethylene^[3].

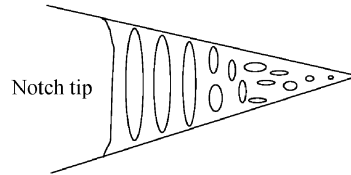


Fig. 3 Schematic illustration of the development of a craze-like structure

In addition, one notices that there is a distribution of strain directions at the crack tip — as derived from the scattering patterns of the tilting voids, such as in position 6, and oriented elliptical scattering patterns, for example in position 3, as shown in Fig. 2. As a consequence, the main strain directions around the crack tip can be determined from the scattering patterns. It is thus straightforward to obtain a distribution of stress around the crack tip. The result is given in the Fig. 4. Additionally, we use the thickness of the arrows to denote qualitatively the amplitude according to the degree of deformation occurring in the sample. If voids show up, the higher scattering intensity in 2D-SAXS patterns implies greater strain and thus the stress. In the other case, where the deformed long spacing scattering is observed, the shorter minor axes of the elliptical pattern indicate greater strain and stress.

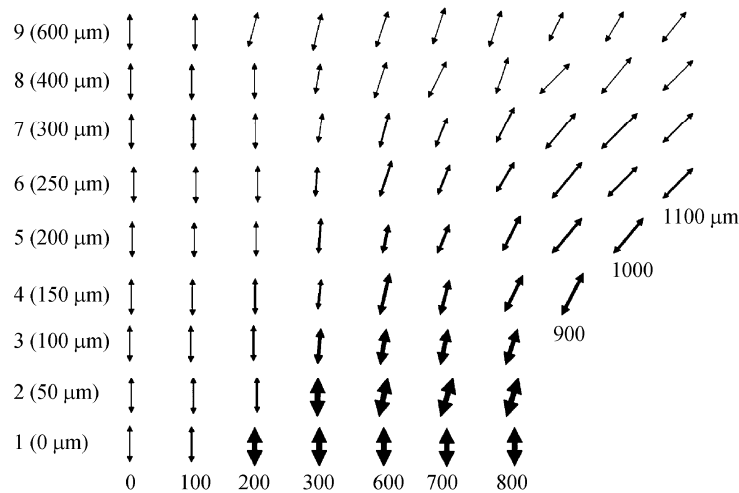


Fig. 4 Schematic diagram of strain distribution in the plastic zone around the crack tip

Combining the result in Fig. 4 with the 2D-SAXS patterns in Fig. 2, it is seen that closer to the crack tip larger strains occur implying also larger stresses in accordance with the mechanics analysis^[4]. Furthermore, such a strain distribution together with morphological observations^[2] implies a flow behavior of the material toward the crack tip.

CONCLUSIONS

The morphological evolution around the crack tip was characterized by microfocus SAXS scanning. The method provides a powerful tool with microscopic spatial resolution. From the scattering data, several results are obtained: (1) the development of a craze-like structure near the crack tip is proposed based on the observation of the evolution of voids; (2) there is a distribution of strain and thus the main stress, both with respect to its strength and its orientation, in the plastic zone near a crack tip.

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