

Initiation, Development and Stabilization of Cavities during Tensile Deformation of Semicrystalline Polymers

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Abstract By using polybutene-1 as a typical example, we illustrate the initiation, development and stabilization of cavities in the sample during tensile deformation. Samples with the same crystallinity, long spacing and crystalline lamellar thickness but very different sizes of spherulites were prepared *via* changing the melt history. Dimension of cavities during stretching the samples was determined by *in situ* ultra small angle X-ray scattering techniques. It turned out that the size of the cavities was bigger in the sample with larger spherulites than the one with smaller spherulites. The results show clear evidence of initiating cavities within crystalline phase at the grain-boundary of crystalline blocks, growing of cavities passing through parallel stacked lamellar crystals and amorphous layers and finally stabilized by tilted lamellae at both ends of the plate-like cavities within the spherulites.

Keywords Cavitation; Deformation; Polymer; Polybutene-1; Spherulite

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INTRODUCTION

Upon tensile stretching, semicrystalline polymers with isotropic spherulitic structure undergo complicated structural evolution^[1]. The main feature of such tensile stretching in semicrystalline polymers is a large extent plastic deformation. Over the years, there have been extensive studies dealing with the underlying mechanism of the plastic deformation in semicrystalline polymers^[2–5]. In short, slips of inter- and intra-lamellar nature^[6–9] and stress induced melting and recrystallization^[10–12] have been proposed to be responsible microscopic mechanism accomplishing macroscopic shape change during stretching. *Via* employing true stress-strain measurements and recovery property analysis, Strobl *et al.* pointed out that block slips within crystalline lamellae took place at small deformation followed by a stress induced disaggregation and recrystallization process at certain strain depending on the stability of the crystals and the state of amorphous network^[13–16].

Very often, stress whitening shows up during the tensile stretching of semicrystalline polymers, indicating cavitation phenomenon around the mechanical yield point^[17–21] or at the late stage of deformation^[22, 23]. Compared to plastic deformation, studies on cavitation are rare and less systematic. With respect to the cavitation at large strain, we were able to clarify its origin being stress induced breakage

of inter-fibrillar load bearing tie chains, which then resulted in disentanglement of the highly stretched inter-fibrillar network, thus creating cavities along stretching direction in between the fibrils/microfibrils^[22]. Contrary to this quite clear view of cavitation mechanism at large strain, the mechanism of cavitation around yield point during tensile deformation of semicrystalline polymers is still under heavy debate. Two models have been put forward in the literature. On one hand, it was proposed that the cavities appearing around yield point were initiated in the amorphous phase between adjacent crystalline lamellae^[17]. On the other hand, we proposed that the cavitation around yield point during stretching a semicrystalline polymer should be initiated first within those crystalline lamellae with their normal perpendicular to the stretching direction^[20, 21]. Both models found certain experimental evidences supporting some aspect of the view. However, neither model provided detailed information about the initiation, growth, and stabilization mechanism during tensile deformation.

In this work, we thus aim to establish detailed mechanism of cavity initiation, growth, and stabilization in semicrystalline polymers around yield point during tensile deformation. This is achieved *via* selecting polybutene-1 samples possessing similar crystallinity, long spacing and crystalline lamellar thickness but very different spherulitic sizes.

EXPERIMENTAL

Materials and Sample Preparation

The PB-1 was supplied by Basell Polyolefins with a trade

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name of PB0110M, whose melt flow rate (MFR) is 0.4 g/10min (190 °C/2.16 kg). In order to prepare samples with the same crystalline lamellar thickness but different spherulite sizes, two processes were employed. In one case, the pellets were compression molded at 180 °C into films of 0.5 mm and 50 µm in thicknesses. The film was held at 180 °C for 10 min to remove any thermal history and then transferred to a thermal bath preset at 80 °C. Solidification occurred during isothermal crystallization at this temperature for 5 h. In the second case, after being compression molded at 180 °C using the same procedure described above, the molten film was quenched into ice water to promote quick crystallization of the polymer into much smaller spherulites. The film was remolten at 135 °C for 10 min and then transferred to the same thermal bath preset at 80 °C and kept at this temperature for 5 h to allow completion of crystallization of the system. The isothermal crystallized samples were then aged at room temperature for 60 days to complete the polymorphic transformation from metastable form II to stable form I. The transition is known to be solid-solid form transition without disturbing the microscopic spherulitic structure^[24, 25]. The transition yields clear blocky substructure of crystalline lamellae due to the density difference between form II and I in PB-1^[26].

Measurements

Polarized optical microscopy (POM)

POM images of the samples with a thickness of 50 µm prepared according to different thermal histories were recorded using POM of Axio Imager A2m (Carl Zeiss, Germany). All optical micrographs presented were taken under cross-polarized light.

Differential scanning calorimetry (DSC)

The DSC measurements were carried out with a DSC1 of Mettler Toledo (Switzerland) under N₂ atmosphere. Samples (5–10 mg) were heated up from 25 °C to 180 °C at a rate of 10 K·min⁻¹ after crystallized under different conditions. Crystallinity values were obtained by considering an ideal value of heat of fusion for a 100% form I crystalline structure of PB-1 as 142 J·g⁻¹^[27]. Peak melting temperature and crystallinity values of the two samples used are included in Table 1.

Table 1 Basic physical properties of the samples used in experiments

Sample	ϕ_w (%)	T_m (°C)	d_{ac} (nm)	d_a (nm)	d_c (nm)
T_m180-T_c80	65.1	131.0	40.9	9.9	31.0
T_m135-T_c80	65.5	130.9	41.3	10.3	31.0

ϕ_w and T_m : obtained from DSC measurements. d_{ac} , d_a and d_c : obtained from SAXS measurements.

Small and ultra-small angle X-ray scattering (SAXS and USAXS)

SAXS and USAXS measurements were carried out in a modified Xeuss system of Xenocs SA, France. The system is equipped with a multilayer focused Cu K α X-ray source (GeniX^{3D} Cu ULD), generated at 50 kV and 0.6 mA. The wavelength of the X-ray radiation was 0.154 nm. The X-ray beam was then collimated with two pairs of Scatterless slits system located 2400 mm apart from each other. Scattering

data were recorded with the aid of a semiconductor detector (Pilatus 100K, DECTRIS, Swiss). In the case of measuring crystalline lamellar structure, the sample-to-detector distance was 2505 mm, and the effective range of the scattering vector q ($q = \frac{4\pi \sin \theta}{\lambda}$, where 2θ is the scattering angle and λ is the wavelength) was 0.048–0.963 nm⁻¹. Each SAXS pattern obtained in the center of the sample was collected within 1 h, background corrected and normalized using the standard procedure. Beside one-dimensional scattering intensity distributions integrated from 2D SAXS patterns, the technique of one-dimensional electron density correlation function analysis has also been used to give detailed structural information of the systems, such as long period (d_{ac}), crystalline lamellar thickness (d_c) and amorphous thickness (d_a). *In situ* USAXS measurements during tensile deformation of the samples were carried out at a sample-to-detector distance of 6558 mm which yielded an effect q range of 0.017 nm⁻¹ to 0.246 nm⁻¹. USAXS patterns were collected after the samples were stretched horizontally to different strains within 300 s and were treated as described above. True strains were determined using photographs of the deformed samples with respect to the undeformed ones. The Hencky measure of strain ε_H is used as the true strain, which is defined as

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

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

RESULTS AND DISCUSSION

Microstructures of the Samples

Before discussing cavitation behavior, we present characteristic structural features of the prepared samples. Table 1 collects some basic physical properties of the samples used in the experiments. Clearly, the samples prepared following two different thermal histories show nearly identical physical properties such as crystallinity, melting point, crystalline lamellar thickness, amorphous layer thickness, and long spacing due to the same isothermal crystallization temperature used.

As the samples were molten at different temperatures before isothermal crystallization, one could expect different spherulite sizes in the final products because the low melt temperature of 135 °C was only few degrees higher than the melting temperature of the materials that may not be high enough to produce a homogenous melt. Indeed, POM results of the two samples revealed such cases. In Fig. 1, the sample crystallized from the melt at 135 °C shows much smaller spherulites than the one from the melt at 180 °C. Clearly, we have successfully prepared two samples with identical microstructures with respect to lamellar thickness, amorphous layer thickness and crystallinity but very different in size of spherulites.

USAXS Results

Selected USAXS patterns taken during the tensile deformation of the samples at different strain values are

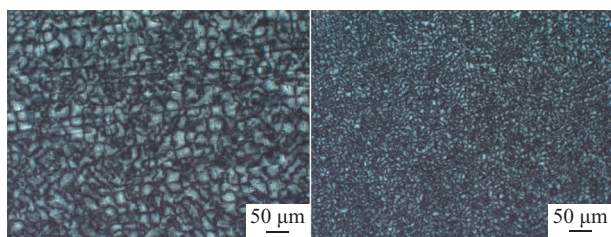


Fig. 1 Polarized optical microscopy images of the samples after isothermal crystallization at 80 °C from the melt at 180 (left) and 135 °C (right). Scale bar: 50 μm.

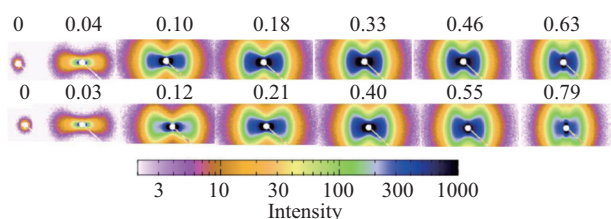


Fig. 2 USAXS patterns of the samples drawn at room temperature. Top: sample isothermally crystallized at 80 °C from a melt at 180 °C; Bottom: sample isothermally crystallized at 80 °C from a melt of 135 °C. The stretching direction is horizontal. Numbers on top of the patterns denote strain values of the sample at which the USAXS patterns were recorded.

presented in Fig. 2. Undeformed samples showed only very weak scattering intensity homogeneously distributed around the beam stop. Such weak scattering might be generated by large scale inhomogeneities in the samples. Scattering intensity due to stacked lamellar crystalline structure was not observed in the USAXS measurements because of the long sample-to-detector distance that weakens the scattering signal at such q range significantly. Upon stretching strong scattering signals started to appear along stretching direction at very small q range at small deformation, indicating the generation of large scale structures of different electron density with respect to the polymer matrix, *i.e.* the occurrence of cavitation. The shape of the scattering pattern at small deformation represents scattering of plate-like cavities with normal parallel to the stretching direction. Before discussing characteristic size of the cavities, we plot in Fig. 3 the integrated scattering intensity over the whole

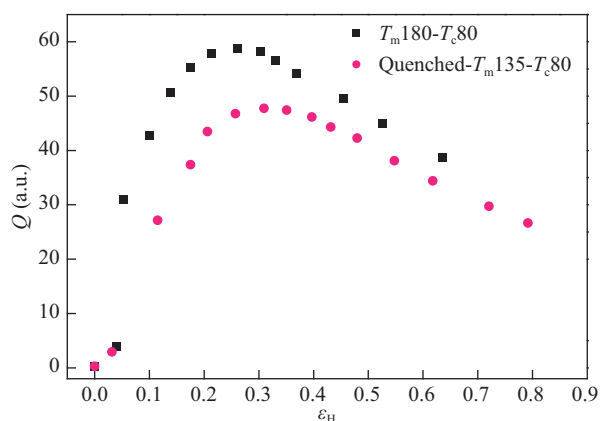


Fig. 3 Integrated scattering intensity as a measure of the scattering power of the systems at different deformations

scattering pattern as a function of strain. This integrated scattering intensity represents volume fraction of the cavities in the samples during stretching. Clearly, the scattering intensity increased at the small to moderate deformation followed by a decrease at the larger strains. The increase in the integrated scattering intensity in the first step clearly demonstrated an increase in the overall volume fraction of the cavities during stretching. The decrease of the intensity after moderate strain came from two factors. Firstly, there was a continuous reduction of the sample thickness so that the scattering volume decreased during stretching. Secondly, some of the plate-like cavities tilted to different directions with respect to the stretching direction thereby shrank in size.

Quantitative discussion of the characteristic features of the cavities can be performed *via* analyzing scattering intensity distribution along stretching direction. Fig. 4 presents such data. Here, we corrected the scattering intensity $I(q)$ by multiplying $I(q)$ with q^2 for the reason discussed below. Theoretically, the scattering intensity distribution of plate-like cavities^[28] reads:

$$I(q) = A \frac{2\pi}{q^2} (\Delta\rho)^2 d^2 \left(\frac{\sin qd/2}{qd/2} \right)^2 \quad (2)$$

where A is the lateral cross section of the plate, $\Delta\rho$ is the electron density difference between the cavities and its surrounding phase, and d is the thickness of the plate. It is evident from the above Eq. (2) that a plot of $I(q)q^2$ versus q yields maxima at $q = 0$ and at $q = [(2n + 1)/d]\pi$ (where $n = 1, 2, 3, \dots$). In Fig. 4, the intensity maximum shifted to smaller q values with the increase of the strain, indicating a continuous opening of the plate-like cavities during stretching. The volume fraction of cavities decreased at large deformation, which was evidenced by the decrease of the scattering intensity. The thickness of cavities along the stretching

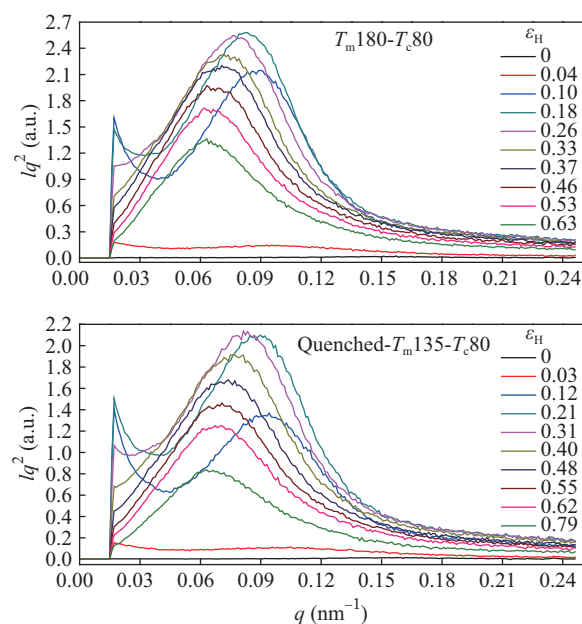


Fig. 4 One dimensional USAXS intensity distributions along stretching direction of samples stretched to different strains. The scattering intensity values were corrected by multiplying with q^2 as described in the text.

direction at different strains could be calculated using the maximum scattering intensity position $q_{\max}$ according to Eq. (3)

$$d = \frac{3\pi}{q_{\max}} \quad (3)$$

In the top of Fig. 5, the thus obtained d values are shown. Two characteristic features can be read from the strain dependency of the opening size of the cavities. First of all, both samples with spherulites of different sizes showed the same trend of increasing in opening of the cavities during tensile deformation. Secondly, the sample with bigger spherulites gave obviously larger opening of the cavities at the same strain than the one with smaller spherulites. It must be emphasized that both samples possess the same crystalline lamellar thickness and crystallinity. The sample with bigger spherulites has even slightly smaller amorphous layer thickness than the one with smaller spherulites. The results shown in the top of Fig. 5 thus strongly suggest a correlation between the cavitation and spherulites structure. Before going one step further to discuss possible structural models to clarify the cavitation process in semicrystalline polymers during tensile deformation, we investigated the relative change in the opening size of the cavities during stretching by plotting the strain of such opening as a function of macroscopic strain in the bottom part of Fig. 5. Clearly, the change of the opening of the cavities with macroscopic

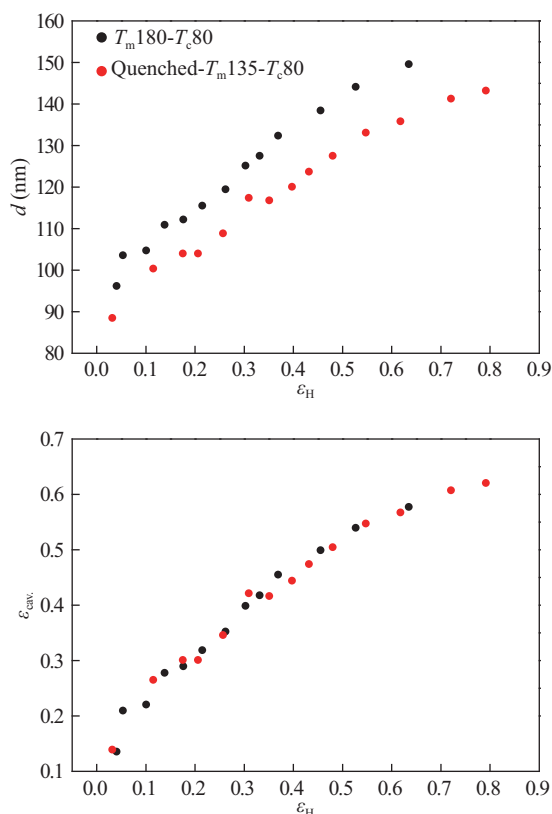


Fig. 5 Opening size of the cavities in samples having different thermal history (top) and strain of the cavities along drawing direction (bottom) as a function of macroscopic strain of the samples

deformation in both samples showed similar dependency. This result indicates that after their initiation in the samples the opening of the plate-like cavities was rather in a controlled manner depending on the macroscopic strain only.

Cavitation Model

To account for above mentioned experimental findings, especially the spherulitic size dependence of the cavity opening dimension, we propose in Fig. 6 a structural model for cavitation process in semicrystalline polymers during tensile deformation.

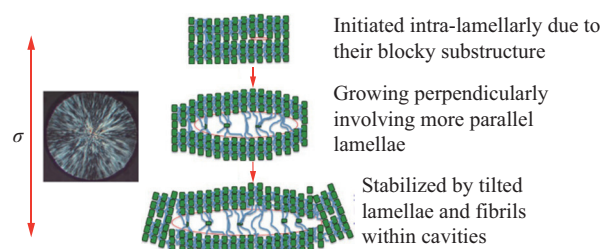


Fig. 6 Structural model of cavitation process in semicrystalline polymers during stretching

Upon stretching, nucleation of cavities takes place at the grain-boundaries of crystalline blocks within stacked lamellae with normal perpendicular to the stretching direction. In isotropic spherulitic samples, there is always a portion of the crystalline lamellae within the spherulites possessing such orientation at the polar region of the spherulites. Locally, the lamellae are parallel stacked with amorphous entangled network in between. It is thus not surprising that such cavities grow rapidly passing through several parallel crystalline lamellae forming low density spaces with irregularly placed amorphous chain aggregations and/or fragmented crystalline blocks filled. An entirely empty cavity cannot be easily formed because those amorphous entangled chains cannot be easily broken during the cavitation process in the manner discussed above. However, the growth of the cavities is limited by tilted lamellae in the spherulites when the cavities span away from the polar region of the spherulites. Moreover, this mechanism implies a spherulitic size dependence of the cavity size which was perfectly observed in this work. Clearly, isotropic distribution of the lamellae in the spherulites together with fibrils formed by the irregular aggregated amorphous chains and fragmented crystalline blocks provides a natural stabilization mechanism of the cavities during tensile deformation of a semicrystalline polymer.

In above mentioned cavitation model, we did not consider possibility of initiation of cavities at the boundaries of spherulites for two reasons. First of all, the sample used in this investigation possesses high crystallinity forming effectively highly interlocked crystalline skeleton with spherulites growth within each other at the grain boundary regions. In such case, macroscopic deformation can be effectively transformed into microscopic deformation at spherulitic level. Secondly, the observed characteristic USAXS intensity distribution in Figs. 2 and 4 showing high

orientation and rather small polydispersity of the cavity thickness indicates that cavities cannot be attributed to the failure of spherulitic boundaries as they are randomly distributed in orientation.

CONCLUSIONS

In conclusion, by using two polybutene-1 samples of the same crystallinity, lamellar thickness, and long spacing but of very different spherulitic size, we investigated the cavity size as a function of structural parameters of the samples. The results led us to propose a model counting basic features of cavitation in semicrystalline polymers during tensile deformation. It turns out that cavities are primarily initiated at the crystalline block grain-boundaries of lamellae with normal perpendicular to the stretching direction which then grow rapidly passing through parallel stacked lamellae forming low density spaces with fibrils linking both surfaces of the plate-like cavities. Eventually, the growth of the cavities is limited by the tilted lamellae when they span away from the polar region of the spherulites. Experimentally observed larger cavities in sample possessing larger spherulites strongly support the applicability of our model in explaining cavitation in semicrystalline polymers around yield point during tensile deformation.

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