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Plastic deformation and cavitation in semicrystalline polymers studied by X-ray methods*)

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Abstract: This paper is a literature review presenting the relation between the cavitation phenomenon and plastic deformation of polymers. The cavitation phenomenon, meaning the formation of numerous micro and nano size voids (cavities), is observed in many semicrystalline polymers deformed at temperatures above the glass transition. Cavitation occurs when crystals in the polymer are stronger than the amorphous phase. This means that the phenomenon may be controlled by applying an appropriate crystallization procedure. Thicker and less defected crystals usually grow when the time for crystallization is longer and it is easier to deform the amorphous phase with voiding. The cavitation process also depends on the deformation conditions. Faster stretching at lower temperatures is favorable for deformation with voiding. The cavities are observed only during tensile deformation as local triaxial straining is necessary for cavitation. Usually, cavities are formed when the strain is close to the yield point and voids have a nanometer size. Larger, micrometer cavities dominate at higher strains, near the end of the deformation process.

Keywords: cavitation, plastic deformation, polyolefins, semicrystalline polymers.

Odkształcenie plastyczne i zjawisko kawitacji w polimerach częściowo krystalicznych badanych metodami rentgenowskimi

Streszczenie: Artykuł stanowi przegląd literatury dotyczącej zależności pomiędzy zjawiskiem kawitacji a odkształceniem plastycznym polimerów. Zjawisko kawitacji, tzn. tworzenie się licznych nano- i mikrometrowych dziur (kawitacji) można obserwować w wielu polimerach częściowo krystalicznych,

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odkształcanych w temperaturze wyższej niż temperatura zeszklenia. Kawitacje pojawiają się wówczas, gdy wytrzymałość kryształów jest większa niż wytrzymałość fazy amorficznej. Oznacza to, że można wpływać na przebieg tego zjawiska w wyniku doboru odpowiednich warunków krystalizacji. Dłuższy czas krystalizacji sprzyja wzrostowi w polimerze grubszych i mniej zdefektowanych lameli, co oznacza, że podczas deformacji łatwiej się tworzą dziury w fazie amorficznej. Proces kawitacji zależy również od warunków odkształcania. Szybsza deformacja, prowadzona w niższej temperaturze, sprzyja powstawaniu dziur. Ponieważ lokalne trójosiowe rozciąganie jest niezbędnym warunkiem powstania kawitacji, to są one obserwowane tylko podczas rozciągania. Zazwyczaj kawitacje powstają już w warunkach odkształceń bliskich granicy plastyczności i mają wtedy nanometrowe wymiary. Większe, mikrometrowe dziury pojawiają się przy dużych odkształceniach, blisko końca deformacji.

Słowa kluczowe: kawitacje, odkształcenie plastyczne, poliolefiny, polimery częściowo krystaliczne.

The cavitation phenomenon, meaning the formation of numerous voids (cavities) inside a volume of solid polymer, is observed in many semicrystalline polymers tensely deformed at temperatures above their glass transition. Recent studies showed that the phenomenon influences the plastic deformation of polymers and their mechanical properties [1—3]. Semicrystalline polymers have a complicated internal structure, composed of crystalline elements — lamellae — and an amorphous phase, often forming a higher level spherulitic structure [4, 5]. During deformation under tension or compression, the spherulitic structure is transformed into a fibrillar structure. The deformation of semicrystalline polymers has been the topic of many studies for the past 50 years and a general description of the micro processes occurring in polymer during deformation has been formulated.

The majority of experiments dedicated to understanding deformation are performed under uniaxial tension so it is easier to present the steps of this process in the following general example. When the external force is applied to a polymer, elastic deformation occurs first. This phase of deformation is quickly finished and the plastic deformation is initiated with a further increase in the applied force. At the beginning, plastic deformation is localized to the amorphous component of the polymer because the crystalline elements are stiffer than the amorphous phase. This deformation is accompanied by observable events such as the separation of lamellae, as well as the intralamellar shearing or rotation of lamellar stacks. The possibilities of deformation in the amorphous phase are quickly exhausted before reaching the macroscopic yield point. The initiation of the plastic deformation of crystals represents the only further opportunity for deformation of the polymer without breaking its structure. There are three possible deformation mechanisms: a martensitic transition into another crystallographic form, twinning or chain slips. Only the last mechanism is really significant because it acts on a large scale in many semicrystalline polymers. The deformation of lamellae by chain slips is possible only in those crystallographic planes that contain macromolecular chains. There are two variants of slips: fine, continuously modifying the lamellar structure, and coarse, leading to the formation of blocks. The main reason for chain slips is the presence of screw dislocations moving through the crystals under the action of shear forces [6]. New dislocations are generated with an increase of deformation so the process of crystal deformation is continued and fragmentation of lamellae is observed. The mechanisms of plastic deformation of crystals appear to be independent of the mode of deformation: tensile or compression. However, the disentanglement of macromolecules present in the amorphous phase may additionally happen in tensile deformation. Often processes of plastic deformation are initiated first in a small volume of sample where the effective cross-area is smallest. The localization of plastic deformation is macroscopically visible as a neck formation. During stretching, the neck propagates through the polymer specimen and a highly deformed material of initial neck is almost unchanged for larger strains because the so-called natural draw ratio is reached. At the end of the deformation, when the easiest possibilities of transformation are exhausted, a strain hardening is observed, leading to the final break.

The plastic deformation of polymers may be realized in several different ways. In amorphous polymers below the glass transition temperature, shear yielding may happen and shear bands, resulting from the contribution of many micro scale shearing processes, can be observed. The alternative process is the formation of crazes, which are elongated structures of voids containing oriented microfibrils [7, 8]. Due to the presence of microfibrils, the crazes are able to transfer stresses so may actively participate in deformation. In semicrystalline polymers, crazing is not restricted to low temperatures and it may also occur at temperatures above the glass transition. The third possibility of deformation is by formation of voids. If the voids (cavities) are small they locally influence the process of deformation, but because their expansion (enlargement) is slow they do not quickly convert to cracks leading to the breaking of the material. The voids in semicrystalline homopolymers deformed above their glass transition temperature (which gives some deformation possibilities for amorphous phases) are small: micro and nanometer size.

This paper presents the state of knowledge about cavitation phenomenon and the relationship between cavitation and tensile deformation of semicrystalline polymers. In the following sections are discussed: the concurrency between cavitation and deformation of crystals, development of cavities with deformation, morphological and deformational factors supporting cavitation and the influence of cavitation on further deformation.

METHODS OF VOID DETECTION

Before the analysis of cavitation processes, the methods of void detection requires a short presentation. Two main groups of methods are available: microscopic and scattering [3]. Microscopic methods include: polarizing-light, scanning electron microscopy (SEM) and atomic force microscopy, detecting voids with sizes in the micrometer to nanometer range. The weakness of microscopy is that it is usually applied in studies of samples after the mechanical test, when the strain relaxation has taken place. The voids present in a polymer sample scatter electromagnetic radiation. It is widely accepted that micrometer size voids are responsible for the scattering of light, which is visible as a whitening of the material. Nanometer size voids scatter X-ray radiation [9]. Because the nano size voids are more numerous than micro size voids and are distributed between lamellae, then they play a more important role on the beginning of plastic deformation. This is a reason why studies of cavitation are focused on nano voids, detected by small angle X-ray scattering (SAXS). Unfortunately, even with modern equipment, the time for acquiring SAXS data is long. The solution is to use a synchrotron radiation source. This reduces the time of SAXS pattern registration to 10—30 s and provides an opportunity to observe the cavitation process in-situ during tensile deformation [10].

Cavitation and crazing are processes that increase the local volume. The measurements of volume give supporting information about the occurrence of cavitation and its range. Usually, the local volume is calculated from sample dimensions in three directions, determined by video extensometry [11]. Sometimes, voiding (cavitation) is characterized with the help of other techniques like densitometry or acoustic detection. The latest approach for the detection of cavities and for examining morphological changes is X-ray microtomography [12].

CAVITATION PROCESS

Microscope and X-ray studies showed that cavitation is often, but not always, observed in semicrystalline polymers: polyethylene (PE-HD), polypropylene (PP), poly(vinylidene fluoride) (PVDF), poly(methylene oxide) (POM), poly-1-butene, poly(ε-caprolactone), poly(ethylene terephthalate) (PET), polylactic acid (PLA). The phenomenon usually begins at yield, i.e. occurs at the same range of strains as the plastic deformation of crystals. It is not trivial to determine what happens first: cavitation or crystal deformation. With an increase of applied force, the local stress in the polymer increases too. There are two values of stress at which processes in the micro scale are initiated: shear stress activating the plastic deformation of crystals and stress of breaking the amorphous phase leading to cavitation (cavitational stress). Which process is initiated first with increased applied force — cavitation or crystal deformation — depends on which of the above stresses has a lower value. These characteristic stresses depend on the microstructure of the respective phase that in turn results from the previous solidification process.

There are no direct methods for the measurement of amorphous phase strength. However, the stress at break may be estimated from studies of polymer melt. This assumes that the amorphous phase is similar to the frozen melt from which it was formed, i.e. that the arrangement of molecules in the amorphous phase, especially chain entanglements and tie molecules, resembles the melt state. There is a body of literature about the strength of the melt of different polymers based on the observations of spherulitic crystallization, during which negative pressure is built up in the melt, leading to cavitation. The negative pressure required for breaking the melt structure was found to be -3.5 to -10 MPa for high density polyethylene, -13 to -19 MPa for polypropylene and -10 to -18 MPa for poly(methylene oxide) [13, 14]. Typical macroscopic stresses for these polymers at yield are equal to 25, 34 and 69 MPa, respectively when tested under tension and 32, 50, 95 MPa, respectively when tested under plane strain compression [15]. In tensile deformation the pressure, p, is theoretically equal to $p = -1/3 \cdot \sigma$, where σ is the tensile stress [16]. However, the polymer is locally non uniform, which means that the value of the pressure should be modified by a stress intensity factor, K. It is reasonable to assume that $K = 2—3$. When the stress at yield is estimated from calculations, it is easy to show that the conditions for cavitation are fulfilled for PE-HD, PP and POM [15]. The cavitation in these polymers was experimentally observed near the yield points.

It is accepted that deformation of crystals is initiated when the Coulomb criterion is fulfilled [17]. Shear resistance, τ, is dependent on the normal stress, σ_n, acting across the glide plane, according to the relation:

$$\tau = \tau_o - K_s \sigma_n \tag{1}$$

where: τ_o — the plastic resistance of crystal for simple shear, K_s — the stress sensitivity factor, for many polymers equal to 0.1. As the easiest slips are initiated when crystals are oriented at 45° in relation to force direction, and yield is a moment of massive deformation of crystals, the equation (1) has the modified form at yield of:

$$\sigma_y = 2\tau_o/(1 - K_s) \tag{2}$$

where: σ_y — the macroscopic yield stress.

It was found that the easiest slip for polypropylene, acting in the (010)[001] direction, is initiated at τ_o = 22—25 MPa [18, 19]. This means that τ_o is higher, when comparing absolute values, than the stress of cavitation (-13 to -19 MPa). In polyethylene crystals, the easiest chain slips are initiated at τ_o = 10 MPa in the direction (100)[001] and at $\tau_o = 15$ MPa in the direction (010)[001] [20]. As the yield stress is related to the resistance of the crystal, it is often taken as a measure of crystal strength. This strength increases with a reduction of the number of defects present in the lamellar crystal. The number of defects in the polymer is high, at the level of 10^{12} up to 10^{16} m^{-2} [21, 22], but may be limited by an appropriate selection of crystallization conditions.

Humbert et al. [23] proposed mathematical formulas describing the relationship between shear stress, cavitation stress and lamellar thickness. They found that the stress of crystal shear is related to crystal thickness, L_c, by the equation:

$$\sigma_{shear} \sim L_c^{0.7} \tag{3}$$

The stress of cavitation depends on L_c by the relation:

$$\sigma_{cav} \sim E + \alpha(1/L_c^{0.5}) \tag{4}$$

where E and α are constants. The relations $\sigma_{shear} = f(L_c)$ and $\sigma_{cav} = f(L_c)$ determine the range of crystal thicknesses for which polymers cavitate. For polyethylene, this range begins at 19 nm. When $\sigma_{shear} < \sigma_{cav}$, but the difference is small, the cavitation might be initiated after the plastic deformation of crystals, during neck formation, at engineering strains of 30—100 %.

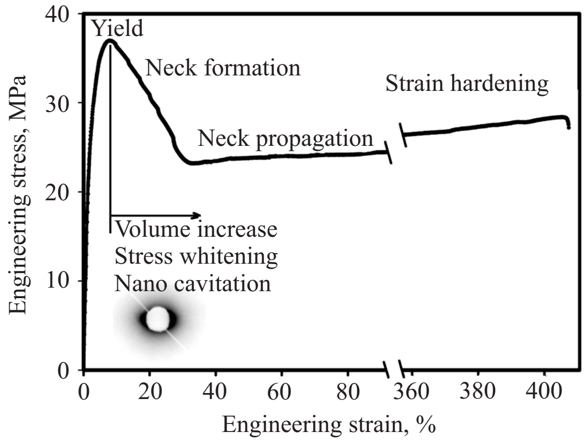

Fig. 1. The phenomena observed in cavitating polymer showed on example of tensely deformed polypropylene; SAXS pattern with intensive scattering on cavities is presented as insertion

Figure 1 presents a typical sequence of events in a tensely deformed cavitating polymer. The X-ray scattering from nano voids and whitening of polymer are observed at the same moment of time when the stress reaches maximum at yield. The yield is also the starting point for a rapid increase of volume. The SAXS pattern registered at yield is elongated in the deformation direction, which means that voids are elongated perpendicularly to the deformation direction and most probably are ellipsoidal in shape. At this moment, at relatively low strains, the separation of lamellae happens in the equatorial parts of spherulites. It is very probable that the source of most of the scattering are voids formed in the amorphous layers between separated lamellae. SEM observations performed for the samples strained beyond the yield show that only a limited number of micrometer-sized voids are visible under medium strains but nano sized voids are much more numerous. The relation between SAX scattering intensity (I) and volume occupied by nano cavities is described by the equation:

$$I(s) = I_o(\rho_1 - \rho_2)^2 v^2 \exp(-4\pi^2 s^2 R^2/3) \tag{5}$$

According to this equation the scattering intensity, I, depends on the initial intensity I_o, difference of electron densities ρ_1-ρ_2, volume of scattering objects v, scattering vector s, and gyration radius of scattering objects R. In non-deformed polymers, electron densities represent the crystalline and amorphous phases. However, in the cavitating polymer, ρ_1-ρ_2 is the difference between the mean electron density of the polymer as whole and the electron density of voids. The gyration radius is often the base for the calculation of void size. However, for non-circular objects additional assumptions are necessary.

When strains are higher than the yield strain, plastic deformation is localized to a small part of the specimen and the formation of a macroscopic neck occurs. The local strain in the neck is much higher than the engineering strain. During formation of the neck, the intensity of scattering usually increases and also the local volume is much higher than at yield. It is observed that the existing nano voids enlarge with deformation and some of them may fall outside the detection range of SAXS. Some new nano voids can be formed at this step of deformation.

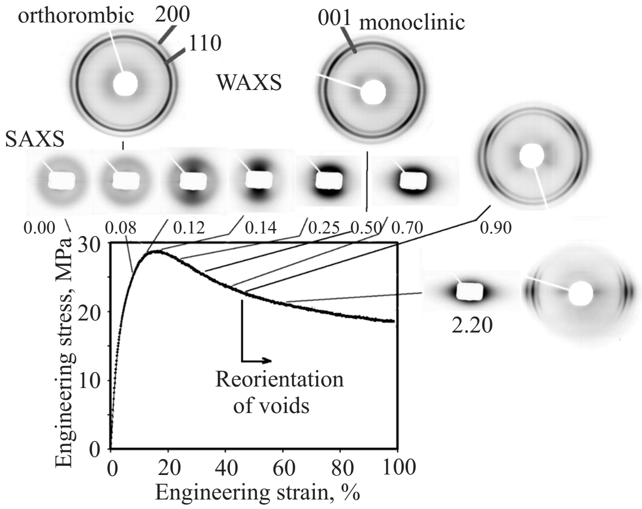

Fig. 2. The stress-strain dependence, SAXS and WAXS patterns for PE-HD sample crystallized in iced water and annealed for 6 h at 120 °C; the number means local strains: (L-L_o)/L_o; deformation direction on patterns is vertical; the transformation of orthorhombic form into monoclinic is visible (WAXS) and also reorientation of voids (SAXS); the results published in [26] were used for the preparation of this figure

Their location is not restricted to the equatorial parts of spherulites. However, the diagonal, shear areas are still prohibited for voiding [24]. The polymer structure transforms inside the neck with the fragmentation of lamellae, building of fibrillar structures from lamellar blocks, and partial disentanglement of macromolecules in the amorphous phase. The transformation of the lamellar structure has an influence on voids present near crystals, which as the softer elements of the structure are oriented in the deformation direction by the movement of lamellar blocks. This is known from a comparison of WAXS (Wide-angle X-ray scattering) and SAXS patterns (Fig. 2).

When the natural draw ratio is reached [25], the polymer is highly oriented and the neck propagates into another part of specimen. Only a small increase of stress and local strain happens in the initial neck area and new cavities are not formed. The macro size voids are clearly observable at this step of deformation when examined by scanning electron microscopy or microtomography.

At the end of deformation, i.e. in the strain hardening phase, some additional cavitation and volume increase are usually observed. Voids of nano and micrometer size are highly elongated in the deformation direction at large strains. Often rows of micro size voids are formed between fibrils.

FACTORS SUPPORTING AND LIMITING CAVITATION

The ability of materials to cavitate depends on morphology and deformation conditions. As polymers are usually solidified from melts, then the cooling conditions determines the final structure of a polymer. A fast cooling rate results in low levels of crystallinity and thin crystals with many defects. When the cooling rate is slower, and the time for crystallization is longer, then the degree of crystallinity is higher, the growing lamellar crystals are thick and the number of dislocations is reduced. Many observations show that cavitation occurs in structures prepared by slow cooling. Similarly, if the crystallization process is isothermal, the conditions for cavitation depend on the time of crystallization as determined by temperature. Studies of polyethylene and polypropylene showed that the growth of thicker crystals at higher crystallization temperatures is accompanied by an increase of crystallinity and decreased number of tie molecules present in the amorphous phase. These changes support a more intensive cavitation process.

The perfectness of crystals and crystallinity may be improved by annealing in the solid state. This was tested on an example of high density polyethylene, which after rapid solidification from melt had 20 nm thick crystals and a 66 % level of crystallinity. The same polymer, after 3 h of annealing at a temperature of 120 °C, had crystals with a thickness of 27 nm and crystallinity level of 78 %. Annealing completely changed the ability of the polymer to form cavities during deformation. The yield stress of PE-HD increased from 21 to 29 MPa and the polymer intensively cavitated at yield as detected by SAXS. The local volume in non-annealed PE-HD was constant to a local strain of 3.0. However, in the annealed specimen it showed a continuous increase since yield until the local strain of 4.0. A 30 % increase of volume confirmed the presence of intensive cavitation [26].

In some polymers crystals of different crystallographic forms may grow, depending on the crystallization conditions. A well-known example is polypropylene, which usually crystallizes in the monoclinic α form. However, when a nucleant is added to the polymer, the lamellae and spherulites of β form may dominate. The α spherulites have a cross-hatched structure, which means the presence of both radial and tangential lamellae. The β form spherulites have a pure radial lamellar architecture with a less restricted amorphous phase, which makes cavitation easier. Na et al. [27] compared the cavitation in the polypropylene α and γ forms and found that the range of cavitation is smaller in the γ sample because the

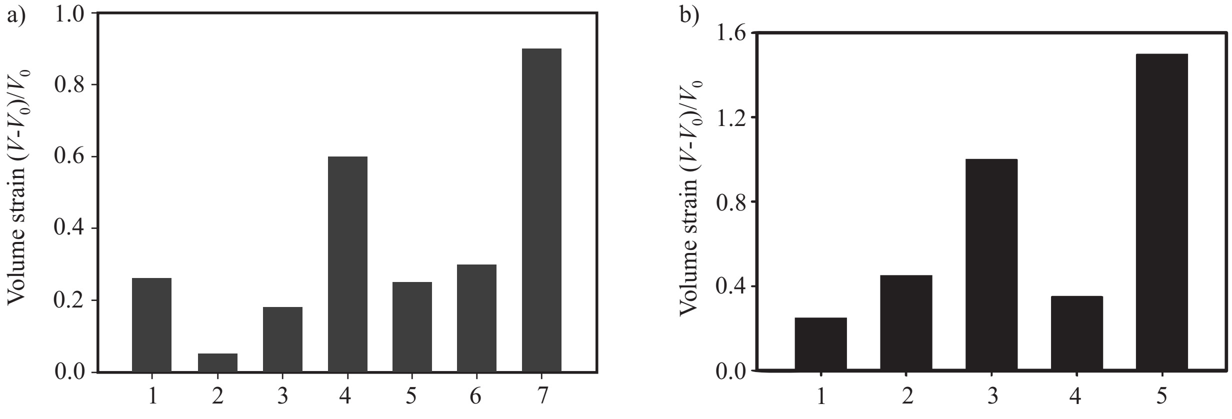

Fig. 3. Volume strain determined for different samples deformed to engineering strain of 70 %: a) PE-HD Lupolen 6021D: 1 — injection molded, 2 — cooled in iced water, 3 — cooled in iced water and annealed, 4 — cooled in air, 5 — crystallized non isothermally with cooling rate 10 °C/min, 6 — crystallized isothermally at 122 °C, 7 — crystallized isothermally at 125 °C; b) PP Novolen 1100: 1 — injected, $M_w = 4.0 \cdot 10^5$, 2 — injected, $M_w = 2.5 \cdot 10^5$, 3 — compression molded, cooled in air; PP Malen P F401: 4 — α form, 5 — β form; according to literature data [24, 26, 30, 31]

fraction of tie molecules is higher. Polyethylene is an example of a polymer in which martensitic transitions occurs (see Fig. 2). Butler et al. [28] proposed that such transformation is a reason of cavitation. However, more recent studies (e.g. Schneider et al. [29]) did not confirm this supposition.

Other structures may grow in the polymer under special conditions of crystallization, like shish-kebabs or oriented lamellar stacks. It was observed that, in injected PE-HD specimens, the macromolecules in the skin layer are highly oriented and the growing lamellae are nearly perfectly aligned. When an external force is applied, the whole deformation is localized to the amorphous phase. It leads to cavitation at a very small strain, 0.1 %, much less than the yield strain for this PE-HD (i.e. 10 % for BASF Lupolene 6021D) [30]. A different structure was observed in injected thick polypropylene bars with the size of spherulites decreasing when going from center to skin and with small grains present in the skin layer, visible when examined by polarizing light microscopy [31]. The influence of the above discussed different morphologies of crystalline structure on volume increase, i.e. on cavitation, is presented in Fig. 3.

In the process of polymer solidification the attention is usually focused on the morphology of crystalline phase. The amorphous phase is less sensitive to the preparation conditions. However, it is formed in the same process when crystals grow, so the phase morphology depends to some extent on the structure of the crystalline phase. In the amorphous phase, the most important factors are elements bonding crystals and transferring stress, i.e. tie molecules and entanglements of macromolecules. The number of tie molecules depends on crystal architecture and, for example, may be reduced when the folded chain crystals grow at higher temperatures. The density of entanglements depends on the molecular mass of the polymer. It was shown for example of polypropylene that an increase of molecular mass and entanglement density leads to decrease in the number of generated cavities (see Fig. 3b, curves 1 and 2) [31]. Rozanski and Galeski [32, 33] discovered that the presence of free volume in the amorphous phase is profitable for cavitation. In a series of experiments, they showed that when the free volume was filled by a low molecular liquid the cavitation was suppressed, but when in a second experiment the impurities and molecules with low molecular mass were removed, then the free volume was larger and voiding was more intensive.

The process of cavitation depends on the experimental conditions. Two of the most important conditions are strain rate and temperature. Fast deformation limits the possibilities of relaxation in the structure, which is visible as an increase in the stress, including yield stress. The increase of yield stress and crystal strength is not compensated by an increase in the strength of the amorphous phase. This means that initiation of cavitation is easier when the semicrystalline polymer is tested more quickly. It has been observed that, in polypropylene formed from melt by cooling in iced water, cavities were not observed for strain rates below 50 %/min. However, strong SAXS pattern from voids was detected beyond this limit [31].

It is known that when the tensile deformation of polymers is performed at elevated temperature, the force needed for the initiation of plastic deformation is smaller and elongation to break may increase significantly. The easier plastic deformation of crystals at higher temperatures also means that the polymer, as a whole, deforms without cavitation. The measurements of PP specimens solidified slowly from melt showed that nano voids were formed at yield when the temperature was in the range 20—40 °C. However, cavitation was not observed at temperatures of 70 and 100 °C [24]. Cavitation in high density polyethylene is even more sensitive to temperature [34, 35]. The whitening of this material was observed at temperatures of deformation in the 20—32 °C range, but not when the temperature was higher. SAXS measurements showed that the last traces of nano cavitation are visible at 40 °C (Fig. 4). The limit of yield stress for transformation from cavitational to non-cavitational deformation (based on SAXS observations) was 19 MPa.

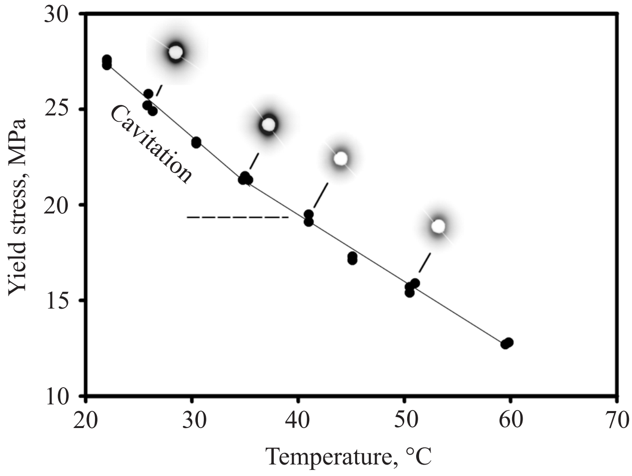

Fig. 4. The influence of temperature on yield stress and cavitation in PE-HD samples cooled in air; the presented SAXS patterns were registered at yield; this figure was prepared with using author's data discussed in [34]

The relations between cavitation conditions and possible lamellar slips were discussed by Addiego et al. [36]. At higher temperatures of deformation, or at lower strain rates, fine chain slips are preferentially activated instead of coarse chain slips. As only coarse slips favor cavitation, the cavitation is delayed or does not occur when in the fine slips mechanism dominates the polymer.

One of the requirements for cavitation is the presence of local three dimensional tensile stress (i.e. negative pressure), also described as triaxiality. For uniaxial stretched polymers, the pressure is always negative. However, as discussed above, this contribution might be too low for breaking the amorphous phase. In real materials, the local stress differs from this externally applied, so locally triaxiality depends on structure. It was found that triaxiality also depends on the shape of the tested specimen, especially on the presence of curvatures and notches, which localize deformation.

Castagnet et al. [37] studied PVDF samples of different shapes: conventional dumbbell (known also as dog-bone) and diabolo (i.e. rod — like samples with preformed neck), exhibiting more or less triaxaility. In diabolo type samples, the greater curvature in the narrow section results in higher hydrostatic stress at the center. PVDF specimens with highest negative pressure cavitated even at testing temperatures of 120 °C, which was not possible for samples with the smallest curvature, i.e. with lower triaxiality. Laiarinandrasana et al. [38] defined stress triaxiality ratio T for such kind of samples as:

$$T = 1/3 + \log\,[(1+r)/(2R_n)] \qquad (6)$$

where: r — the minimal cross section-radius, R_n — the notch radius. Recent studies of Addiego et al. [39] showed that the triaxiality is largest in the center of thick injected samples, which together with the presence of more perfect crystals in this area lead to intensive cavitation, observed in PP specimens. The general conclusion from the above observations is that the shape of tested sample is important because the presence of curvatures, manufactured necks etc., enlarges triaxiality and by this supports cavitation.

There are substantial difficulties in the determination of mean void size and size distribution. Micrometer-sized voids are usually observed after tensile testing by scanning electron microscopy. The individual voids might be easily detected. However, it is difficult to have a statistic of the dimensions from a limited number of photographs. Additionally, the observed objects might not be fully representative due to relaxation of the material after mechanical testing and due to the applied preparation procedure. The main obstacle in the measurements of nano voids by SAXS method is the presence of a beam stop, protecting the detector from damage by the primary beam. The beam stop also covers the radiation scattered at very small angles. This means that the method cannot be used for the detection of large scattering objects and that it is not possible to directly determine the shape and size of voids. However, there are some methods helpful in the calculation of approximated void size from the SAXS pattern. One method is based on the determination of the radius of gyration (R) from Eq. 5, which may be easily done if the dependence $\ln(I) = f(s^2)$ is linear. Yamashita and Nabeshima [40] showed that if this dependence is not linear, it may be divided into parts representing populations of cavities. The contribution of each group of voids to the total scattering is then determined from modified Eq. 5 and the radii of gyration is calculated. If an ellipsoidal shape for cavities is assumed then their dimensions can be evaluated from the relation:

$$R^2 = (a^2 + 2b^2)/5 \qquad (7)$$

where: $2a$ and $2b$ — the lengths of ellipsoid axes [41]. Pawlak [30] found that three populations of voids with radii of gyration: 4—5, 6—8 and 9—11 existed in PE-HD deformed to a strain of 0.3. Assuming that $b = 3.5$ nm, i.e. is equal to half of the amorphous layer thickness, then the longer axis of an ellipsoid representing the largest cavities is equal to 48 nm. Similar calculations for polypropylene [31] strained to yield point gave the dimensions of the largest voids $80 \cdot 7$ nm

Humbert et al. [23], assuming a cylindrical shape of voids in PE, calculated that cavities have a size of $40 \cdot 60$ nm immediately after generation. The presence of only large cavities seems be unrealistic. The other approach for the calculation of length of ellipsoidal cavities was proposed by Grubb and Prassad [42]. The method is based on the determination of integral breadths of many scattering profiles taken in the direction of the longest size of void, but at different distances from the center of the pattern. Because the integral breadth of the scattering profile at the center is unavailable due to the presence of a beam stop, it is approximately calculated from the interpolation of known integral breadths. The integral breadth Δz of this central scattering profile is related to the length of scattering objects according to the equation (8):

$$(\Delta z)^2 \cos(2\theta)/(\lambda D) = 1/2l + [1/(4l^2)+q^2\sin^2\beta/(4\pi^2)] \qquad (8)$$

where: $q = 4\pi \sin\theta/\lambda$, 2θ — the scattering angle, λ — the wavelength of the X-ray, D — the sample–detector distance, l — the length of voids, and β is the misorientation factor. The length l and factor β can be obtained by a nonlinear fit of Δz vs q. Calculations for the uniaxially deformed polypropylene samples based on the above approach gave a value $l = 59$ nm at a strain of 0.07 [31].

Sometimes other methods than SEM or SAXS are used for the characterization of void sizes. Chu et al. [43] measured the size of pores in drawn film of β form polypropylene using a mercury intrusion method and gas (N_2) adsorption method. A film previously prepared at 20 °C had a smaller average pore radius (14.5 or 9.5 nm, depending on the applied method) than film prepared at a crystallization temperature of 110 °C and drawn at 130 °C (radius of pores 56.1 or 9.8 nm).

The whitening of polymer is usually explained by the presence of micro size voids. It is evidently true for large deformations where many voids exist, as was observed by SEM. However, the whitening is visible the first time at yield, when only a couple of these voids is visible on SEM photographs and the total increase of volume is very small. Recently, Farge et al. [44] proposed another explanation of early whitening at yield. Incoherent polarized steady-light transport method and microtomography were applied for studies of tensely deformed polypropylene. The conclusion from these experiments was that assemblies of nano voids, giving a similar scattering effect as the individual micro voids were responsible for whitening at yield.

INFLUENCE OF CAVITATION ON THE FURTHER DEFORMATION

Voiding provides some degree of freedom to the constrained structure. The voids appear before large scale breaks of crystals. There are three experimental proofs of the influence of voiding on further deformation of the polymer. It was observed for many polymers that stress at yield and stresses after yield are lower in tension than in compression [15]. Compression occurs without cavitation. However, processes of crystal deformation are in principle the same as under tension [2]. The explanation of lower stress values is the rapid change of local stress state during cavitation, promoting the deformation of the crystal at decreased macroscopic level of stress.

It is known that during plastic deformation of crystals, heat is generated and the temperature of sample increases if the conditions of experiment are quasi-adiabatic. The measurements for polypropylene show that a rapid increase of temperature is observed after yield, during neck formation. Initiation of cavitation at yield stimulates the additional heat generation, which happens after yield and being a result of more numerous processes of plastic deformation in crystals [45]. Because the WAXS measurement did not show more intensive fragmentation of crystals in blocks in cavitating polymer, it means that the main reason of the additional heat is intensification of fine chain slips.

Liu et al. [46] analyzed the changes in WAXS diffractograms obtained for polypropylene samples deformed with different strain rates at temperatures of 21 and 56 °C. Using the Scherrer equation (9), they determined the lengths of the lamellae in the direction normal to the selected crystallographic plane. The Scherrer equation has the form:

$$L_{hkl} = 0.9\lambda/(\beta_o \cos \theta) \tag{9}$$

where: L_{hkl} — mean crystal size in the direction perpendicular to the (hkl) plane, λ — the wavelength, β_o — the half-width of the diffraction peak, and θ — the Bragg angle [47]. The results of calculations for highly deformed polymers are summarized in Table 1.

Table 1. The characteristic dimension of lamellar crystals in polypropylene determined for (110) plane from eq. 9; according to results of Liu et al. [46]

Temperature, °C	Strain rate, s^{-1}	Length of crystals, nm
21	Untested	28.8
56	$8.33 \cdot 10^{-3}$	13.1
56	$8.33 \cdot 10^{-1}$	9.3
21	$8.33 \cdot 10^{-3}$	5.0
21	$8.33 \cdot 10^{-1}$	2.6

Liu et al. [46] observed a decrease of lamellae size when the experimental conditions preferred cavitation, i.e. when the test was faster and/or was performed at lower temperatures. This means that more intensive cavitation supports the fragmentation of lamellar crystals into blocks.

CONCLUSIONS

Cavitation appears when chain mobility is insufficient for lamellar deformation by crystal slip systems alone. This happens in many semicrystalline polymers tensely deformed at temperatures above the glass transition. The high crystallinity, reduced number of defects in lamellae, low temperature and high speed of deformation are factors supporting cavitation. The necessary condition for cavitation is a local presence of three-dimensional stretching stress, i.e. presence of negative pressure. Usually the cavities are formed before the large scale plastic deformation of crystals is initiated at yield. The generation of the cavity rapidly changes the stress state in its surroundings, which is an impulse for earlier (i.e. at lower stress) and more intensive deformation of crystals by the chain slip mechanism. Typically, the voids at this step of deformation are nano size. The larger, micrometer cavities are developed later when the lamellar structure is transformed into a fibrillar structure. These micro voids play a role at the end of deformation when their presence make a fracture process easier.

The cavitation phenomenon is negative in many applications of homopolymers because it decreases the barrier for plastic deformation. However, there are applications where the phenomenon is positive. Examples of such applications are semi-transparent membranes for packaging or materials for production of sportswear with good ventilation.

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