

# Cavitation and morphological changes in polypropylene deformed at elevated temperatures

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## **Abstract**

Polypropylene thick films were subjected to tensile drawing at various temperatures from the room temperature to 100°C. Morphological alterations during drawing were followed by WAXS, SAXS, SEM of sectioned and etched samples, volume strain measurement, light transparency measurement at various level of strain. The morphological observations were paralleled with stress-strain determination. Samples drawn at 25 and 40°C undergo severe cavitation contributing to their volume increase up to 90-95%. The volume increase contributes greatly to the engineering strain. Polypropylene drawn at 70 and 100°C does not cavitate. At the strain up to 1.2 a high lamellae orientation is observed in SEM while the 2D WAXS patterns show in contrary circular diffraction rings indicating low orientation of crystals. The rotation of lamellae towards drawing direction is associated with reverse rotation of chains in crystals due to fine chain slips. These two rotations in opposite directions counterbalance resulting in a much weaker crystal orientation than expected from the SEM images. Non-cavitating samples retain their translucency up to a high strain.

**Keywords:** voids, poly(propylene), plastic deformation, mechanical properties, SAXS.

## Introduction

Plastic deformation of crystalline and amorphous phases in polypropylene is often accompanied by the formation of cavities<sup>1-10</sup>. Cavitation process is then initiated in tensile drawing shortly before or at the yield point<sup>11</sup> if the resilience of the amorphous phase is lower than the strength of crystals<sup>3,9,10</sup>. Formation of a cavity changes rapidly the local distribution of stresses in surrounding crystals and initiates their plastic deformation, mainly by crystallographic slips<sup>3</sup>.

Cavitation is usually studied by small angle X-ray scattering (SAXS) from the nanometer size voids<sup>11-13</sup>. Larger cavities, if present in the polymer, scatters light, which is seen as a whitening of a material<sup>14-16</sup>. Another useful technique for detection of micrometer size voids and larger cracks in PP is a scanning electron microscopy (SEM)<sup>6,17,18</sup>. Liu et. al.<sup>14</sup> examined whitening process in polypropylene and observed that it occurs for samples drawn with high rates or at low temperatures. At the temperature of 40 °C and above the whitening during drawing was not visible.

Cavitation is considered as the main reason of volume increase in deformed polymer samples<sup>19-23</sup>. G'Sell et al.<sup>22</sup>, Pawlak et al.<sup>10</sup> and Na and Lv<sup>19</sup> observed that the volume of deformed polypropylene substantially increases with increasing strain. According to Bucknall's proposition for similar behavior of amorphous polymers<sup>24</sup> the overall volume variation is the sum of three components: elastic, plastic and cavitational. The elastic component of volume strain is a function of strain and Poisson ratio. Bucknall assumed that the plastic component of volume increase is negligible, however, Addiego et al.<sup>23</sup> have shown for polyethylene that the compaction of amorphous chains and the destruction of crystals during drawing may not sum up to zero.

Recently, we have shown that both cavitational and non-cavitational behavior may be observed in the same polymer -polyethylene or polypropylene- depending on the conditions of

the tensile drawing (e. g. rate of deformation) and polymer morphology controlled by solidification process<sup>9-10</sup>. At slow drawing rates the samples with less perfect smaller crystals do not show cavitation. That is because the plastic deformation of crystals is initiated before the stress reaches the resilience of the amorphous phase. Increasing of the drawing rate leads to an increase in the yield stress and the cavitation mechanism of deformation is preferred under these circumstances. Such change of a behavior was observed for polypropylene (PP)<sup>10</sup>.

The formation of voids rapidly changes the local state of stress, which should promote easier fragmentation of surroundings crystals. Liu et al.<sup>14</sup> observed more frequent fragmentation of crystals in cavitating polymer as compared to non-cavitating. The easier crystal deformation on a microscale has the influence on the entire process of plastic deformation on a macroscale and polymer drawability. It is known that the yield stress is decreased when cavitation sets in. That was shown by comparison of tensile and compression experiments for several polymers<sup>3</sup>. In a compressed polymer the cavitation is prohibited by a positive pressure component. The influence of cavitation on mechanism of plastic deformation leads to changed mechanical properties and determines the possible applications of a polymer.

It is known that the increase of drawing temperature influences the mechanical properties, among them a macroscopic yield<sup>25</sup>. The yield stress decreases with the increase of the temperature. Hartmann et al.<sup>25</sup> observed that the yield parameters: yield strain and a non-recoverable permanent deformation both have a maximum at the temperature of deformation around 60-70 °C and also that the dependence of the yield stress on the temperature changes in this temperature range. They did not analyzed whether cavities were formed in their polymer during drawing or not. However, since the yield stress decreases with the temperature it is probable that at some elevated temperature the plastic deformation occurs without cavitation in a polymer that cavitates at lower temperature.

The goal of this paper is to show the existence of such cavitation-non-cavitation transition in polypropylene deformed at elevated temperatures. We also want to present the relations between the changes in internal morphology of PP and the cavitation process.

## **EXPERIMENTAL**

### **Materials and methods.**

Polypropylene Novolen 1100 N produced by BASF was used in these studies. According to the producer data it has the density of 0.91 g/cm<sup>3</sup>, molecular weight  $M_w = 2.5 \cdot 10^5$  g/mol, polydispersity  $M_w/M_n = 5.0$ , melt flow index of 11.0 g/10 min, (at 230 °C, 2.16 kg). Samples for tensile tests were prepared by compression molding at 200 °C. Compression molded polypropylene in the form of 1 mm thick sheets was cooled slowly in air. Dog-bone samples for mechanical tests were cut from those sheets, accordingly to ASTM D 638 standard. The length of gauge section was 9.5 mm and its width was 3.18 mm.

Mechanical properties of PP were studied in tension at room and elevated temperatures (25, 40, 70, 100 °C) using an Instron tensile testing machine equipped with the environmental chamber. Samples before the test were conditioned at least 15 min at the drawing temperature. Engineering strain rate was of  $8.3 \cdot 10^{-4}$  s<sup>-1</sup>. Usually the deformation was stopped at a selected engineering strain, below 80%, because the observations were focused on the initial (around yield) and intermediate stages of deformation. Yield stress and yield strain were determined from engineering stress-strain curve at maximum engineering stress. The momentary shape and the dimensions of a sample during deformation was recorded by a “Minolta Dimage” digital camera. A mirror was applied for simultaneous recording of the third dimension of a sample, the thickness. Actual cross-section was calculated from measured dimensions of the sample.

For the measurement of local deformation, black ink marks were placed on the surface of a sample, at distances of 1 mm. The local strain was determined as the change of the distance between marks,  $l-l_0$ , divided by the original distance  $l_0$ . The local volume strain was calculated as a local change of the volume,  $\Delta V=V-V_0$ , divided by the initial volume,  $V_0$ , measured in the most deformed part of a sample. The accuracy of volume strain measurements strongly depends on the resolution of imaging system and usually is estimated to be 1-3% of measured value. Besides there are small individual differences within the set of samples requiring an averaging of mechanical data over several samples.

The small angle X-ray scattering technique was used for the detection of cavities. A 0.5 m long Kiessig-type camera was equipped with a pinhole collimator and a Kodak imaging plate as a recording medium. The camera was coupled to a Philips PW 1830 X-ray generator (Cu  $K_{\alpha}$ , operating at 50 kV and 35 mA) consisting of a capillary collimator, allowing for resolution of scattering objects up to 40 nm. Exposed imaging plates were read with a PhosphorImager SI system (Molecular Dynamics). The objects of the studies were deformed samples after stress relaxation with fixed ends for several hours.

The small angle X-ray scattering (SAXS) was also performed in the synchrotron beamline A2 at Hasylab (Desy) in Hamburg. The goal of these experiments was to elucidate the healing of cavities and orientation relaxation during drawing and keeping the sample with fixed ends. X-ray wavelength from synchrotron source was 0.15 nm and the sample to detector distance was 2.6 m. Scattering patterns were collected by a two-dimensional detector operated in 2048\*2048 pixel mode. The tensile in-situ observations of voids formation were possible because a self-custom made tensile tester testing machine that was fitted to the beamline.

The wide angle X-ray scattering (WAXS) photo camera was used for observations of lamellae orientation. A source of Cu $K_{\alpha}$  radiation, operating at 50kV and 35mA was used. Two-dimensional scattering images were recorded by a camera equipped with a Kodak

imaging plate. The distance between a sample and the recording plate was 5 cm. Exposed imaging plates were analyzed with PhosphorImager SI system (Molecular Dynamics).

The degree of crystallinity was determined from the heat of melting by using a DSC 2920 differential scanning calorimeter (TA Instruments). The 8-9 mg samples were heated up from 20 °C to 200 °C, at the rate of 10 K/min.

Morphology and shape of cavities in the deformed samples of polypropylene were examined by scanning electron microscopy (SEM). A specimen after 20 min freezing inside a tank with a liquid nitrogen was split along the tensile direction with a razor blade. A revealed surface of the sample interior was then treated by a permanganic etchant in order to expose a lamellar structure. Specimens were etched according to the procedure developed originally by Olley and Basset<sup>26</sup> in 2 wt% KMnO<sub>4</sub> solution in H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (1:1 vol). The time of etching for this particular polymer was extended to 6 hours. The etching process was terminated by immersing the specimen in cold diluted H<sub>2</sub>SO<sub>4</sub>. Then, the specimen was subsequently immersed into four tubes in an ultrasonic bath, containing the following liquids: diluted cold H<sub>2</sub>SO<sub>4</sub>, cold H<sub>2</sub>O<sub>2</sub> (diluted, 30%), H<sub>2</sub>O and acetone. Time of immersion in each tube was 3 minutes. The etched specimens were sputtered with gold and examined in a Jeol 5500 LV scanning electron microscope in a high vacuum mode.

The small pieces, cut from original and deformed PP samples, were used for the measurements of density by the gradient column filled a mixture of ethyl alcohol and water at 23°C. The gradient column was calibrated with floating glass beads whose densities were determined with the precision of 0.0001 g/cm<sup>3</sup>.

The Poisson ratio was measured using the instrument and procedure described by Bielinski et al.<sup>27</sup>. The concept of the experiment is based on the compression of cylindrical specimen fitted to a barrel and the measurements of Young's and bulk moduli. The Poisson ratio is then calculated from the values of both modulus. We assumed the same value of

Young's modulus in tension as it was determined in compression.

## Results

The samples before and after drawing were characterized by differential scanning calorimetry (DSC). In the melting thermogram only one melting peak with a maximum at 161.9 °C was observed for undeformed PP. The crystallinity of this material, determined on the basis of the heat of melting equal 97 J/g, was around 59%. The heat of melting for crystals equal 165 J/g was assumed in these calculations<sup>28</sup>.

The DSC measurements showed also that the elevated temperature during the mechanical testing had only a little influence on the melting temperature but it slightly increased a sample crystallinity. For example the polypropylene sample conditioned 20 min at 100 °C, showed an increase of the melting temperature to 162.2 °C and the heat of melting to 109 J/g, which means 7% increase of crystallinity. Further increase of crystallinity was caused by plastic deformation at 100 °C (heat of melting 113 J/g; 68% of crystallinity) however, two separate maxima of melting were observed at 158.3 and 165.1 °C.

In Fig 1a the engineering stress-engineering strain dependences are presented for PP samples drawn at temperatures of 25, 40, 70 and 100 °C. In all cases the deformation with yielding was observed. The yield stress decreased with the increase of drawing temperature and it was equal: 37 MPa at 25 °C, 28 MPa at 40 °C, 18 MPa at 70 °C and only 11 MPa at 100 °C. Some increase of an engineering strain at yield was observed: from 14% at 25 °C, through 16% at 40 °C, 17% at 70 °C to 18% at 100 °C. In this range of deformation the value of engineering strain at yield is nearly equal to local yield strain (compare Fig. 1b). The increase of strain at yield with temperature is in contrary to the conclusions in some papers<sup>8,29</sup> claiming the strain at yield independent of temperature. However, in those papers the yield strain was determined from the true stress-strain curves and because those curves do not show



maximum at a yield point there is a quite significant uncertainty in the determination of strain at yield.

The deformation beyond the yield point in all these samples was strongly localized and as a result the local strain inside the neck part was much larger than the average strain. In Fig. 1b the maximum local strain as a function of engineering strain is presented. The maximal local strain increases slightly with the increase of engineering strain to the point of yielding. Then the rapid increase of local strain begins at around 25% of the engineering strain. The dependence for engineering strains higher than 25% is described by a straight line nearly identical for all temperatures. It must be noticed that the plot in Fig. 1b is characteristic for a particular shape of the gauge of a tensile sample and it reflects the development of the neck. Nearly linear increase of the local strain, visible in Fig 1b, is the result of the formation of the neck that is not yet fully developed at 70% of engineering strain. For this particular PP and utilized template for tensile samples the propagation of neck along the gauge length begins at the engineering strain larger than 100%<sup>10</sup>. Apparently the maximum local strain in the developing neck for similar engineering strain does not depend on the temperature, at least for that particular brand of polypropylene. However, the observations for other materials, for example for high density polyethylene, show that it is not a general rule. The localization of neck (in HDPE) is lower at higher temperatures: at engineering strain of 70% it is 2.2 at 20 °C and only 0.8 at 40 °C<sup>30</sup>.

The samples of PP drawn at 25 and 40 °C undergo stress whitening around the yield point. Then the necking sets in and is always localized in the whitened zone. The whitening means a loss of transparency by initially translucent sample and it is a result of a formation of more strongly light scattering objects in the internal structure, having the size in the micrometer and sub-micrometer range. The voiding is usually the cause of strong light scattering due to a large polarizability contrast between a polymer and voids. Also the

reorientation of crystalline elements and strain induced crystallization must be taken into consideration.

At higher drawing temperature the translucency is preserved even for large deformations. As an example the PP sample drawn at 100 °C was still translucent at the engineering strain of 50%, which was equivalent to a maximum local strain of 2.2.

The changes of whitening during deformation were monitored by the photographic method. The light source was located behind the sample. Figure 2 shows the intensity of light registered by the camera detector as a function of engineering strain. The intensity of light transmitted through the samples decreased after the yield point, when the engineering strain was 20-30%, i. e. when the neck was formed. The decrease depended on the testing temperature and was more rapid at  $T=25$  or  $40$  °C. Intensities changed slower with the increase of deformation temperature. The intensities of transmitted light remained constant for large strains. The final level of transparency of the deformed samples was higher at the higher temperatures.

Existing difference between the shapes of curves for low and high temperatures indicates that the nature of whitening is not the same in both cases. The reasons of whitening in semicrystalline polymers are the increase of crystallinity level, molecular orientation or formation of voids, formation of voids being the most weighty. The increase of crystallinity as it was determined by DSC and discussed above is not significant. Our previous investigations for PP and PE<sup>3,9,10</sup> suggest that the rapid decrease of transmitted light intensity at low temperatures may be attributed to cavitation appearing just beyond the yield, but the whiteness change at high temperatures (70 and 100 °C) is the result of orientation of structure due to the transformation from lamellar to fibrillar structure, with a possible presence of large voids, formed much later at larger deformation.

The most often used technique of voids detection in deformed polymers is a small angle X-ray scattering (SAXS). Fig. 3 presents a collection of scattering patterns for the samples deformed to various degrees at different temperatures. The patterns were recorded after releasing the stress. It is known that the scattering from voids is much more intensive than the scattering from crystal lamellae stacks and due this fact it is usually easily recognizable. The scattering from voids is clearly visible in Fig. 3a for strains of 0.2 and more, when the sample was deformed at 25 °C. Similar scattering from voids is seen for the PP sample deformed at 40 °C for the strain range from 0.2 to 2.5. Figs. 3c and 3d show that there is no cavitation component in the scattering from the samples deformed at higher temperatures.

The range of sizes of detected cavities by our SAXS experiments is from 2 to 40 nm. From the shape of scattering pattern it is possible to deduce the shape of voids. Initially they are elongated perpendicularly to the drawing direction, that is horizontal in Fig 3. Comparison of x-ray scattering patterns from samples that were deformed in the synchrotron experiment and kept with fixed ends (maximum scattered intensity 31 000) with x-ray scattering from samples during deformation (maximum scattered intensity 35 000) shows that the scattering patterns retain their character with only small decrease in intensity. That means that the cavities do not have a strong tendency to healing, similarly as in polyethylene<sup>9</sup>. Also the clear scattering signal from voids after removing the samples from the clamps indicates that the formed voids are rather stable.

The shape of scattering patterns from voids changes at the strain of 0.9 (see Fig 3 a, b), which means that the reorientation of cavities happens and at higher strains the cavities are elongated in the deformation direction. The intensity of scattering decreases for strain of 4.0. It is specially visible at 40 °C, where the signal from the voids nearly disappears. Smaller but significant decrease of intensity is noticed at 25 °C. We observed previously that the disappearing of voids scattering at room temperature occurs for other highly deformed

polymers<sup>3</sup>. The reason of this effect is that cavities enlarge with deformation and finally most of them scatter x-ray outside of SAXS detection limit.

The cavities are not observed in samples deformed at high temperatures (Fig. 3 c,d) and the x-ray scattering in these cases reflects only the internal crystalline structure. At the strain of 2.3 some x-ray streaks perpendicular to the drawing direction develop for all drawing temperatures. The streaks are the result of x-ray scattering from long and narrow fibrils that are transformed from packets of lamellae in spherulitic structure. The transformation occurs apparently within the strain range from 1.1 to 2.3, it is rather independent of the drawing temperature and develops also in samples without cavitation.

The Figure 4 shows the intensities of scattering from PP samples as a function of a scattering vector  $s$ . These are horizontal scans of selected patterns presented in Fig. 3. They show the differences in intensities between non-deformed sample, with low intensity scattering from crystalline arrangement (Fig. 4, curve a), a sample deformed at 25 °C to the strain 0.2 with cavitation (Fig.4, curve b) and a sample deformed at 70 °C to the strain 0.5 (Fig.4, curve c). In the last case the cavitation was not detected, as it is discussed above. The intensity of x-ray scattering in the cavitated sample,  $I$ , (Fig.4, curve b) is a one order of magnitude larger than in non cavitated samples (Fig. 4, curves a and c). That is because the scattering intensity depends on the second power of the difference of electron densities of material components  $\rho_1$  and  $\rho_2$ , i. e.  $I \sim (\rho_1 - \rho_2)^2$ , where  $\rho_2$  being the electron density of air inside the cavity. The difference between electron densities of amorphous and crystalline components of a polymer is much lower, resulting in much lower scattering intensity<sup>31</sup>.

The observations of whitening and SAXS measurements showed that the cavitation occurs in samples deformed at low temperatures (25 and 40 °C) but not in those deformed at high temperatures (70 and 100 °C), which perfectly agrees with the results of volume strain measurements. Figure 5 presents changes of volume strain with strain for various temperature

of tensile drawing. An increase of the volume with the strain was observed for all polypropylene samples. Initially, before the yield (i. e. below strain of 0.15-0.2), the volume change is reversible and has elastic character. With further drawing the volume change become inelastic and is irreversible<sup>11</sup>. The reason of changes observed at this step is the stretching of amorphous phase, with accompanying interlamellar separation, and later with reorientation of crystals inside the amorphous environment<sup>32</sup>. The volume change associated with elastic deformation is described by equation of:

$$\Delta V/V_0=(1-2\nu)*\epsilon \quad (1)$$

where  $\Delta V/V_0$  is the volume strain,  $\nu$  is the Poisson ratio,  $\epsilon$  is the strain. The Poisson ratio of our samples was 0.38 at 25 °C and 0.46 at 100 °C, so the calculated elastic volume strain was 0.05 for T=25 °C and 0.02 for T=100 °C, i. e. positive and close to those observed at the yield as illustrated in Fig. 5.

Starting with the yield the plastic deformation sets in: chain slips in crystals<sup>33</sup> and respective deformation of amorphous phase caused by lamellae glide and lamellae rotation<sup>8,34</sup>. The intensity of these processes increase with increasing deformation. At large strain also the fragmentation of PP crystals occurs along with the voiding localized in the amorphous phase. It is clear from Fig. 5 that the volume increases beyond the yield (strain of 0.15-0.2 and over) differently for polypropylene samples deformed at a higher temperature (70, 100 °C) and at a low temperature: 40 °C and 25 °C. At a high temperature the dependence is flat, on the level of volume strain around 0.1, and a significant increase is observed for the strain larger than 2.5. This increase may be associated with the final stage of the transition from lamellar to fibrillar morphology and formation of some openings between fibrils. These openings give weak oriented SAXS streaks (see Fig. 3) and are poorly discernible by SEM (see later discussion of Fig. 7).

The rapid increase of the sample volume beyond the yield point was observed for the drawing temperature of 25 °C . It reached 0.35 for the strain of 0.5 and 0.8 for the strain of 2.0. Similar in the scale changes of volume in deformed polypropylene were previously described in the literature<sup>19,22</sup>. The reason for the volume increase is the intensive cavitation. The volume increase dependence with increasing strain for polypropylene deformed at 40 °C is intermediate between the dependencies for 25 and 70 °C: the volume continuously increases beyond the yield and reaches 0.2. for the strain of 2.0, which documents again cavitation in the material, however, less intense than in the sample drawn at 25 °C. .

For each sample the values of volume strain are much larger than those determined from the density changes by floatation method. The cavitation voids are shrinking when the tensile drawing is interrupted and the stress released by unclamping the sample. These discrepancies are also caused by the presence of open voids, forming channels inside the material. that are penetrated by water-alcohol mixture during density measurements.

The evolution of voids shape, as seen in Fig 3, is governed by the changes of structure around them, i. e. fragmentation of lamellae, their reorientation, stretching of amorphous phase<sup>8,10</sup>. The evolution of structure for cavitating and not cavitating samples was followed by wide angle X-ray diffraction on the lamellar level and on the spherulitic level by scanning electron microscopy.

Fig. 6 presents the wide angle X-ray diffraction patterns from PP samples deformed to increasing strains. For low deformation the diffraction from the following crystallographic planes: (110), (040), (130) and (111) overlapped with (-131) and (041) represent the concentric rings<sup>35</sup>. Preferential orientation of crystallographic planes is not considerable for low strain in the range of 0-0.9. Apparently the most part of strain stored in the sample can be attributed to cavities and not to the orientation of crystallites. In more deformed samples the reflections from (110), (040) and (130) planes tend to concentrate in the direction

perpendicular to drawing. The planes for those reflections contain macromolecular chain axes and they are equatorial in a so-called fiber diffraction pattern. The concentration of the reflexes from (040) and (110) planes at equatorial positions in the fiber diffraction pattern with increasing of deformation suggests that the rotation of crystals either by crystallographic slip or by rotation of lamellae takes place. The orientation of crystallographic planes becomes significant at the strain of 1.1 for the specimens drawn at 25 °C. In the samples deformed at a higher temperature the random, circular pattern is still visible at larger strains, i. e. 1.1 at 40 and 70 °C and 1.2 at 100 °C, which means that the amorphous phase accommodate most of the orientation and that the reorientation of crystals occurs at later stages of deformation at higher temperatures. This is also confirmed by a shift of the engineering yield strain from 14% at 25 °C to 17% and 18% at 70 °C and 100 °C, respectively (see Fig.1a).

Outer ring of scattering patterns in Fig. 6 represents overlapped reflexes from three planes (111), (041) and (-131), difficult to separate for low strain. However, at a local strain of 1.1-1.6 the four-point pattern of outer ring emerges, representing two populations of differently oriented lamellae.

WAXS patterns from highly deformed samples reveal also a presence of the meso phase, that is visible on the patterns as a diffused dark halo in the regions of equatorial reflexes from planes (110), (040) and (130) vertical in Fig. 6. For better visualization of the presence of the meso phase the  $2\Theta$  scans are presented in Fig. 6 for each temperature and for the largest deformation. The meso phase exists only in samples deformed at 25 and 40 °C, but not when the temperature was higher. Several authors observed the formation of meso phase in deformed polypropylene<sup>36,37</sup> and it was explained as a transition from monoclinic crystallographic phase, occurring when the polymer is deformed at the temperatures below 60 °C<sup>37</sup>.

A strong reorientation of crystalline elements at strain of 1.0-1.3 coincides with reorientation of cavities, as it was presented in Fig. 3. It suggests that the shape of cavities depends on the spatial arrangement of surrounding lamellae.

The morphological changes during deformation, observed on the micrometer level by scanning electron microscopy, are illustrated in Fig. 7. Deformation direction on micrographs is horizontal. The spherulitic structure is clearly visible. It is seen that the changes of morphology with deformation depend on the deformation temperature. The top row of micrographs is for 25 °C. When the strain reaches of 0.3 some cavities in polar regions of spherulites appear. They are elongated perpendicularly to the deformation direction. However, these voids are larger than those detected by SAXS. The large cavities become more numerous with increasing deformation and at the strain of 0.7 additional voids appear in the equatorial parts of spherulites. The spherulites gradually deform and become elongated in the deformation direction. At the strain 1.2 the spherulites are so highly elongated that it is difficult to recognize spherulitic arrangement. The micrographs in Fig. 7 also illustrate that the cavities enlarge with deformation, they become more circular in shape and for these at larger strain the groups of cavities appear between oriented stacks of lamellae. Similar tendencies are observed on the second set of micrographs, representing morphologies of polypropylene deformed at 40 °C.

The evolution of morphology of deformed polypropylene proceeds differently when strained at higher temperature of 70 and 100 °C. The cavities are now not detected by SAXS. Examples of morphological changes at 70 and 100 °C are also presented in Fig. 7. Similarly as for lower temperatures the initial spherulitic structure deforms when the strain exceeds yield point. However, cavitation does not occur. In Fig. 7 only the evolution of spherulites shape is seen with increasing orientation of lamellae toward the deformation direction. At larger magnification (micrograph not shown here) the cavities are also not



revealed. The results of SEM, SAXS and light transparency of the samples deformed at 70 and 100 °C lead to the conclusion that the cavities with size larger than 2 nm are not formed in the samples.

The SEM observations at higher magnifications for the samples deformed at 25 or 40 °C, indicate that apart from large cavities a lot of small voids exist between oriented and deformed lamellae. This is illustrated in Fig. 8, where the morphology of surface and interior of the highly deformed polypropylene sample (strain approx. 2.0) is shown. The surface (Fig.8a) is shown as it is, while the central part of sample was exposed by sectioning followed by permanganic etching. On the surface of the sample there are numerous small holes, with a diameter in the range of 50-100 nm. Fig. 8b is related to the micrograph on Fig. 7, representing strain of 1.2 at T=25 °C. The voids are also visible here. They are larger, with diameter of 100-500 nm, more elongated and the number of smaller voids is much lower than in the surface layer (Fig. 8a). Apparently the material surrounding small cavities was etched away and they disappeared while the edges of largest cavities were enlarged by etching.

## **Conclusions**

The presented experiments showed that polypropylene that cavitates during tensile drawing at the room temperature may not cavitate at a higher temperature. The increase of the temperature changes the properties of crystalline and amorphous phases, however, the response of both phases is different. The barrier for plastic deformation of crystals by chain slips decreases with the temperature as the polymer crystal plasticity is unambiguously a thermally activated process. It is seen on a macroscale as a decrease of the yield stress for

increasing temperature of deformation. The strength of amorphous phase subjected to a negative pressure above its glass transition temperature is apparently much less affected by the increase of temperature. There is a critical temperature above which it is easier to initiate plastic deformation of crystals than to break the amorphous phase with formation of voids. This critical temperature for polypropylene is in the range between 40 and 70 °C.

The cavities, if present, are first detected by SAXS just beyond the yield point. The differences between voids formation at temperatures of 25 and 40 °C are rather not significant. At the onset of cavitation the nanometer size voids appear and they are oriented perpendicularly to the deformation direction. These nanovoids are located in the equatorial parts of spherulites<sup>38</sup>, where the amorphous phase is subjected to stronger dilatational strain. SEM observation shows that small voids are accompanied by larger ones, micrometers in size, also similarly oriented as smaller voids. Those cavities, observed at slightly larger strains, beginning from the strain 0.3, are the main reason of whitening of samples.

With further drawing the other microvoids form at polar regions of spherulites, where the lamellae breaks. The number of voids increases with deformation, which is seen as further increase of whiteness, volume strain and intensity of SAXS scattering. The SEM examination shows that spherulites become elongated in the deformation direction. However, the orientation of crystalline phase is rather weak as detected by WAXS. This observation means that the stretching at this step is in a significant amount by creation of cavities (compare Fig. 5) with rotation of crystalline lamellae perpendicular to the drawing direction but without significant reorientation of the crystallographic planes due to compensation by rotation of crystallographic planes in the opposite direction. The explanation for this phenomenon is presented in Fig. 9 where the rotation of lamellae in 45° fans of spherulites and respective crystallographic slip are depicted. The rotation of lamellae towards drawing direction is associated with the reverse rotation of chains in crystals due to fine chain slips. These two

rotations in opposite directions counterbalance resulting in a much weaker crystal orientation than expected from the SEM images. Such rotations occur also when cavitation and lamellae fragmentation are in action during drawing at lower temperature.

The rapid changes in morphology and cavitation process are observed when the strain reaches the value of 0.9-1.3. The voids shape changes from elongated perpendicularly to elongated parallel to the deformation direction. This phenomenon is first observed at the strain of 0.9. It is evident that some new cavities oriented in the deformation direction are also formed because the intensity of SAX scattering at the strain of 0.9 is increased (see Fig. 3). At the strain of 1.0-1.3 crystalline elements become more and more oriented in the deformation direction (Fig. 6). Macroscopically this phase of deformation corresponds to approaching the plastic flow on the engineering stress-strain curve (Fig. 1a).

With further increase of strain the volume of cavities increases however, the SAX scattering from voids is becomes less visible because most of the cavities are larger than the SAXS detection range. The structure of specimen is then highly oriented and the smectic phase is formed.

The deformation of polypropylene at temperatures of 70 and 100 °C occurs with yield, however, without cavitation. It is confirmed by SAXS, volume strain and SEM investigations. It seems from SEM images in Fig. 7 that lamellae do not fragment up to the strain of 1.2 when PP is drawn at 70 and 100°C. The orientation of lamellae within spherulites in the drawing direction is already highly advanced at the strain of 1.2. However, in contrary to high lamellae orientation, the 2D WAXS patterns in Fig. 6 show still circular diffraction rings from weakly oriented crystalline planes indicating far lower crystal orientation than the orientation of lamellae. The explanation for this phenomenon is presented in Fig. 9. The rotation of lamellae towards drawing direction is associated with the reverse rotation of crystallographic planes due

to fine chain slips. These two rotations in opposite directions compensate resulting in a much weaker crystal planes orientation than expected.

In the samples drawn at  $T=70$  and  $100$  °C the meso phase is not detected because its melting temperature is around  $60$ °C. Polypropylene drawn at a temperature above  $40$  °C remains translucent (see Fig. 2) even at the strain of 4-5.

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FIGURES

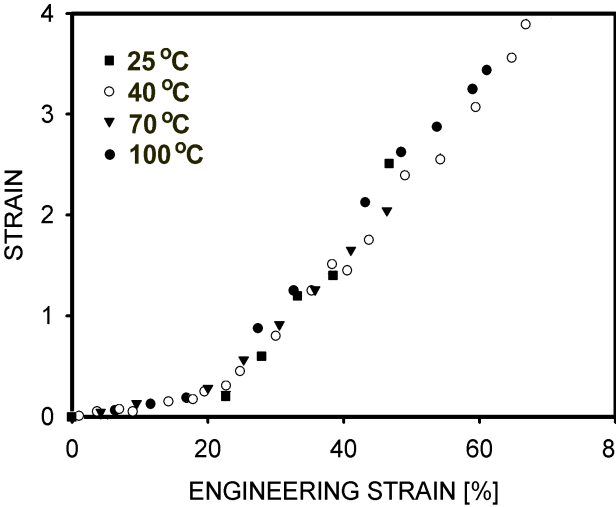
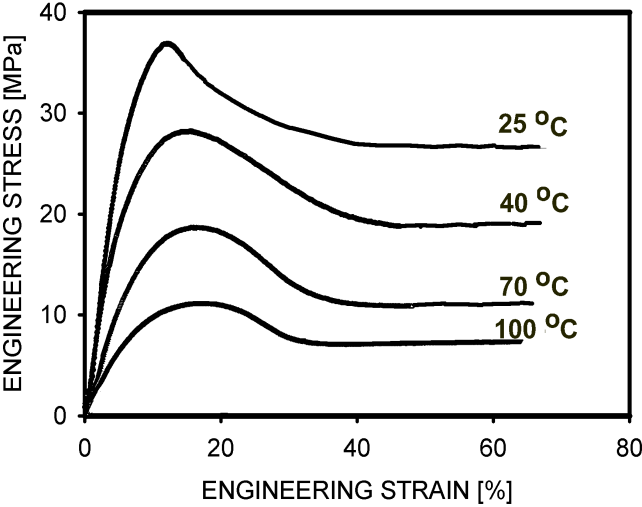


Fig 1. (a) Engineering stress-strain relation for PP tested at different temperatures; (b) Maximum local strain as a function of engineering strain.

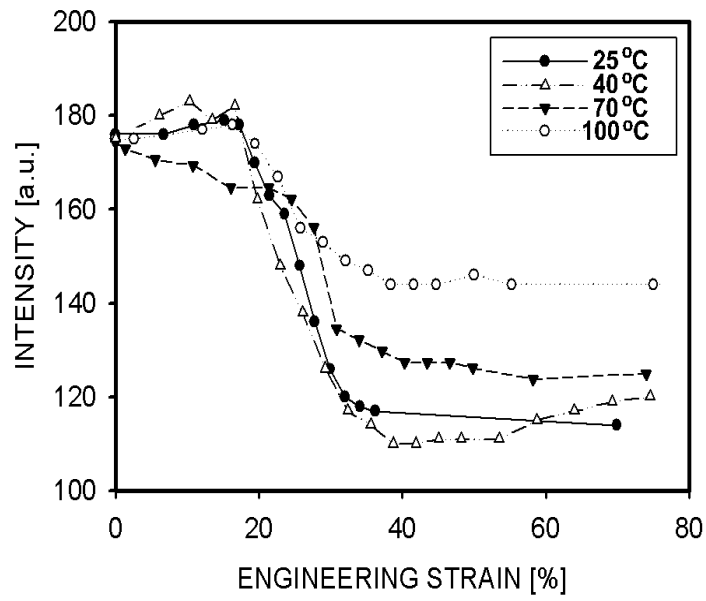


Fig. 2. Dependence of intensity of light transmitted through samples on the engineering strain.

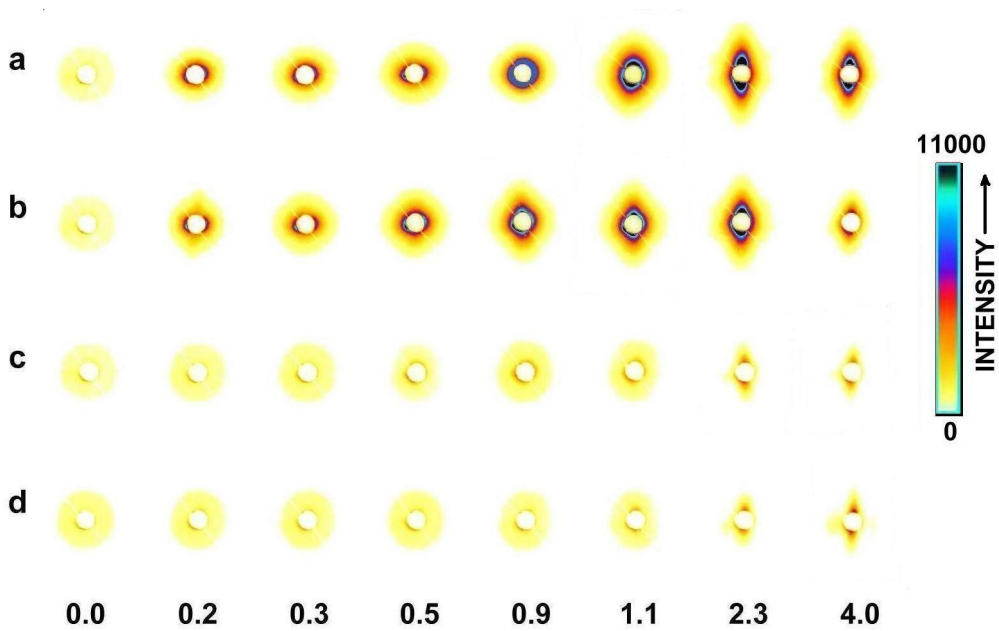


Fig. 3. Small angle X-ray scattering from PP samples after deformation. Numbers indicate local strains. Temperatures of deformation: a-25 °C, b-40 °C, c-70 °C, d-100 °C. Drawing direction horizontal.



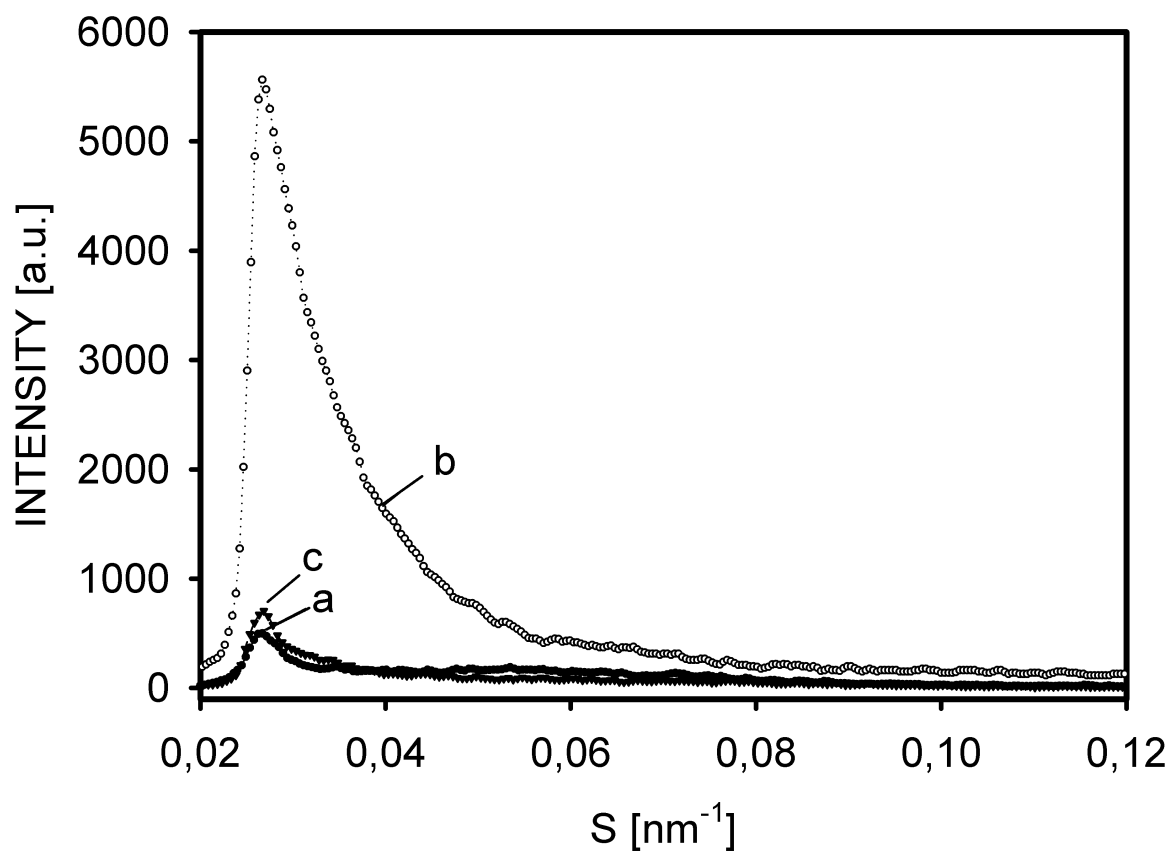


Fig. 4. The intensities of small angle x-ray scattering measured in the horizontal direction, outside the beamstop, for selected patterns presented on Fig 3.  $S$  is the scattering vector. The curves represent scattering from the non-deformed sample measured at 25 °C (a), from the sample strained to 0.2 at the temperature of 25 °C (b), and from the sample strained to 0.5 at the temperature of 70 °C (c)

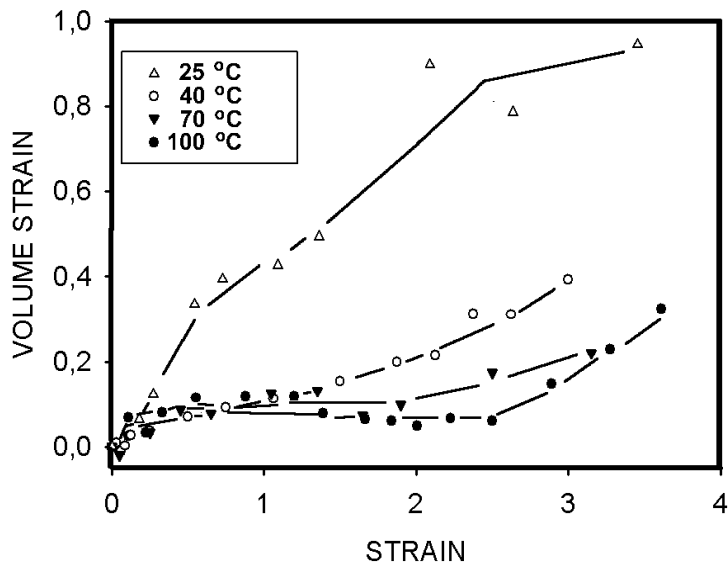


Fig. 5. Volume strain as a function of strain during tensile drawing at various temperatures.

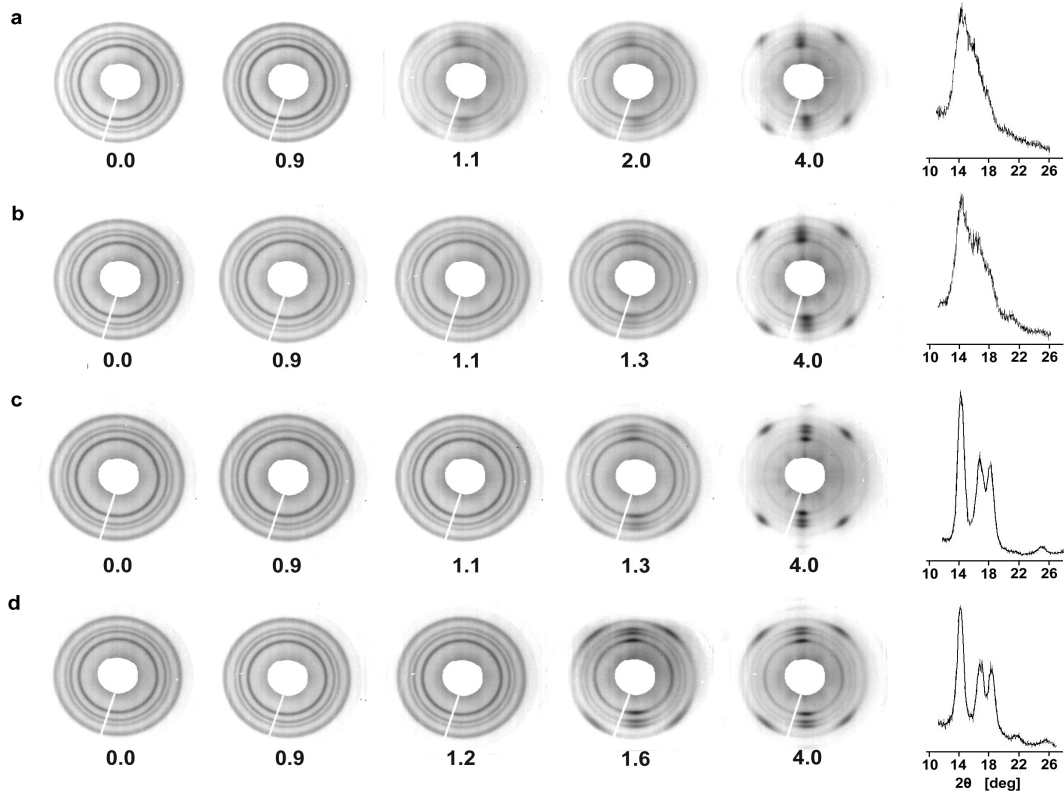


Fig. 6. Wide angle X-ray scattering from differently deformed PP samples. Numbers indicate local strains. Temperatures of deformation: a-25 °C, b-40 °C, c-70 °C, d-100 °C. Deformation direction was horizontal.

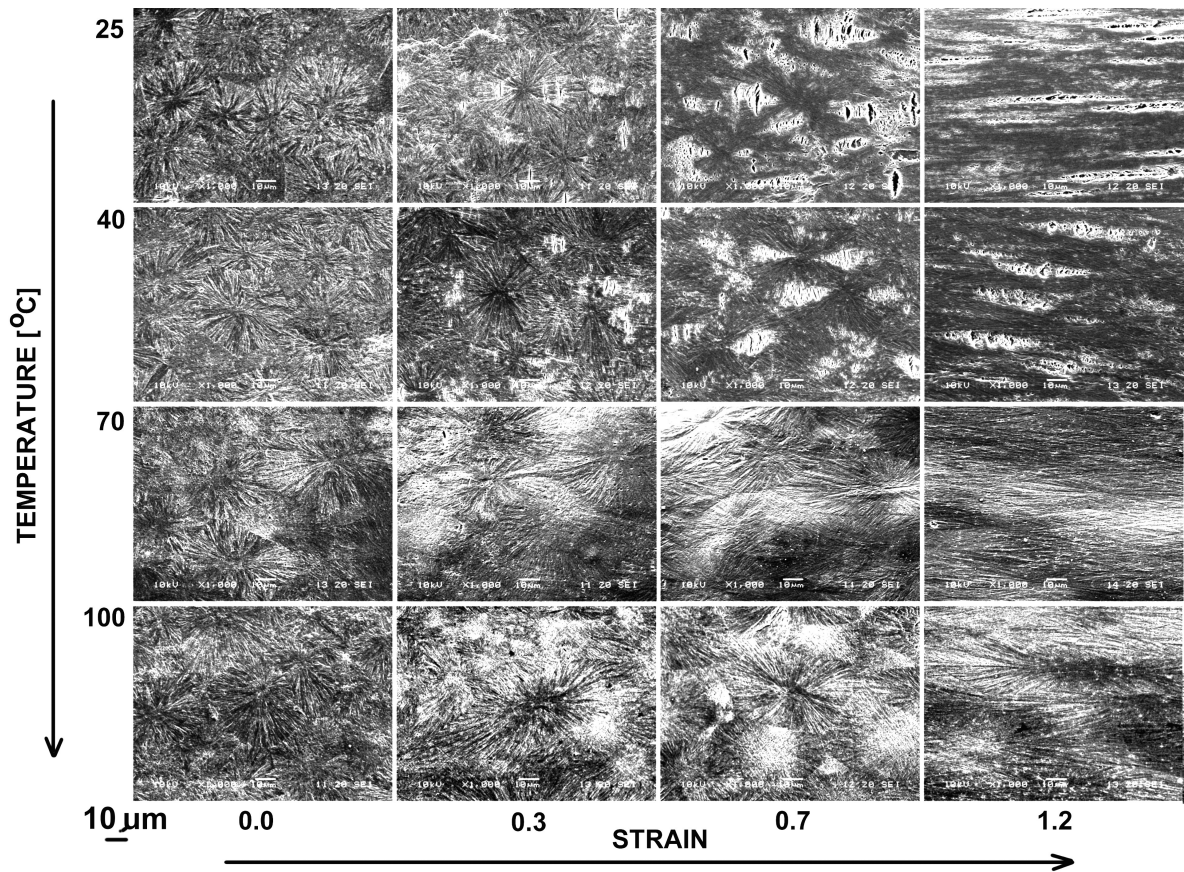


Fig 7. Evolution of internal structure of PP samples deformed at different temperatures. Morphology at different strain is presented: initial, 0.3, 0.7, 1.2. Deformation direction is horizontal.

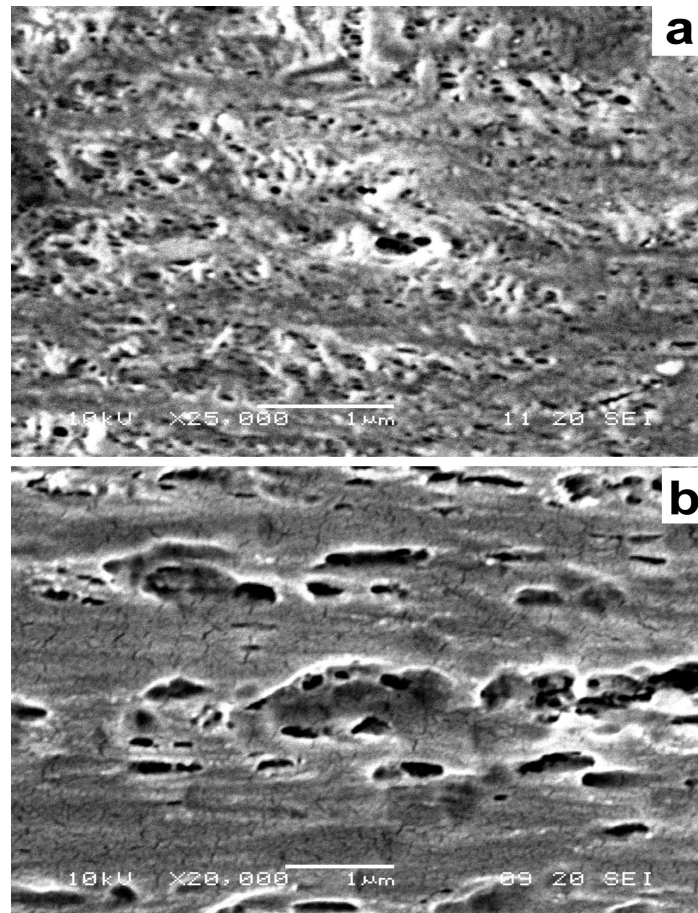


Fig. 8. Morphologies of polypropylene sample deformed to strain of 2 at the temperature of 25 °C: a) surface of sample, b) interior after etching.

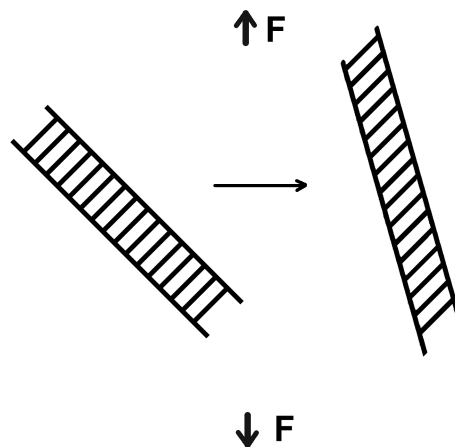


Fig. 9. Scheme of lamellae rotation in 45° fans of spherulites during tensile drawing. Associated crystallographic slip causes the reverse rotation of chain axes in crystals counterbalancing the orientation.