The cavitation in amorphous phase is often observed during tensile deformation of semicrystalline polymers. The progress in understanding of voiding mechanism and conditions at which it appears is noticed in the literature published for last 10 years. Our previous studies shown that not all polymers cavitate and that these able to cavitate do it only at some deformation conditions [1, 2]. The reason of cavitation is a competition between two possible mechanisms: plastic deformation of crystalline elements, usually by chain slips and the break of stretched amorphous phase with a formation of numerous voids. The selection of deformation way depends on the relation between strength of amorphous phase and strength of crystals. It is known that perfection and strength of crystalline lamellae may be modified by processing condition among them by annealing. Annealing in the solid state results in some increase of crystallinity degree, and in thickening of crystals. The second one is more important for cavitation process.

The subject of our studies in HASYLAB was influence of annealing in solid state on cavitation in strained high density polyethylene BASF Lupole 6021D. The presence of cavities were detected by small angle X-ray scattering (SAXS) measurements, done in situ on A2 beamline during uniaxial deformation of polymer. The time of annealing was 0, 3 or 6 hrs.

Figure 1: SAXS scattering measured in situ during the tensile test. a) non annealed sample, b) sample annealed 1 h, c) sample annealed 3 h, d) sample annealed 6 h. Numbers below photographs represents local strain in sample at the moment of SAXS registration. Arrow shows the deformation direction.
Figure 1 presents stress-strain curves for tensily deformed, differently annealed samples. It is visible that all samples deformed with the neck formation. The yield stress increases with annealing time from 21.0 MPa to 29.6 MPa. Figure 1 also illustrates the small angle X-ray scattering from our samples, recorded during mechanical deformation. It is visible that the voids formation rapidly increases scattering intensity. The scattering patterns of polypropylene change with deformation. In the case of non annealed sample (see Fig. 1a) initially only scattering from periodic crystalline structure is visible. The scattering image representing local strain of 0.5 has an additional, more intensive signal, localized in the centre. It may be interpreted as a result of limited voiding, preceded process of transformation from lamellar to fibrillar structure of polymer. The shape of signal from voids indicates their elongation perpendicular to deformation direction at strain of 0.5 and parallel to deformation direction for strains of 1.0 and more. The scattering patterns from sample annealed 1 h are similar to previously discussed, only the intensities are higher.

A really strong scattering from voids is observed for the sample annealed 3 h before the mechanical test (Fig. 1c). The vertical signal, exceeding crystalline scattering background, is seen first time for strain of 0.12, i.e. shortly before yield. The intensity rapidly increases at the yield and less strongly during further deformation. The scattering profiles evolves during the test. Initially the voids are oriented perpendicularly to deformation direction. At some moment, close to the strain of 0.7 the scattering pattern is approximately circular and for larger strain elongated perpendicularly to deformation direction. It may be interpreted as reorientation of existing voids into deformation direction. The scattering from HDPE specimen annealed 3 h is much stronger than the scattering from HDPE sample annealed 1 h. The X-ray scattering from sample annealed 6 h is similar to scattering observed for the shorter annealing time, which agrees with observation that the mechanical properties (yield) and crystal thickness are only a little larger for the samples annealed 6 h as compared with 3 h annealing. The two difference in relation to 3 h annealing material are that the total scattering intensities are slightly bigger and that the reorientation of voids occur later, at the strains of 0.8-1.0.

The results of measurements in HASYLAB strongly supports supposition about the role of crystal perfection and thickness on the process of plastic deformation of semicrystalline polymers. It was shown that the massive cavitation occur in the annealed polyethylene.

References