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Controlling Cavitation of Semicrystalline Polymers during Tensile Drawing

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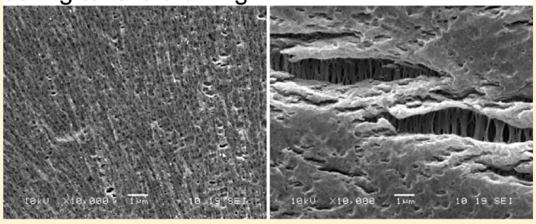
ABSTRACT: A common belief is that liquids have no strength. An example is tap water. However, liquids devoid of dissolved gases and impurities exhibit strength. By analogy, it was expected that purification would reduce cavitation and would increase polymer strength. In contrast to expectation, purified polymers exhibited surprisingly more intense cavitation during tensile deformation than pristine ones. It was concluded that cavitation is initiated in amorphous phase from homogeneous nuclei that are fluctuations of free volume. It seems that introducing a liquid penetrant into interlamellar regions should lead to filling free volume pores and to a decrease of intensity of cavitation. Polyethylene, polypropylene, and polyamide were selected for experiments. Modification of amorphous phases of polymers was conducted by introduction chloroform and hexane for polyolefins and water for polyamide. Chosen liquids penetrate amorphous phase of polymers but do not influence their crystalline phase. Samples whose amorphous phase had been filled with low molecular weight molecules remained transparent up to rupture without evidencing cavitation during tensile drawing. It appears that blocking cavitation in crystallizing polymers is possible by removing homogeneous cavitation nuclei by filling the free volume of amorphous phase of the material with low molecular weight liquids. The type of liquid is not relevant, except that it should not dissolve polymer crystals. The above observation is valid for polyethylene, polypropylene, and polyamide; however, it seems that other crystallizing polymers should also reflect similar dependencies. By infusing low molecular weight penetrants, one may control cavitation. Moreover, liquids that can be used are not limited to the ones described in the paper.

Controlling cavitation of crystalline polymers during tensile drawing



INTRODUCTION

A common belief is that low molecular weight liquids have no strength. An example is tap water. However, water devoid of bubbles, dissolved gases, and other impurities exhibits a very strong ability to transfer tensile stresses. For example, a value of −27.5 MPa at 8 °C was found for highly purified water by Briggs.[2] For other liquids their strength after purification is also significant; extensive research allowed to determine the maximum strength of some liquids and to assess the temperature at which the strength achieves the biggest value, for example: −28.8 MPa at 23 °C for acetic acid,[3] −15 MPa at 19 °C for benzene,[3] −30 MPa at 0 °C for aniline,[3] −27.6 MPa for tetrachloromethane,[3] and −31.7 MPa for chloroform.[3] It is now accepted that low strength of ordinary liquids is caused by heterogeneous nuclei that originate cavitation. However, the strength of water calculated in complete absence of any heterogeneous cavitation nuclei and using homogeneous nucleation concept gave the value of −140 MPa.[4] According to Speedy,[5] the strength of water at the temperature 35 °C is even higher and should reach up to −200 MPa.

In amorphous phases of crystalline polymers above their glass transition the stress necessary for cavitation reaches also exceptionally high values: polypropylene (−13.7 MPa),[6] poly(methylene oxide) (−35.8 MPa),[6] and polyethylene (−15.1 MPa).[6] This is very unusual considering that commodity polymers contain additives, stabilizers, low molecular weight fractions, catalyst residue, and other impurities such as dissolved gases. It was anticipated that removing those additives and impurities would further increase the strength of amorphous phase of crystalline polymers. In a recent paper by the authors the effect of removal of stabilizers, additives, and low molecular weight fractions on cavitation during tensile drawing was studied in details in polypropylene.[1] The additives were extracted from compression-molded samples, and dissolved gases were evacuated. The extract was an oily liquid composed of antioxidants, processing stabilizers, and a spectrum of low molecular weight fractions of polypropylene. In contrast to expectation, purified polypropylene exhibited surprisingly more intense cavitation than pristine polypropylene. As it was shown purification was associated with a drastic increase in free volume of the amorphous phase as it was determined by volume measurements and by positron annihilation lifetime spectroscopy.[1]

Intensification of the cavitation process in the purified samples was explained by the changes in the amorphous phase, namely the changes in free volume by eliminating low fractions and soluble additives. The dominant role of the free volume of amorphous phase, which is an integral part of unordered regions of all crystalline polymers, in formation of cavitation pores in crystalline polymers proves that initiation of the phenomenon is of a homogeneous nature. This anticipation is strongly supported by unusually high stress necessary for cavitation for several

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commodity crystalline polymers.[6] It appears also that in crystalline polymers a heterogeneous nucleation of cavitation is nearly inactive. More intense formation of cavitation pores in purified polypropylene proves that initiation of cavitation in polypropylene has a homogeneous nature.

The size of these empty spaces of free volume (0.139 nm^3 for polypropylene, average value from positron annihilation lifetime spectroscopy[1]) is considerably smaller than the thickness of amorphous layers, though it can increase under the influence of mechanical stress during tensile drawing of a polymer, which is when they may become cavitation nuclei. The amorphous phase of polymers is characterized by a more unordered structure than amorphous low molecular weight materials due to steric hindrances introduced by chemical bonds of long chains. Hence, an intrinsic element of polymers' amorphous phase is a fraction of so-called "free volume" resulting from its incomplete packing. This results in difference in density between well packed polymer crystals and amorphous phase. At the temperatures above glass transition amorphous phase exhibits certain dynamics of free volume—"empty" spaces change in time as a result of thermal movements of polymer chains.

Since purification of amorphous phase of crystalline polymers by extraction leads to an increase of free volume, then the reverse action to purification, i.e. introducing some low molecular weight mobile species, should take the place of extracted impurities and low molecular weight fraction. Therefore, it seems that introducing molecules of a low molecular weight liquid penetrant into interlamellar regions, i.e. into amorphous phase, should lead to at least partial filling of the free volume of amorphous phase and thus a decrease in size or significant elimination of the "empty" spaces which constitute an integral part of the unordered regions. Hence, introducing a low molecular weight liquid into amorphous phase, that is, to a region where cavitation is initiated, should result in a change in the intensity of the phenomenon.

Because cavitational voids at the moment of their generation are having sizes on the nanoscale level, as it follows from SAXS investigations, e.g., refs 7 and 8, there is an issue of their stability. On each nanopore the surface tension is exerted from the very beginning of their formation, which tends to close a pore. In order to preserve a pore, an action of a negative pressure is required at the level which is reciprocally proportional to the radius of a pore: $p = -2\tau_s/r$, where τ_s is the surface tension and r is the size of a pore. It follows then that for the stability or further development of small pores into cavities the negative pressure must be significantly larger than for large pores, larger than the negative pressure generated during tensile drawing. An inadequate level of negative pressure will lead to a spontaneous healing of cavitational pores, and no cavitation will be observed; otherwise, pores can grow in the course of drawing. When a fraction of large pores are filled with low molecular weight liquid, then the stress level required for cavitation should increase; one should observe less intense cavitation, or even cavitation will be suppressed.

Filling free volume pores with molecules of low molecular weight material could become a means of controlling cavitation.

In order to study the effect of penetration of molecules of low molecular weight materials into free volume pores, solidified samples of several crystalline polymers were used. Isotactic polypropylene, high density polyethylene, and polyamide 6 were selected for the studies in the form of 1 mm thick compression-molded crystallized films.

In order to avoid unwanted changes of the samples and limit the number of variable parameters, penetrants were carefully chosen based on the following criteria: (i) should not dissolve polymer crystals and (ii) should penetrate amorphous phase of polymers only.

We chose chloroform and hexane for the modification of the amorphous phases of polypropylene and polyethylene. Chloroform is a common solvent in the laboratory because it is relatively unreactive, miscible with most organic liquids, and conveniently volatile. It is known that it does not dissolve polypropylene at room temperature but swell polypropylene and polyethylene. Chloroform molecules have sizes of the order of 0.5 nm in diameter, as it was determined from the carbon−carbon radial distribution functions between two chloroform molecules.[9] They would fit perfectly into an average dynamic free volume pore of polypropylene that was measured by positron annihilation lifetime spectroscopy in our previous work.[1] We expect a similar relation for polyethylene.

The other selected penetrant, hexane, is used for removing atactic and soluble fractions of polypropylene, and it is known not to dissolve polypropylene crystals. The size of hexane molecules[10] is similar to free volume pores of polypropylene, and we expect that it is similar to free volume pores of polyethylene. Hexane was also used by others,[11,12] in a mixture with chloroform and ethyl alcohol, to extract additives and antioxidants from polyethylene or polypropylene without disturbing their crystalline structure and morphology. Hence, the modification of the amorphous phases of polypropylene and polyethylene can be conducted by introduction of chloroform or hexane.

Polyamide 6 is known to be hygroscopic due to the presence of hydrogen bonds. While amorphous phase plasticization by water sorption has been identified, water effect on the crystalline phase was not noticed. However, some authors have reported slight changes in the crystal unit cell of polyamide 6 and polyamide 66 in the presence of water.[13−17] Nevertheless, measurements of elastic modulus of the α form crystals of polyamide 6 in the presence of water strongly supports the fact that water is only absorbed by the amorphous phase.[13] Other papers describing the results of solid state nuclear magnetic resonance studies confirmed negligible water absorption in the crystals.[18−20] Hence, water seems to be appropriate penetrant for amorphous phase of polyamide 6.

Chosen liquids will penetrate amorphous phases of polymers but will not influence the crystalline phases. A gradual saturation of the amorphous phase with penetrants will allow to follow changes in cavitation process.

■ EXPERIMENTAL SECTION

Studies presented in the paper have been conducted for a number of crystalline polymers, whose deformation was accompanied by cavitation. The materials used are presented and characterized as follows. Polypropylene: Borclean HB300BF (M_w = 608 kg/mol, M_n = 72 kg/mol, M_w/M_n = 8.44; manufacturer data), of melt flow index MFI = 2.5 g/10 min (for 230 °C, 2.16 kg according to ISO 1133), by Borealis. High density polyethylene: Lupolen 6021D (HDPE) (M_w = 182 kg/mol, M_n = 25 kg/mol, M_w/M_n = 7.2; manufacturer data), of melt flow index MFI = 2.6 g/10 min (for 190 °C, 2.16 kg according to ISO 1133), by BASF. Polyamide 6: polycaprolactam (PA6) (M_w = 35 kg/mol; manufacturer data), of relative viscosity 4.1 by Polysciences, Inc.

Results presented further in the paper were obtained on the basis of a number of research methods and techniques. Measuring equipment used to characterize materials which are the subject of the paper included a tensile testing machine, scanning electron microscope (SEM), small-angle (SAXS) and wide-angle (WAXS) X-ray diffractometer, differential scanning calorimeter (DSC), and thermogravimetry (TGA).

Mechanical properties of the materials examined in the paper were assessed using a tensile testing machine (Instron 5582) of load range 0−100 kN. Shape of samples was according to ISO 527-2 standard, with 1 mm thickness and 4 mm width. The gauge length was 25 mm. Tests were performed at room temperature at a standard rate 3.3×10^{-3} s^{-1}. The actual shape of a sample during deformation was recorded using Nikon D50 digital camera. In order to determine the local strain, markers of sputter-coated gold located along the entire gauge length at a distance of 1 mm from one another were being placed on surfaces of the samples using an ion sputter coater and a mask obtained with the use of photolithography. A similar measuring technique was used earlier in the papers.[21−24]

Local strain was calculated as a change in distance between the markers according to the relation $(l - l_0)/l_0$, where l_0 is a distance between markers for the undeformed sample and l is a distance between markers for the deformed sample. Volume strain for local strains was determined using the following relation: $(V - V_0)/V_0$, where V_0 denotes the volume of the undeformed sample. To do so, a small mirror was set up during photographic register of deformation, which directed an image of the sample's thickness to a digital camera. The volume of the sample between markers was determined on the basis of a distance between markers and the thickness of the photographed sample.

Deformation of samples during small-angle synchrotron radiation scattering studies was performed on a specially designed testing machine which enabled tension of samples with a simultaneous register of SAXS scattering patterns. Symmetrically stretched samples were monitored with the use of a camera, which enabled precise calculation of local strain of the sample on the basis of change in distance between the markers. Tests were performed at room temperature at a standard rate 3.3×10^{-3} s^{-1}. Deformation was conducted for 6 s, and next a scattering pattern for a given strain (calculated on the basis of images obtained with a photographic camera, with no tension) was registered. The entire procedure was cyclically repeated up to rupture of the sample.

Thermal analysis of the examined materials was conducted using an indium-calibrated DSC apparatus (TA 2920, Thermal Analysis). Samples of total mass of 6−8 mg were being placed in aluminum pans and pressed slightly in order to ensure good contact with the DSC cell surface. The data was registered during heating at a constant rate of 10 °C/min, under nitrogen flow. The degree of crystallinity of the studied samples was determined according to the formula $X_c = \Delta H_m/\Delta H^\circ_m$, where ΔH_m is the measured specific heat of melting and ΔH°_m is the heat of fusion of the crystal. For polypropylene the value of ΔH°_m = 209 J/g has been assumed.[25] To measure the density of the samples, a gradient column with a vertical linear liquid density gradient (a mixture of ethanol and water) was used. The gradient column was calibrated with beads, whose density in temperature was determined to an accuracy of 0.0001 g/cm^3.

The desorption of penetrants was studied by means of thermogravimetry (TGA). A thermogravimetric analyzer Hi-Res TGA 2950 by TA Instruments was used with the heating rate of 1 °C/min in a nitrogen environment.

The bulk morphology of the samples was studied using a scanning electron microscope (SEM, JEOL JSM 5500LV). The internal part of a sample was exposed by cutting with an ultramicrotome (Power Tome XL, Boeckeler Instruments, Inc.) equipped with a diamond knife (Diatome Ltd.). The exposed surfaces were etched for 2 h at room temperature in a solution composed of $KMnO_4$ (0.7 wt %) dissolved in a mixture of concentrated sulfuric acid, orthophosphoric acid, and distilled water in the volume ratio 5/4/1, in accordance with the procedure proposed by Basset[26] and refined by us.[27] To improve etching, the mixture was placed in an ultrasonic bath running periodically for short time periods during the etching process (for ∼2 min every 20 min). After completion of etching, the samples were immersed into four tubes in the following order: with diluted sulfuric acid (sulfuric acid/water 2/7 vol), perhydrol, distilled water, and acetone. Washing was run in the presence of ultrasounds, so as to ensure more efficient transport from/to the surface of impurities/liquids. Dried sample was coated with a fine gold layer (about 20 nm) by ion sputtering (JEOL JFC-1200) and examined with a scanning electron microscope JEOL JSM-5500 LV. Microphotographs were registered in a high-vacuum mode at the accelerating voltage of 10 kV. Microscopic image was created using secondary electron detector (SEI).

Analysis of the crystalline structure of the materials was performed using wide-angle X-ray scattering measurements by means of computer-controlled goniometer associated coupled to a sealed-tube source of Cu Kα radiation (Philips), operating at 50 kV and 30 mA. The Cu Kα line was filtered using electronic filtering and the usual thin Ni filter.

The small-angle X-ray scattering technique was used for detection of cavities and for determination of long period. The 0.5 m long Kiessig-type camera was equipped with a tapered capillary collimator combined with additional pinholes (300 μm in diameter) forming the beam and an imaging plate as a detector and recording medium (Kodak). The camera was coupled to a X-ray source (sealed-tube, fine point Cu Kα filtered radiation, operating at 50 kV and 40 mA; Philips). The time of collection of the pattern was usually around 3 h. Exposed imaging plates were read with Phosphor Imager SI scanner and ImageQuant software (Molecular Dynamics).

In situ studies with the use of synchrotron radiation, wavelength 0.1542 nm, were performed at A2 beamline in Hasylab (Hamburg, Germany). Two-dimensional scattering patterns were registered with the use of MarCCD 165 detector (Mar Research, Norderstedt, Niemcy) of resolution 2048 × 2048 pixels. The distance between the sample and the detector was 2513 mm. The exposure time was 12 s for polyethylene and polypropylene and 30 s for polyamide 6. Long periods were determined from one-dimensional sections of 2-D pattern. Background and Lorentz corrections were applied to the curves. A long period was then calculated from position of the maximum of corrected curves using the Bragg law.

From 1 mm thick polymer films, obtained by compression molding and cooled between metal plates, samples were cut out for mechanical and X-ray studies. The first batch of samples (soaked samples: SS) has been placed in a vessel containing a penetrant for the period of at least 72 h in order to obtain full saturation of the amorphous phase of the material with a low molecular weight liquid. The second batch of samples (reference samples: RS) provided reference material. We selected chloroform and hexane for polyolefins and water for polyamide as low molecular weight penetrants.

■ RESULTS

The modification of amorphous phases of polymers was conducted by introduction of chloroform and hexane for polyolefins and water for polyamide.

Modification of the Amorphous Phase of Polypropylene with Chloroform and Hexane. From 1 mm thick film, obtained by compression molding at the temperature of 230 °C and cooled between metal plates, samples were cut out for mechanical and X-ray studies. The first batch of samples (soaked sample: SS) has been placed in a vessel containing a penetrant (chloroform or hexane) for the period of at least 72 h in order to obtain full saturation of the amorphous phase of the material with a low molecular weight liquid. The second batch of samples (reference sample: RS) provided reference material.

In order to estimate the amount of modifier present in the examined materials on completion of the conditioning process,

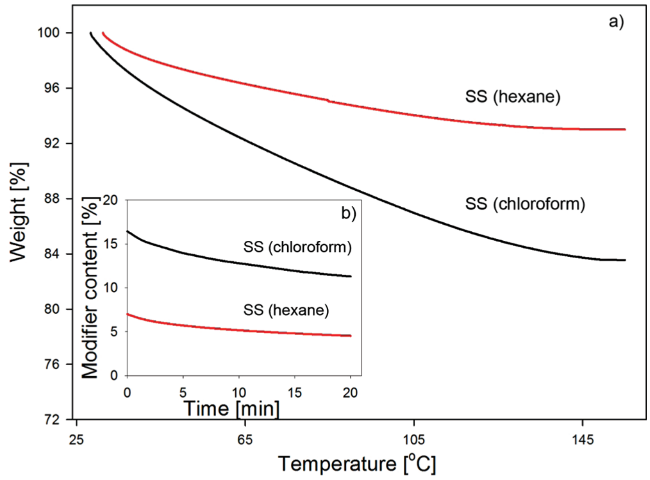

Figure 1. Modifier-soaked polypropylene: (a) TGA thermogram of weight loss in air: chloroform (black), hexane (red). (b) Kinetics of modifier desorption for SS samples, after removal from a liquid, under laboratory conditions: chloroform (black), hexane (red).

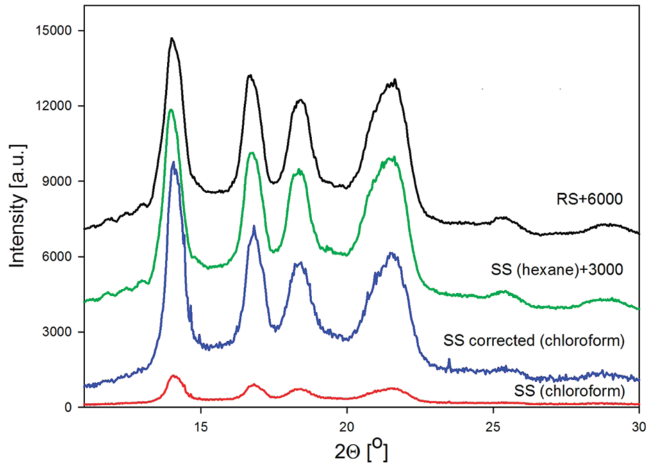

Figure 2. Diffractograms in transmission of polypropylene samples: saturated with modifiers, SS, and reference, RS. Diffraction intensity for SS sample (chloroform) was corrected for X-ray absorption, SS corrected. Curves RS for plain PP and SS for hexane-soaked PP shifted up for better visualization.

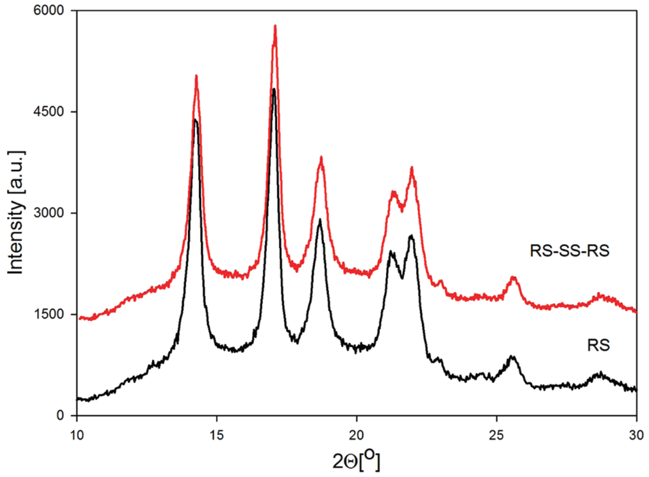

Figure 3. Diffractograms of RS and RS−SS−RS polypropylene samples. Curves have been shifted along the vertical axis for better visualization.

TGA examination has been conducted in nitrogen. Figure 1 presents the relevant thermograms of weight loss.

The amount of modifiers has been estimated (18 wt % (12.3 vol %) in the case of chloroform, 7.2 wt % (10.7 vol %) in the case of hexane) in the analyzed materials on completion of the conditioning process. Additionally, Figure 1b presents the kinetics of penetrants desorption at room temperature on extraction of the material from the conditioning vessel. Desorption of penetrants under laboratory conditions was found to be a relatively quick process; therefore, all measurements were performed within a minute after removal of the modifier-soaked sample from the conditioning vessel.

Figure 2 presents WAXS diffractograms for reference (RS) and modified (SS) polypropylene. In the case of the SS sample (chloroform) significant reduction in the intensity of peaks is observed, which is the result of the introduction of chlorine atoms strongly absorbing X-ray radiation. The diffraction curve for SS sample in transmission was corrected based on the following equation:

$$I = I_0 \exp[-\mu t/\cos(2\Theta)]/\mu/[1 - 1/\cos(2\Theta)]\{1 - \exp(-\mu t[1 - 1/\cos(2\Theta)]\} \qquad (1)$$

where μ is the increase of absorption of the sample caused by introduction of penetrant, 2Θ is the diffraction angle, and t is actual thickness of the sample. The corrected curve for SS sample plotted in Figure 2 is nearly identical with the diffraction curve for RS sample. It means that introduction of chloroform to polypropylene has not disturbed crystalline structure of the sample, neither the level of crystallinity, peak height and width, nor crystallographic form.

The diffraction profile for hexane-soaked sample also indicates no significant differences of diffraction reflections in height and width, which indicates no changes in the crystalline structure of the material caused by the penetrant.

DSC thermograms (not presented here) indicate the lack of substantial changes in the crystalline structure of the material as a result of sorption and desorption of the penetrants: the melting peak temperature of polypropylene samples before sorption was 164.7 ± 0.2 °C and heat of melting 98.4 ± 0.2 J/g while after sorption and desorption of chloroform the melting peak temperature was 164.4 ± 0.2 °C and heat of melting 98.9 ± 0.2 J/g; after sorption and desorption of hexane the melting peak temperature was 164.4 ± 0.2 °C and heat of melting 98.9 ± 0.2 J/g.

In order to further check whether chloroform is not affecting crystalline phase of polypropylene, a WAXS diffractogram was recorded for polypropylene sample prior to the conditioning process (RS) and for the material which was initially saturated with chloroform and next deprived of penetrant as a result of the drying process (RS−SS−RS).

Wide-angle X-ray diffraction measurements presented in Figure 3 indicate not only complete reversibility of the process of chloroform sorption but also the lack of significant changes in the crystalline structure of polypropylene as a result of introduction and desorption of the penetrant. The presented results indicate that chloroform sorption occurs exclusively in the area of

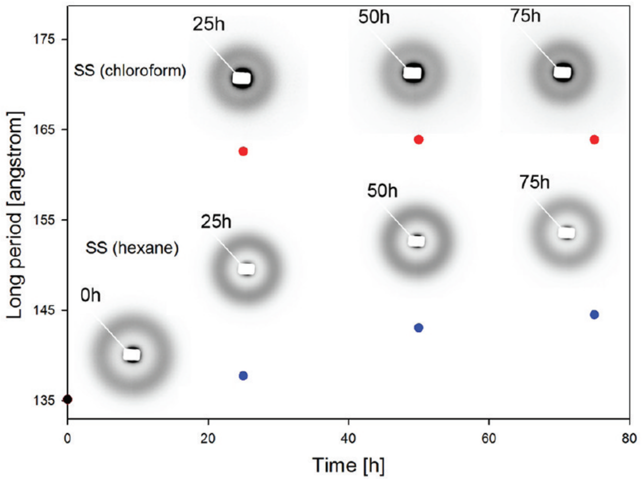

Figure 4. Change in a long period of polypropylene as a function of time of sorption of chloroform and hexane.

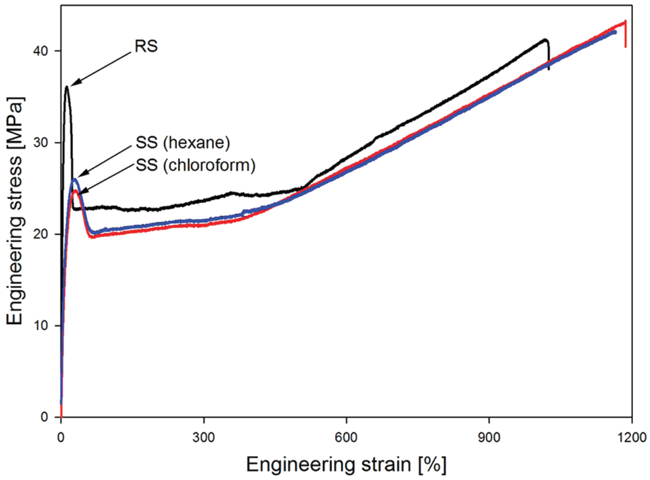

Figure 5. Engineering strain—engineering stress curves for samples of unmodified polypropylene and saturated with modifiers. Deformation rate: 3.3×10^{-3} s^{-1}.

amorphous phase of material, and it is mainly there that the molecules of low molecular weight penetrant accumulate.

Figure 4 presents results of a measurement of a long period as a function of time of sorption of a low molecular weight penetrant (chloroform and hexane). Clear changes in the values of a long period in the samples saturated with a low molecular weight penetrant (13.5 nm for reference sample, 16.4 nm for chloroform-soaked sample, 14.4 nm for hexane-soaked sample), with minor changes in the crystalline regions, indicate an increase in the interlamellar distances as a result of strong swelling and deformation of unordered regions with molecules of chloroform. However, the parameters of the crystalline phase of soaked sample, as proved by X-ray examinations, remain unchanged as a result of chloroform/hexane sorption.

Figure 5 presents engineering strain—engineering stress curves for polypropylene samples subjected to tensile drawing up to fracture. Deformation of unmodified and modifiers-soaked polypropylene was accompanied by the necking process. Deformation of unmodified polypropylene within the region of macroscopic yield point was accompanied by intense whitening of the material, which is the evidence of intense cavitation. At the same time the sample, whose amorphous phase had been filled with low molecular weight molecules (chloroform or hexane) remained transparent up to rupture without evidencing cavitation. The analysis of curves presented in Figure 5 indicates, moreover, strong dependence of stress at yield point on the presence of a penetrant filling the amorphous phase of material. The stress field in lamellae stacks is more complicated than simple osmotic pressure because there is no retraction of the material along lamellae basal planes. Hence, the amorphous phase is subjected to uniaxial tension rather than pressure. Amorphous phase pulls crystals with the uniaxial stress. Since the macromolecular network in the amorphous phase is subjected to uniaxial tension, then a negative pressure is generated. Instead, a penetrant is subjected to positive pressure. Measured stress at yield plus tensile stress from the swollen extended amorphous phase amounts exactly to the stress required for plastic deformation of crystals. This effect is of rather complicated nature and will be the subject of a forthcoming paper.

In order to establish the influence of the presence of molecules of a low molecular weight penetrant, within the amorphous phase of the material, on the phenomenon of cavitation accompanying deformation of unmodified material, small-angle X-ray scattering (SAXS) measurements were performed. Scattering patterns presented in Figure 6 were performed during *in situ* studies using synchrotron radiation.

In the case of unmodified polypropylene the first signals on SAXS scattering patterns evidencing the presence of cavitation in the material were already observed at the local strain equal to 0.08. The registered signal indicates that cavities at this deformation stage are of ellipsoidal shape, forced by the lamellar structure of the material, and are oriented by their long axis perpendicularly to the direction of deformation (signal in the meridional region on a scattering pattern). At further deformation stages an increase in the intensity of the registered signal is observed in the mentioned scattering pattern up to the local strain of 0.8. Meanwhile, a less intense, markedly thin signal is noted in the equatorial region on a scattering pattern for the deformed sample up to the local strain of 0.3. Such shape of scattering pattern obtained for the deformed material evidences the presence of dilatation gaps occurring during deformation of material. The characteristic feature of such discontinuities is the presence of highly deformed parts of material in the form of fibrils which create a peculiar kind of structure of the dilatation gaps. Openings occurring between the neighboring fibrils, which are elongated parallel to the direction of deformation, contribute to X-ray scattering in the way presented in the mentioned scattering pattern.

Deformation of unmodified polypropylene is therefore accompanied by formation of numerous small cavities in the range below tens of nanometers (Figure 7a) as well as individual dilatation gaps occurring mainly in the equatorial region of spherulites (Figure 7b).

In the case of unmodified samples with a higher degree of deformation (>0.8) an increase in the intensity of the scattering signal is observed in the equatorial region at the expense of the signal in the meridional region. The observed change is an effect of the reorganization of the shape of cavities, which orient themselves in the direction of the applied stress as a result of activation of subsequent plastic deformation mechanisms. Finally, for the samples with a degree of deformation of 3.5 or more, the signal narrowing in the equatorial region of a scattering

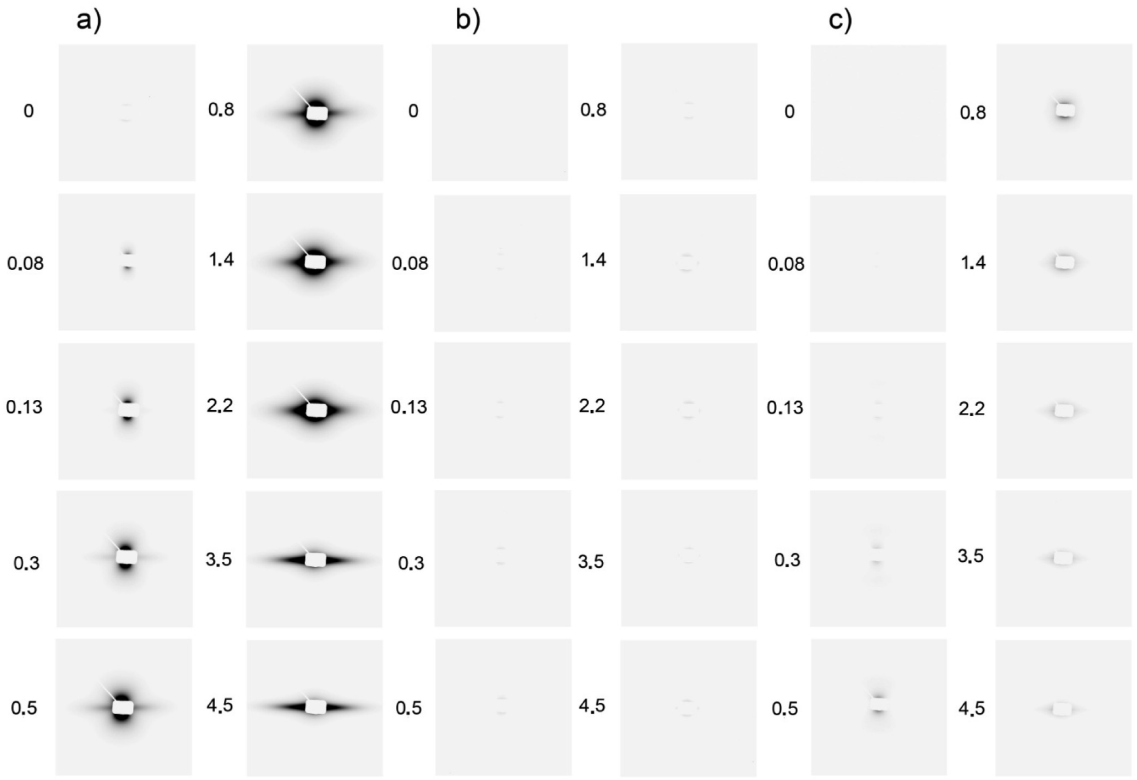

Figure 6. Small-angle X-ray scattering patterns of a series of polypropylene samples: (a) RS; (b) SS (chloroform); (c) SS (hexane). Numbers correspond to local strain of samples. Direction of deformation: vertical.

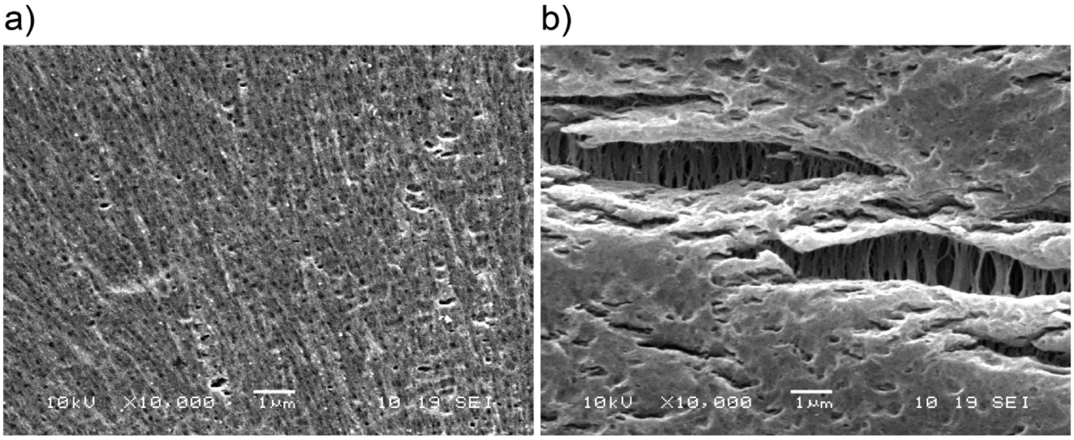

Figure 7. Microphotographs of polypropylene sample deformed to the local strain of 0.5. Details of bulk morphology exposed by sectioning and etching. Direction of deformation: vertical. (a) Polar region of spherulite; (b) equatorial region of spherulite.

pattern appears, which evidence the high degree of orientation of markedly thin cavities. It is difficult, based on small-angle X-ray scattering measurements, to assess changes that occur in the dilatational gaps on further (>0.8) stages of deformation; however, SEM microphotographs (not presented here) indicate a rapid increase in their size combined with the reorganization of shape and destruction of fibrillar structure. Such changes in the morphology of the material are outside detection of the SAXS method.

Scattering patterns presented in Figure 6b performed for modifiers-soaked polypropylene, for local strains analogous to RS sample, indicate complete elimination of the phenomenon of cavitation. No signals indicating formation of discontinuities in the material, both cavities and dilatation gaps, are noted up to the local strain of 4.5. Filling the free volume of the amorphous phase of material successfully eliminates this kind of material response.

In order to check whether the lack of signals on SAXS scattering patterns (Figure 6b) for modified samples, in the case of chloroform-soaked samples, is an effect of elimination of cavitation and not the strong X-ray absorption of chlorine atoms from chloroform filling the amorphous phase of material, small-angle X-ray scattering studies were performed for samples, from which

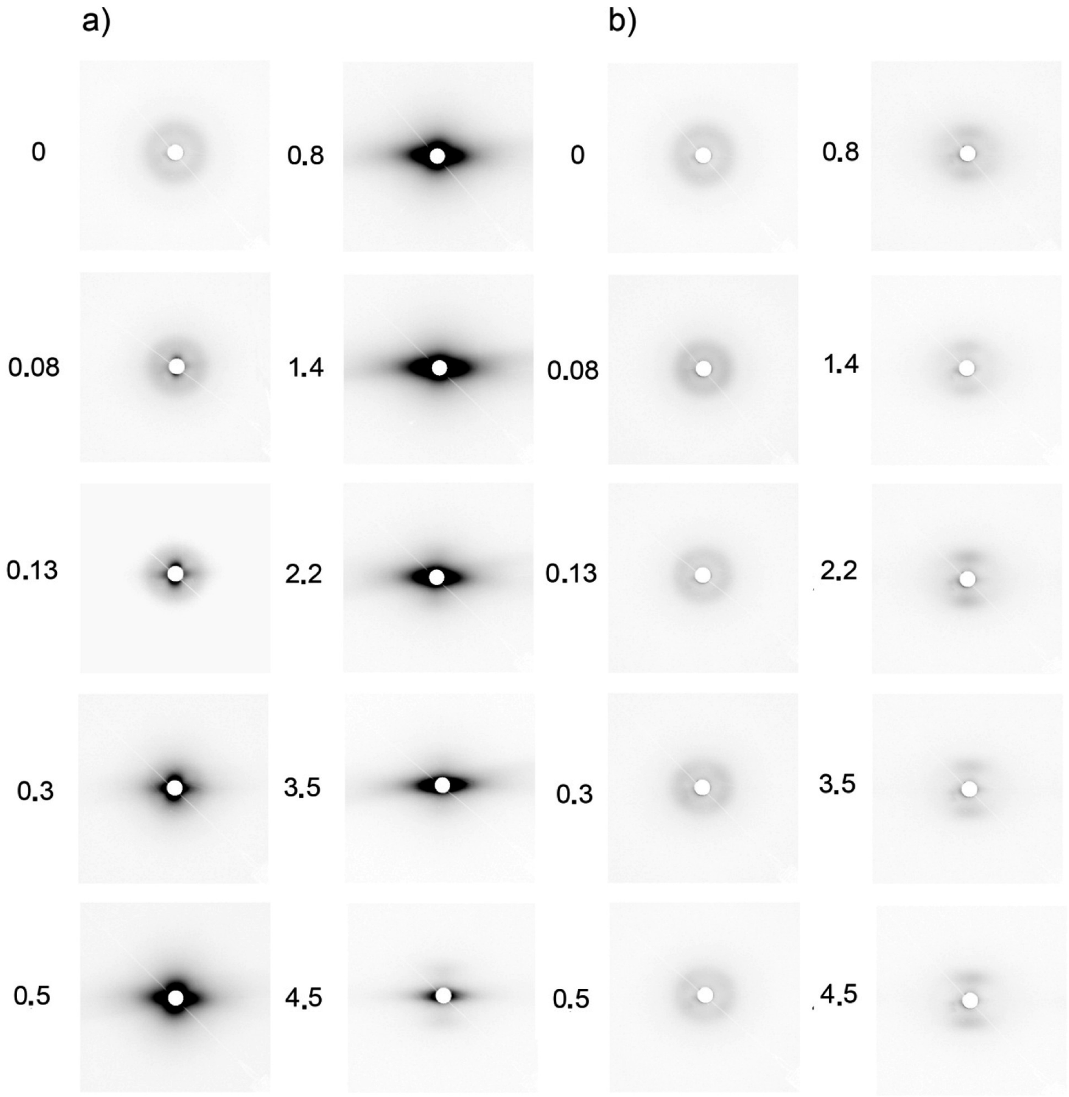

Figure 8. Small-angle X-ray scattering patterns of a series of polypropylene samples: (a) RS; (b) SS (chloroform). Numbers correspond to local strain of samples. Direction of deformation: vertical. SS samples, in the strained state, were being dried at the temperature of 40 °C in order to remove a low molecular weight penetrant. RS samples were subjected to an analogous procedure.

a low molecular weight penetrant was removed after the deformation process. SS samples deformed to selected strains were fixed in a special frame, which enabled removal of the sample from a testing machine while retaining the strain state in the material. Next, the penetrant was removed from samples by drying at the temperature of 40 °C to constant weight. An analogous procedure was applied for unmodified material in order to obtain the reference data. For such prepared samples small-angle X-ray scattering (SAXS) measurements were conducted as presented in Figure 8.

The presented scattering patterns confirmed the results of *in situ* small-angle X-ray scattering (SAXS) studies using synchrotron radiation. Deformation of unmodified polypropylene (Figure 8a) is accompanied by an intensive cavitation process. The first cavities begin to appear at the local deformation equal to 0.08. At further stage of deformation one also observes appearance of dilatation gaps. The presence of this type of discontinuities is manifested by an additional signal in the equatorial region of scattering pattern. For RS polypropylene samples of a higher degree of deformation, an increase in the intensity of the signal is registered in the equatorial region of scattering pattern at the expense of signal in the meridional zone. The observed changes are the result of the reorganization of the shape of cavities at this stage of deformation of the material. Continuing deformation (>1.4) make the cavities become thinner and elongated parallel to the direction of deformation.

Scattering patterns recorded for SS samples after removal of low molecular weight penetrant confirm earlier conclusions that filling the amorphous phase of material leads to elimination of cavitation during deformation of the material (Figure 8b). Examinations performed after chloroform desorption not only indicate that the process of formation of discontinuities (cavities, dilatation gaps) could be entirely eliminated in SS samples but also enable to trace the changes occurring in the lamellar structure on subsequent stages of deformation. Isotropic signal, typical of nonoriented material, transforms into a four-point pattern with the strain increase (0.3). Such image is an evidence of the formation of two populations of lamellae oriented at an acute angle to

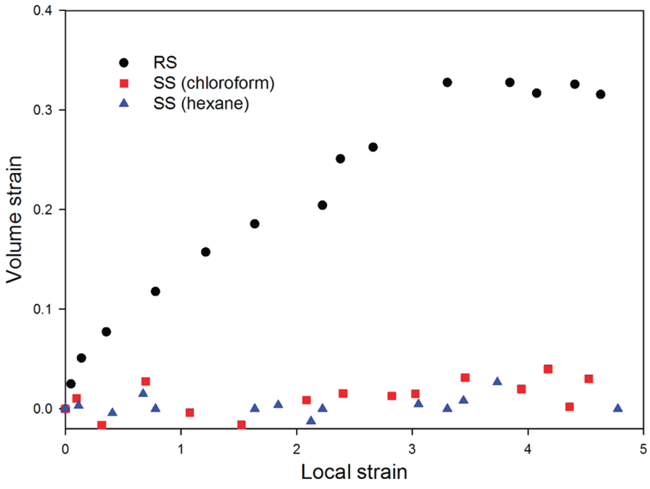

Figure 9. Volume strain as a function of local strain for unmodified polypropylene (RS), saturated with chloroform (SS, red), and saturated with hexane (SS, blue).

the direction of deformation. With the strain increase, the angle between the normals of lamellae and the direction of the applied force decreases. This evidence a systematic change in the direction of lamellar arrangement in the material. Finally, for the local strain of 0.8 or more, a two-point signal is observed in the polar region, which indicates lamellar arrangement (fragments of lamellae) perpendicularly to the direction of deformation.

Such analysis was not possible for cavitating samples because of strong signal from cavities. Only for samples with high strain (4.5), the signal from lamellae can be observed, as in the case of a sample SS, in the meridional region of diffractogram, which testifies to the similar arrangement of lamellae in the material.

Conclusions supported by X-ray examinations, indicating appearance of cavitation in RS samples and excluding the phenomenon in the modified polypropylene samples, are also confirmed by the results of volume strain measurements (Figure 9). Deformation of samples of unmodified polypropylene is accompanied by a significant volume increase (by ~30%), an effect of formation of cavities and dilatation microcracks. Filling the free volume of the amorphous phase of a polymer with a low molecular weight penetrant, chloroform or hexane, eliminates the process of formation of discontinuities in the material, which is manifested by the lack of volume change of samples during their deformation.

In order to check whether the low molecular weight penetrant fills the free volume of the amorphous phase of the material, density measurements of reference and modified material were performed. Macroscopic swelling of the sample should be in fact also related to the process of filling free spaces within the amorphous phase of a polymer. In such a case, the volume of the modifier introduced to the material should be higher than a change in volume of the sample as a result of saturation. Because of fast modifier desorption, density measurements of fully saturated sample were not possible. The density measurement were performed ~16 h after removal of the sample from the conditioning vessel. After 16 h the sample has still a considerable content of the penetrant; however, the rate of the desorption process becomes relatively slow. Relevant measurements and calculations showed that the chloroform-soaked sample increased its volume by 0.033 39 (0.032 75 in the case of hexane), whereas 0.035 76 was the relative volume of infused chloroform (0.034 15 in the case of hexane). The volume of a low molecular weight penetrant introduced during modification of the material is higher than the change in the volume of the sample as a result of saturation. This indicates filling of pores of the free volume of amorphous phase of the material at the level of 0.24% (0.14% in case of hexane) of the volume of the sample before saturation. One may assume that in the sample fully saturated with low molecular weight molecules of a penetrant (immediately after removal of the sample from the conditioning vessel) the degree of saturation of the free volume of the amorphous phase is much higher.

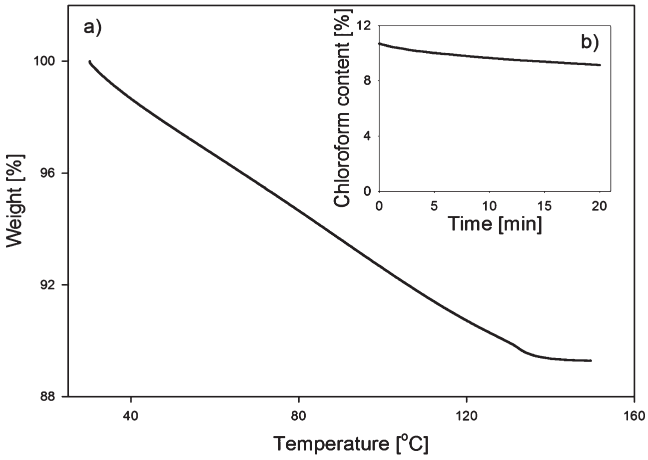

Figure 10. Chloroform-soaked polyethylene: (a) TGA thermogram; (b) desorption kinetics of chloroform for SS sample under laboratory conditions, after removal from a liquid.

Modification of the Amorphous Phase of Polyethylene. Samples for tests were cut out from film, 1 mm thick, prepared by compression molding. The first batch of samples (soaked sample: SS) was placed in a vessel containing a penetrant (chloroform) in order to obtain full saturation of the amorphous phase with a low molecular weight liquid, whereas the second batch of samples (reference sample: RS) was not subjected to conditioning and provided reference material. The process of saturation of material with chloroform was run for at least 72 h (up to full saturation of the amorphous phase).

In order to determine the quantity of chloroform present in the examined material on completion of the conditioning process, the TGA thermogram presented in Figure 10a has been recorded. On the basis of the above thermogram, the amount of chloroform in the examined material on completion of saturation has been determined as 10.7 wt % (7.2 vol %). Figure 10b also presents desorption kinetics of a modifier at room temperature after removal of the material from the conditioning vessel. The desorption of penetrant under laboratory conditions was found to be a relatively slow process; however, some changes in the chloroform content after removal of the sample from a liquid made it necessary to perform all measurements within a maximum of 2 min after removal of the samples from the conditioning vessel.

Figure 11 presents WAXS diffractograms of RS and SS samples. The nature of the presented curves demonstrates no significant changes in the crystalline structure of the material as a result of chloroform sorption. Only decrease in the intensity of individual peaks is observed with the saturated sample, an effect of the introduction of chlorine atoms strongly absorbing X-ray radiation.

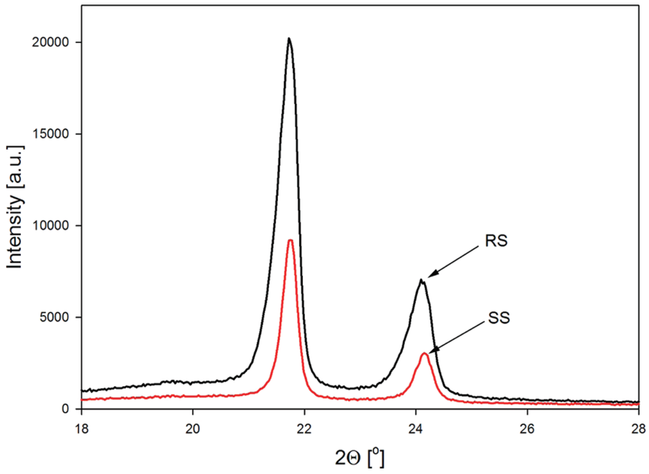

Figure 11. Diffractograms of polyethylene samples: RS: reference sample; SS: sample soaked in chloroform.

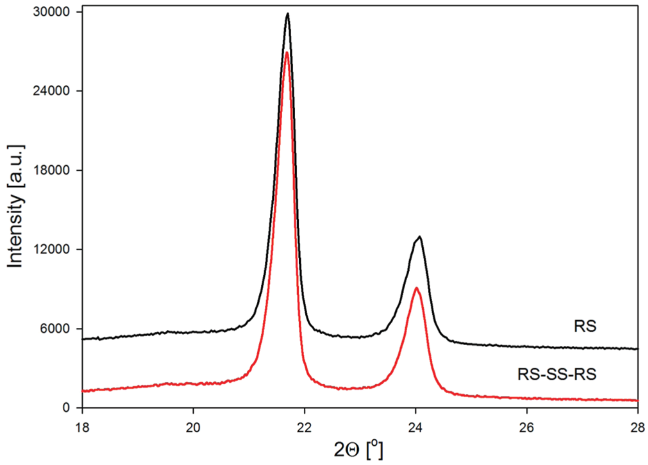

Figure 12. Diffractograms of polyethylene samples. Curves have been shifted along the vertical axis for better visualization.

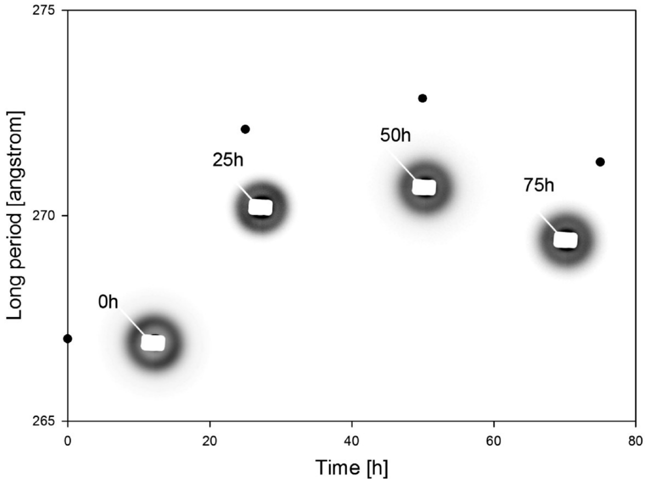

Figure 13. Change in a long period of polyethylene as a function of time of sorption of chloroform.

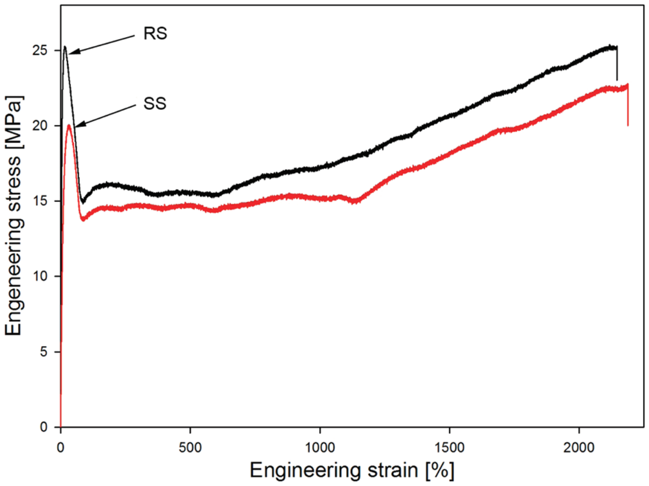

Figure 14. Engineering strain—engineering stress curves for samples of unmodified polyethylene and saturated with chloroform. Deformation rate: 3.3×10^{-3} s^{-1}.

Figure 12 also presents diffractograms of a polyethylene sample prior to the conditioning process (RS) and of the material saturated with chloroform and then deprived of the penetrant as a result of the drying process (RS—SS—RS). Presented wide-angle X-ray scattering measurements demonstrate not only complete reversibility of the sorption process of chloroform but also the absence of any changes in polyethylene crystals as a result of the introduction and desorption of a penetrant. No changes in the parameters of polyethylene crystals prove a low molecular weight penetrant to be localized in the amorphous phase of the material.

DSC thermograms (not presented here) also indicate the lack of substantial changes in the crystalline structure of the material as a result of sorption and desorption of the penetrant: the melting peak temperature of polyethylene samples before sorption was 134.2 ± 0.2 °C and heat of melting 201.5 ± 0.5 J/g, while after sorption and desorption of chloroform melting peak temperature was 134.6 ± 0.2 °C and heat of melting 203.1 ± 0.5 J/g.

Figure 13 presents results of measurements of a long period of polyethylene samples as a function of sorption time of a low molecular weight penetrant (chloroform). Changes in the values of a long period in the samples saturated with a low molecular weight penetrant (26.7 nm for reference sample, around 27.2 nm for soaked sample), with no changes in the crystalline regions, indicate an increase in the interlamellar distances as a result of strong swelling (deformation) of unordered regions with molecules of chloroform.

Figure 14 presents engineering stress—engineering strain curves for polyethylene samples subjected to tensile drawing. Deformation of unmodified polyethylene and saturated with chloroform was accompanied by the necking process. During deformation of the unmodified polyethylene strong whitening of the material occurred in the macroscopic yield point region, whereas the sample saturated with chloroform remained transparent up to rupture. Again this effect was roughly explained in the section Modification of Amorphous Phase of Polypropylene and will be the subject of a forthcoming publication.

In order to assess the impact of the penetrant filling the amorphous phase of material on the phenomenon of cavitation

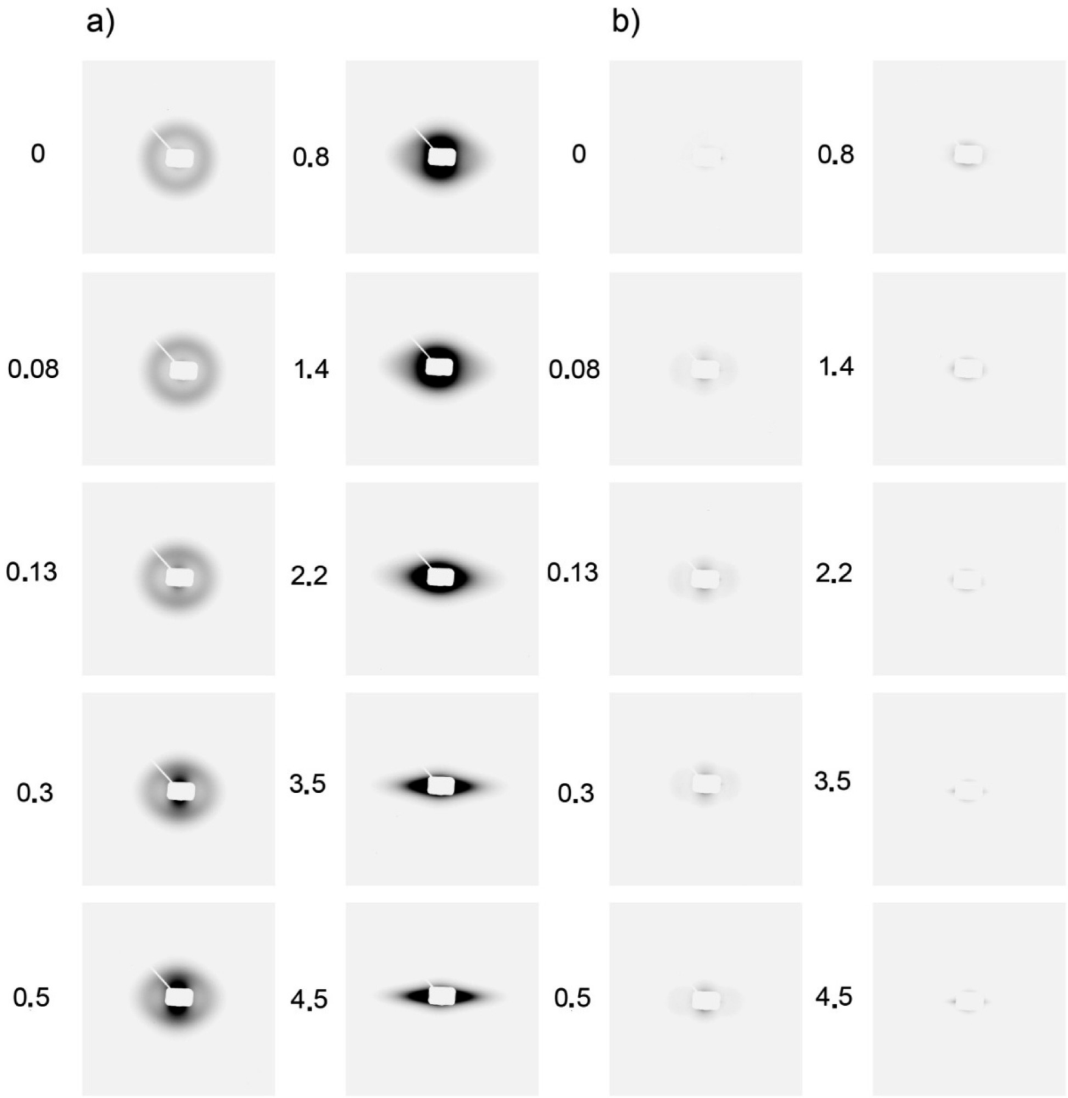

Figure 15. Small-angle X-ray scattering patterns obtained *in situ* during deformation of a series of polyethylene samples (a) RS and (b) SS. Numbers correspond to local strain of samples. Direction of deformation: vertical.

during tensile drawing, *in situ* small-angle X-ray scattering (SAXS) studies using synchrotron radiation have been conducted. Figure 15 presents SAXS scattering patterns recorded for subsequent deformation stages of unmodified and chloroform-soaked polyethylene samples.

Analysis of the presented scattering patterns proves a significant influence of the filling of the free volume of amorphous phase with a low molecular liquid on the phenomenon of cavity formation in polyethylene during its deformation. With unmodified polyethylene, the first signals on SAXS scattering patterns, indicating formation of discontinuities in the material, are observed at the local strain of 0.3. The recorded signal suggests that cavities at this stage of deformation, similarly as in the case of polypropylene, are of ellipsoidal shape and are oriented by their long axis perpendicularly to the direction of deformation (signal in the meridional region on a scattering pattern). At further deformation stages an increase in the intensity of the registered signal occurs in the said region of scattering pattern, up to the local strain equal to 0.8. At this stage the maximum intensity of signal in the scattering pattern was reached, and further deformation of the material is accompanied by strong scattering in the equatorial region at the cost of signal in the meridional region. This indicates change in the shape of cavities in relation to the direction of deformation. Cavities initially oriented perpendicularly to the direction of the applied stress, beyond the local strain of 0.8, are oriented parallel. Above the local strain of 2.2 one observes a strong, thin signal, mainly in the equatorial region, indicating strong orientation of cavities generated in the material parallel to the direction of the applied stress.

Deformation of polyethylene penetrated with a low molecular liquid is not accompanied by the process of formation of cavities. On the presented scattering patterns (Figure 15) up to the local strain of 4.5 one does not observe signals, indicating formation of discontinuities in the examined material. Filling the free volume of amorphous phase of the material effectively eliminates generation of cavities.

Conclusions drawn on the basis of small-angle X-ray scattering measurements are also confirmed by the volume strain measurements performed for the examined materials (Figure 16). Deformation of unmodified polyethylene is accompanied by a strong

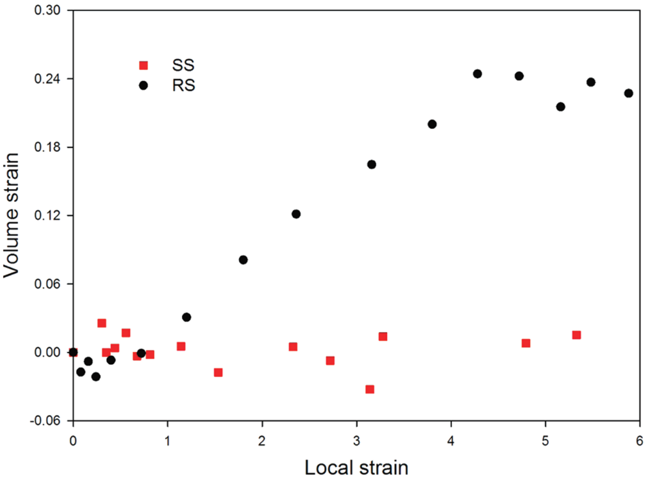

Figure 16. Volume strain as a function of local strain for unmodified (RS) and chloroform-soaked (SS) polyethylene.

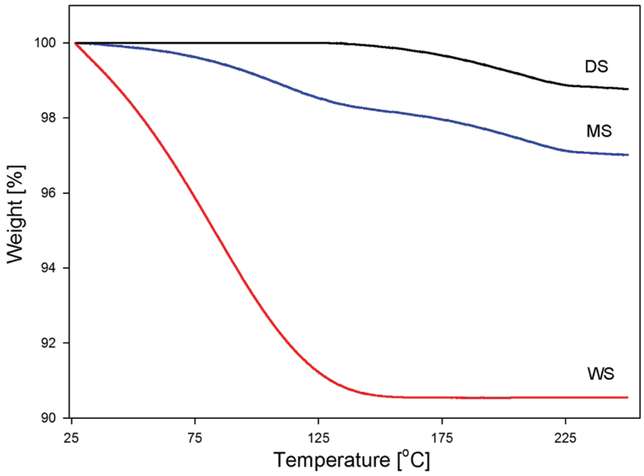

Figure 17. TGA thermograms of polyamide 6 samples of different water content.

volume increase of the sample (up to ∼25%) as a result of cavities generated in the material. X-ray examinations showed that the first cavities appear at the local strain equal to 0.3. Volume strain measurement, as a method less sensitive to subtle changes occurring in the material, demonstrates that only at a strain equal to 0.7 detectable discontinuities are generated in the material.

Volume strain measurements performed for polyethylene modified with chloroform prove the absence of changes in the morphology of the material (presence of cavitation) which would result in volume increase of the sample.

Modification of the Amorphous Phase of Polyamide 6. In the case of polyamide 6 we chose water as a low molecular weight penetrant of its amorphous phase. There are several reports indicating that water infused into amorphous phase of polyamide 6 while crystalline phase is unaltered (see for example Seguela et al.[28] and references cited therein). Three types of samples of polyamide 6 of different water content have been prepared. Samples for studies were cut out from 1 mm thick film, prepared by compression molding. In order to standardize the water content and the crystalline structure of the analyzed material, the prepared samples were annealed under vacuum at 105 °C to a

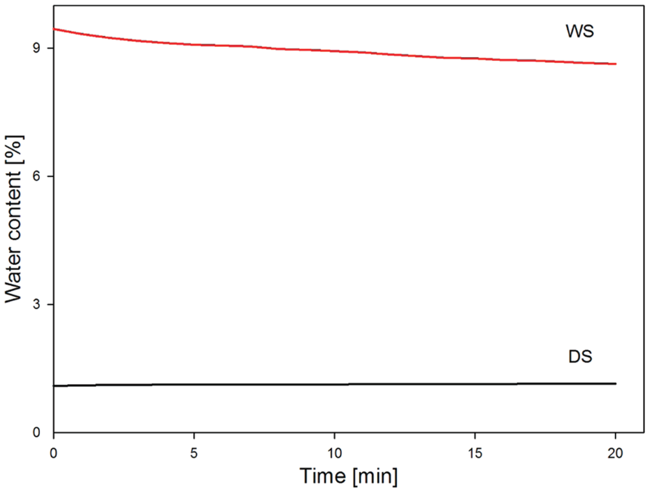

Figure 18. Kinetics of sorption (for DS sample) and desorption of water (for WS sample) under laboratory conditions (relative humidity around 50%, temperature 23 °C).

constant weight. After drying, the first batch of samples (DS: dry sample) was immediately placed in a container with phosphorus(V) oxide. The applied procedure enabled to retain low water content in the samples. Another group of samples (MS: moist sample) was subjected to conditioning under laboratory-like conditions (temperature 23 °C, relative humidity around 50%). The last batch of samples (WS: wet sample) was immersed directly in distilled water to obtain a material with the maximum content of penetrant. For each group of samples conditioning in the given conditions ran for at least 72 h.

Figure 17 presents TGA thermograms recorded for samples of polyamide 6 of different water content. The conditioning procedure of the samples discussed in the previous paragraph, allowed to obtain the material of clearly different modifier content (water). As expected, samples placed in a container filled with a highly hygroscopic substance immediately after the annealing process were characterized by the lowest humidity (1.1%). Samples conditioned at the humidity around 50%, due to a natural tendency of polyamide 6 to absorb water, contained nearly 3 times more water (2.95%). Samples immersed directly in water contained the highest amount of water. For such conditioned samples water content was estimated as 9.45%.

Sorption of water by DS samples after removal from a conditioning vessel, and desorption of penetrant at room temperature for samples with the highest water content, WS (Figure 18) removed from a liquid, are relatively slow processes. Hence, one could assume relative stability of the penetrant content in the examined material, especially during mechanical and X-ray studies.

Figure 19 presents WAXS diffractograms for polyamide 6 samples of different water content. The presented profiles indicate no significant changes in the crystallographic structure of the samples (α-phase: monoclinic with characteristic peaks located at $2\theta = 20.3°$ and 23.3°, corresponding to crystallographic planes (200) and (002) + (202)), as a result of introduction of a modifier, which is confirmed by the literature data[13] demonstrating that during sorption of water modifier is preferentially accumulated in the amorphous phase of the material. One can only observe a slight separation (shift of the maximum of the peak corresponding to crystallographic plane (200) toward lower values of 2θ angle and shift of the signal from (002) + (202)

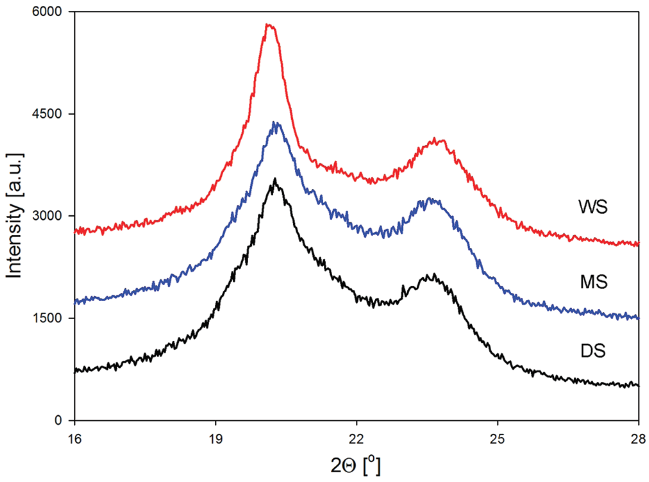

Figure 19. Diffractograms of PA6 samples of different water content. Graphs have been shifted along the vertical axis for better visualization.

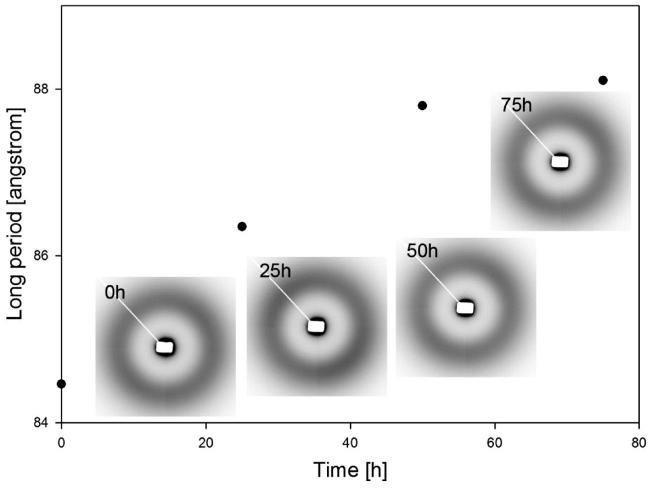

Figure 20. Change in a long period of polyamide 6 as a function of time of sorption of water.

planes toward higher values of 2θ angle) of the registered peaks of the crystalline component. The phenomenon was registered during wetting and annealing of polyamide 6.[18,29,30] Separation of peaks of the crystalline component initiated by wetting of the material is a reversible process. In both cases, the change in the position of the mentioned signals is interpreted as a change in the crystal perfection.[18,29,30]

Figure 20 presents measurement results of a long period as a function of time of sorption of a low molecular weight penetrant (water). Changes in the values of a long period in the samples saturated with a low molecular weight penetrant (8.44 nm for reference sample, 8.81 nm for water-soaked sample), with insignificant (if any) changes in the crystalline regions, indicate an increase in the interlamellar distances as a result of strong swelling (deformation) of unordered regions with molecules of water.

Figure 21 presents engineering stress—engineering strain curves for samples of polyamide 6 of different water content, subjected to tensile drawing. The test was conducted up to rupture of the sample. Deformation of DS samples was accompanied by the necking process. For samples with the highest water content deformation proceeded in a homogeneous manner, along the entire gauge length of the sample. In the case of MS samples deformation ran in an intermediate manner a neck was formed, though the degree of its localization was relatively low. Analysis of curves presented in the Figure 21 points to strong dependence of stress at yield point on the water content in the material. Again, this effect was roughly explained in the section Modification of Amorphous Phase of Polypropylene and will be the subject of a forthcoming publication.

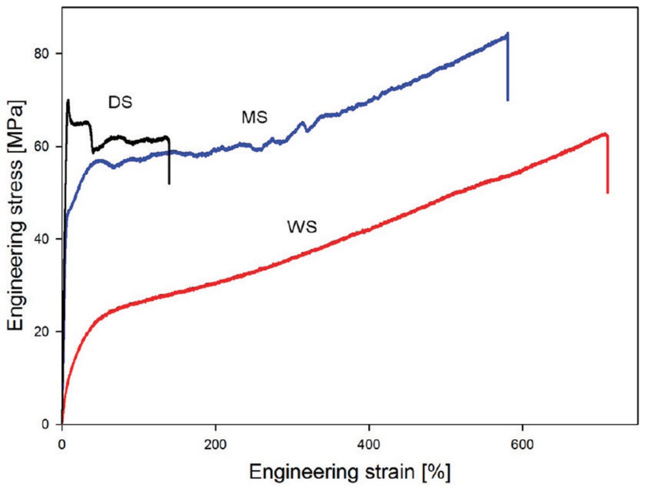

Figure 21. Engineering stress—engineering strain curves for samples of polyamide 6 of different water content. Deformation rate: $3.3 \times 10^{-3}\ s^{-1}$.

In order to assess the influence of the water content in the amorphous phase of polyamide 6 on cavitation during tensile drawing, small-angle X-ray scattering studies (SAXS) have been conducted. As it was mentioned, SAXS method is a very useful tool for examination of cavities in materials. Figure 22 presents SAXS scattering patterns registered for subsequent deformation stages during *in situ* studies using synchrotron radiation. Analysis of the presented scattering patterns proves how strongly the phenomenon of formation discontinuities in the material is influenced by the degree of saturation of the amorphous phase with water. Deformation of the MS sample, that is, a material whose degree of saturation with water is close to the level corresponding to a typical water content in the material during its use in standard conditions, is accompanied by cavitation; however, the intensity of the process is relatively small. This is confirmed by the results which suggested the possibility of formation of cavities in polyamide 6.[31] However, according to the authors of the mentioned paper, cavities formed during deformation are instable due to small size and close during deformation or shortly after the release of stress. The first SAXS signals from cavities are observed at the local strain of 0.7 (Figure 22b). At this deformation stage cavities of ellipsoidal shape, as in the case of polyolefins, are oriented by their long axis perpendicular to the direction of deformation.

The presence of objects with such parameters is confirmed by a signal in the meridional region on a SAXS scattering pattern. Such a shape of cavities is forced by the lamellar structure of the material. Studies on polyamide 6, based on microphotographs recorded using transmission electron microscopy and the process of contrasting samples with the use of osmium oxide, presented by Galeski et al.,[31] indicated the possibility of formation of cavities,

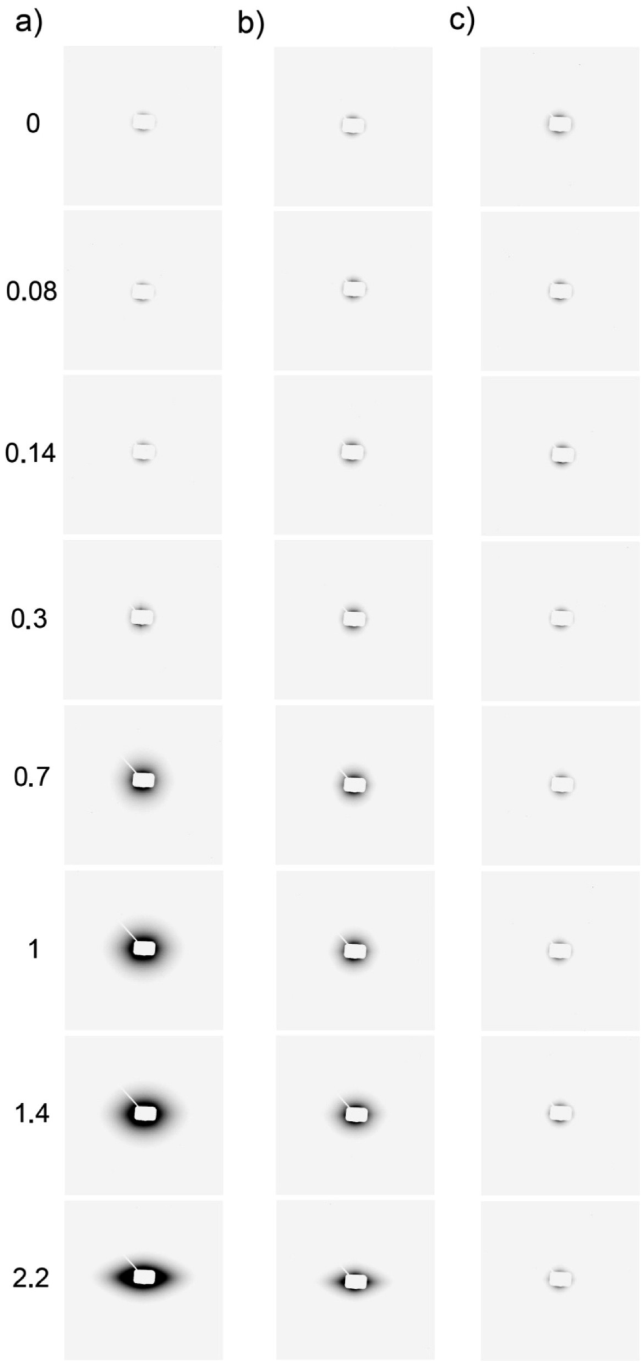

Figure 22. Diffractograms of small-angle X-ray scattering of a series of samples of different water content: (a) DS; (b) MS; (c) WS. Figures correspond to local strain of samples. Direction of deformation: vertical.

particularly intensively in the equatorial region of a spherulite, in which the specific arrangement of crystallites facilitates formation of ellipsoidal cavities in the interlamellar regions. At further deformation stages, at the local strain exceeding 1, one can also note on a scattering pattern a signal from cavities oriented parallel to the direction of deformation (signal in the equatorial region.) The observed effect is the result of changes in the interlamellar distances and lamellar fragmentation taking place at this stage of plastic deformation. At the local strain equal to 2.2 a thin, intensive signal is observed on a scattering pattern, mainly in the equatorial region, indicating strong orienation of the cavities generated in the material parallel to the direction of the applied stress.

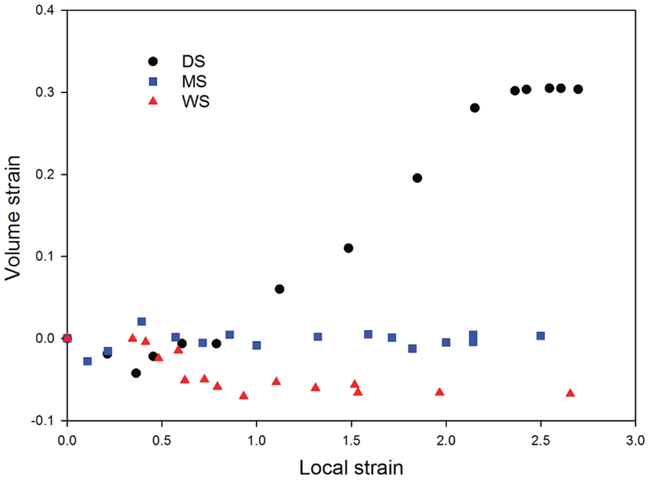

Figure 23. Volume strain as a function of local strain for polyamide 6 of different degree of saturation with water.

Drying of polyamide 6 (DS sample), whose effect is reduction of the water content in the material up to 1.1%, considerably influences the process of cavity formation during deformation of the material (Figure 22a). The first signals from cavities on SAXS patterns begin to appear at the local strain of 0.3. As in the case of MS samples, cavities are initially elongated perpendicular to the direction of the applied stress. At further stages of deformation, as a result from changes taking place in the lamellar structure of the material, one also observes changes in the shape of cavities (signal in the equatorial region on a diffractogram). Although the initial shape of cavities observed in DS samples and the process of their reorganization recorded as a result of activation of subsequent plastic deformation mechanisms is similar to the mechanism of cavitation in MS sample, the intensity of the cavitation process is much stronger in the dried samples.

A reverse effect has been observed for WS samples (Figure 22c). A maximum saturation of the amorphous phase of the material with water led to the complete elimination of cavitation during tensile drawing of such modified material. On presented scattering patterns, up to the local strain of 2.2, no signals indicating the presence of cavities generated during deformation of the material were recorded.

Figure 23 presents measurements of volume strain as a function of the local strain for the given materials. Analysis of these results confirms results obtained from X-ray measurements. In the case of material with the lowest water content, strong increase in volume accompanying deformation was observed, up to 30%. Such a strong change in the parameters of a sample is the result of intensive cavitation during deformation of the material. Only initially tensile drawing of DS sample is accompanied by the negative volume change, which can be accounted for by better packing of the material as a result of the applied stress. At further stages of deformation of the material, when the first signals from cavities are recorded on SAXS scattering patterns, one observes a strong increase in volume as a result of cavitation.

Also volume strain measurements during deformation of the material with the maximum degree of water saturation demonstrate that cavitation in the material is completely eliminated as a result of filling the amorphous phase with the penetrant. The relation between the volume strain and the degree of deformation of WS sample, presented in Figure 23, does not exhibit typical changes observed in the strongly cavitating materials. One observes a few percent decrease in the volume of the sample as a result of tighter packing of the material, resulting from plasticization of the material with molecules of water, elimination of cavitation, and orientation of the amorphous material as a result of tensile drawing.

In the case of polyamide 6 conditioned in laboratory conditions, no significant changes in the volume of the samples at subsequent stages of deformation are observed. Increase in volume, a result of relatively weak cavitation registered during X-ray examinations (Figure 22b), is compensated by changes in the structure of the material leading to closer packing of the material.

CONCLUSIONS

Chosen liquids penetrate amorphous phases of polymers but do not influence their crystalline phases. Neither crystalline fraction nor individual lamellar crystals have been affected by penetration of liquids as it follows from WAXS, SAXS, and DSC.

Infusion of several polymers with a penetrant resulted in complete suppression of cavitation during tensile drawing. Polymers chosen for the studies were hydrophobic or hydrophilic while penetrants were polar or nonpolar provided that they do not disturbe crystalline phase of polymers. Similar results were obtained in the case of PP with chloroform, PP with hexane, HDPE with hexane, and PA 6 with water. In all those cases no trace of cavitation was observed in soaked samples. The observations were made on the basis of SAXS measurements and are also confirmed by the volume strain measurements performed for the examined materials.

All the experiments were designed based on the hypothesis that when penetrant fills free volume pores in the amorphous phase various polymers the homogeneous nuclei of cavitation either become too small to originate stable cavities or they are eliminated. It appeared that the phenomenon depend neither on the type of a crystalline polymer nor on the nature of penetrant. It is rather a rule that when the free volume pores are saturated with molecules of low molecular weight cavitation during tensile drawing is suppressed. By infusing low molecular weight penetrants, one may control cavitation. Moreover, liquids that can be used are not limited to the ones described in the paper.

The reported studies allowed to formulate the following important conclusions:

1. It was undoubtly shown that cavitation during drawing of semicrystalline polymers is initiated in their amorphous phase. Modification of the amorphous phase causes drastic changes in cavitation. Cavitation is inextricably linked with packing of the amorphous phase.
2. Blocking cavitation in crystallizing polymers is possible by removing homogeneous cavitation nuclei by filling the free volume of amorphous phase of the material with low molecular weight liquids. The type of liquid is not relevant, except that it should not dissolve polymer crystals.
3. The above observation is valid for polyethylene, polypropylene, and polyamide. It seems that other crystallizing polymers should also reflect similar dependencies.
4. Special attention has been paid to the above mechanism for polyamide 6, which exhibits a natural tendency to absorb water. The inclination of polyamide 6 to cavitate during drawing when dry and not to cavitate when moist is now clearly explained in terms of dynamic free volume.
5. Most of commodity semicrystalline polymers contain low molecular weight additives and also low molecular weight fractions that are accumulated in their amorphous phase during solidification. The presence of additives and low molecular weight fractions must influence mechanical properties of those industrially important thermoplastics, especially their tendency to cavitate.

Mechanical response of polymers with infused liquids into their amorphous phases is different than the virgin materials in all polymers studied.

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