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Influence of non-polymeric substances localized in the amorphous phase on selected properties of semicrystalline polymers

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1. Introduction

Intensive studies concerning semicrystalline polymers have been conducted for several decades [1–7]. Unfading interest of this class of materials is caused by both their unique properties and complex, hierarchical structure. During the solidification of semicrystalline polymers, lamellar crystals immersed in amorphous disordered regions and supermolecular structures-spherulites are created. Both the crystalline and amorphous component display certain characteristic properties (thermal, mechanical, barrier, etc.). Macroscopic properties of semicrystalline polymers are to some extent a derivative from a relative content of the mentioned components and their characteristic properties.

Using widely available microscopic (OM, SEM, TEM), thermal (DSC) or X-ray (SAXS, WAXS) techniques, it is relatively easy to analyze the structure of crystalline regions and their influence on macroscopic properties of the entire polymer matrix. Meanwhile, the direct analysis of non-crystalline regions (interlamellar and interspherulitic) is difficult. The complications are primarily related to the structure of the amorphous phase [8–10]. It contains regions of different packing density, different microconformation and content of chemical defects (branching) along chains or different connectivity between chains and crystals. In the amorphous phase area, there are the chain ends-cilia (it is believed that up to 90% of the chain ends are being pushed out into the amorphous phase region), folds, loops, macromolecules physically connecting adjacent crystals.

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http://dx.doi.org/10.1016/j.eurpolymj.2015.06.005
0014-3057/© 2015 Published by Elsevier Ltd.

Please cite this article in press as: A. Rozanski, R. Idczak, Influence of non-polymeric substances localized in the amorphous phase on selected properties of semicrystalline polymers, Eur. Polym. J. (2015), http://dx.doi.org/10.1016/j.eurpolymj.2015.06.005
In non-crystalline regions of commercially available semicrystalline polymers, non-polymeric substances may be additionally localized. The desired physical properties of semicrystalline polymers are closely correlated to their molecular weight. Therefore each reaction leading to the change of this parameter is extremely important and should be controlled (eliminated). Negative combination of factors such as temperature, UV and oxygen imposes the necessity of using antioxidants [11]. These kinds of substances should be present not only during the use of polymeric material but also during its processing and storage. The properties of the substances are different in relation to an individual polymer matrix, therefore, they may affect its physicochemical properties. Usually, they are effective at concentrations of fraction of one percent.

The next group of non-polymeric substances filling mainly non-crystalline regions of semicrystalline polymers are oligomers. Due to the specific process of polymerization (mainly as a result of different side reactions, which lead to deactivation of the active center at the end of a growing chain), a fraction of low molecular weight molecules is also generated. The chemical properties of these substances are similar to the chemical properties of corresponding polymer matrix, however their physical properties may be substantially different. The content of such substances usually oscillates between a fraction of one percent to even a few percent.

A complex, non-homogenous structure of the amorphous phase impedes the analysis of the influence of this component on thermo-mechanical properties of semicrystalline polymers. One of the few techniques enabling a direct analysis of the structure of the amorphous phase is positron annihilation lifetime spectroscopy (PALS). PALS technique is usually very fruitful even in the case of complex, porous substances because some of these components in a positron annihilation spectrum which can be relatively easily extracted from the whole measured spectrum, are determined mainly by the size and concentration of the empty spaces (pores) occupied by positronium atoms (Ps-hydrogen-like bound state of an electron and a positron) before their decay. In particular these really useful spectrum components are the long-lived ortho-Ps (o-Ps) ones. The mean lifetime of the long-lived o-Ps component is determined by the size of the positronium traps. Using positronium probes, one can investigate empty spaces (pores) in solids with sizes from about 0.25 nm to about 16 nm. Finally, it is worth noting that the one of the most important advantage of the PALS is its non-destructive nature.

Also, a cavitation phenomenon is activated in interlamellar regions [12,13]. It has to be stressed that the process of generation of cavities in the material is present during the uniaxial stretching of most of the semicrystalline polymers and has a negative influence on their thermo-mechanical properties [12,14,15]. The amorphous phase ability to transfer tensile stress without losing continuity, decides on the presence or absence of the cavitation phenomenon. In case the resistance of non-crystalline regions is higher than the critical stress of activation of mechanisms of plastic deformation of the crystals, the cavitation phenomenon is not observed [15]. Each change of structure and physical state of the amorphous phase leading to the alteration of interlamellar regions resistance should therefore also affect the intensity of the cavitation phenomenon.

In the paper [16], we presented a method of removing the non-polymeric substances mentioned above from non-crystalline regions of polypropylene matrix with the use of supercritical CO₂ extraction and extraction with a non-solvent mixture in Soxhlet apparatus. Meanwhile, in the paper [17,18] we presented the modification method of non-crystalline regions by introducing, selectively only into the amorphous phase, the molecules of low molecular weight modifier. At the same time we proved that the amorphous phase modification methods mentioned above may affect the content and mean size of free volume pores and also the course and intensity of the cavitation phenomenon.

In this paper, for several typical semicrystalline polymers such as polypropylene, high and low density polyethylene, we performed the supercritical CO₂ extraction of non-polymeric substances. At the same time we performed a quantitative/semi-qualitative analysis of extracted substances and we determined their thermal properties. Then, we assessed their impact on the structure of the amorphous phase, thermal, thermo-mechanical and barrier properties of analyzed polymers and the course and intensity of the cavitation phenomenon during uniaxial stretching.

2. Experimental

2.1. Materials

Polypropylene Moplen HP 456H (PP) of melt flow index MFI = 1.8 g/10 min (for 190 °C, 2.16 kg according to ISO 1133), by Lyondell Basell. High density polyethylene Lupolen 6021D (HDPE) (Mₙ = 182 kg/mol, Mₚ = 25 kg/mol, Mₘ/Mₚ = 7.2) of melt flow index MFI = 2.6 g/10 min (for 190 °C, 2.16 kg, ISO 1133), by BASF. High density polyethylene Borstar HE 3490 (HDPE_B) of melt flow index MFI < 0.1 g/10 min (for 190 °C, 2.16 kg, ISO 1133) by Borealis. Low density polyethylene Lupolen 2420H (LDPE) of melt flow index MFI = 2.1 g/10 min (for 190 °C, 2.16 kg, ISO 1133) by BASF.

2.2. Supercritical CO₂ extraction

The process of samples purification has been performed by means of supercritical CO₂ extraction. The extraction was performed in a batch manner. The samples were loaded into the 50-ml extraction vessel of supercritical fluid extractor (SFT-110, Supercritical Fluid Technologies, Inc., Newark, DE, USA). The extraction was conducted by continuously flowing CO₂ through...
the extraction vessel at a rate of 12 ml/min, at temperature 60 °C and pressure 27 MPa for 3 h. The extract was separately accumulated.

### 2.3. Nuclear magnetic resonance (NMR)

$^{13}$C NMR spectra in a liquid phase (deuterated chloroform as a solvent) were recorded using Bruker AV 200 apparatus operating at the frequency of 50.33 MHz. Chemical shifts of signals given in parts per million (ppm) were measured relative to chloroform ($^{13}$C 77.00).

### 2.4. Mechanical testing

Mechanical properties of the materials examined in the paper were assessed using a tensile testing machine (Instron 5582) of load range 0–2 kN. Shape of samples was according to ISO 527-2 standard, with 1 mm thickness and 5 mm width. The gauge length was 25 mm. Tests were performed at room temperature at a standard rate $3.3 \times 10^{-3}$ s$^{-1}$ (the crosshead speed: 5 mm/min). 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 [13,19–21]. 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 $3.3 \times 10^{-3}$ s$^{-1}$ (the crosshead speed: 5 mm/min).

### 2.5. Differential scanning calorimetry (DSC)

Thermal analysis of the examined materials was conducted using an indium calibrated DSC apparatus (TA Q20, 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 recorded during heating at a constant rate of 10°/min under nitrogen flow. The degree of crystallinity of the studied samples was determined according to a formula: $X_c = \Delta H_m/\Delta H_m^0$, where: $\Delta H_m$ is the measured specific heat of melting, $\Delta H_m^0$ is the heat of fusion of the crystal. The following values of $\Delta H_m^0$ have been assumed: 209 J/g for polypropylene [22], 293 J/g for polyethylene [23].

### 2.6. Wide-angle X-ray scattering (WAXS)

Analysis of the crystalline structure of the materials was performed using wide-angle X-ray scattering measurements by means of a computer controlled goniometer coupled to a sealed-tube source of Cu Ka radiation (Philips), operating at 30 kV and 50 mA. The Cu Ka line was filtered using electronic filtering and the usual thin Ni filter. Analysis of diffraction profiles of the examined samples and peak deconvolution were performed using WAXSfit software designed by M. Rabiej at the University of Bielsko-Biała (AHT). The software allows to approximate the shape of the peaks with a linear combination of Gauss and Lorentz or Gauss and Cauchy functions and adjusts their settings and magnitudes to the experimental curve with a “genetic” minimizing algorithm [24,25].

### 2.7. Small-angle X-ray scattering (SAXS)

The measurements were performed with the use of synchrotron radiation, $\lambda = 0.957 + 0.002$ Å, P03 beamline in Hasylab (Hamburg, Germany). Two-dimensional scattering patterns with the use of Pilatus detector (Dectris, Switzerland) were registered. Long periods were determined from one dimensional sections of 2-D pattern. Background and Lorentz corrections were applied to the curves. Long period was then calculated from position of the maximum of corrected curves using the Bragg's law.

### 2.8. Positron annihilation lifetime spectroscopy (PALS)

Positron lifetime spectra measurements were performed using an ORTEC “fast–fast” spectrometer [26]. The resolution of the spectrometer was found to be 300 ps. In this method, positrons emitted by the radioactive source (in this case $^{22}$Na)
penetrate into two samples surrounding the source and annihilate after thermalization process. In the case of polymers, some positrons create a positronium (Ps) in the free volume regions. A mean lifetime of the o-Ps is related to the size of the free volume regions in which the atoms of the o-Ps annihilate. Reconstruction of the distribution of the positronium lifetimes, on the basis of the measured lifetime spectrum and determination of shape of the free volume regions, enables one to determine radius or volume distribution of these areas. Positron lifetime spectra measurements were performed in air at room temperature. Measurement time for one spectrum was 24 h, which corresponds to a total of approximately $2 \times 10^6$ counts under the measured spectrum. LIFETIME software was used for the analysis [27].

2.9. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out on rectangular specimens cut out from 1 mm thick films, in a single cantilever bending mode using a DMTA TA Q-800, Thermal analysis apparatus at the frequency of 1 Hz and at the heating rate of 2 °C min$^{-1}$.

2.10. Barrier properties

Barrier measurements of selected materials, were determined using gas permeation device Lyssy 100–500 (PBI-Dansensor, Germany), according to PN-EN ISO 2556 standard. Permeability parameters for 1 mm thick films were averaged from two measurements.

2.11. Transmission electron microscopy (TEM)

The lamellar structure of analyzed materials was controlled with a transmission electron microscope (TEM), Tesla BS 500 (Tesla, Czech Republic), operating at the accelerating voltage of 90 kV. Samples for TEM examination, in the form of ultra-thin sections 60 nm thick, were prepared by cryo-ultramicrotoming. The cryo-ultramicromtome, type PowerTome PC (Boeckeler, USA) equipped with a 35° diamond knife (Diatome, Switzerland) was used for sectioning. Before cutting polypropylene samples were exposure to the vapor of RuO$_4$ at room temperature for a 24 h. The polyethylene samples, before cutting were immersed in chlorosulphonic acid for a 24 h.

3. Results

In this paper, four typical semicrystalline polymers were selected: isotactic polypropylene (PP), high density polyethylene (HDPE), high density polyethylene containing an increased fraction of oligomers (HDPE_B) and low density polyethylene (LDPE).

As a result of the supercritical CO$_2$ extraction, physically/chemically not-connected non-polymeric substances were removed from the amorphous regions. Table 1 contains the quantity of non-polymeric substances extracted from analyzed materials determined on the basis of the samples weight decrease after extraction process.

Supercritical CO$_2$ extraction enables removing physically/chemically not-connected non-polymeric substances only from the amorphous phase regions. Taking into consideration the degree of crystallinity of individual materials presented further in the paper (Table 2), the data of Table 1 suggest that the content of non-polymeric substances is substantially higher in the disordered regions.

For the purpose of qualitative analysis of the extracted substances, we collected a spectra of nuclear magnetic resonance, $^{13}$C NMR. Fig. 1 presents a spectra performed for the substances extracted from PP and HDPE, dissolved in deuterated chloroform. Fig. S1 presents $^{13}$C NMR spectra for the rest of the analyzed materials (HDPE_B and LDPE).

We may distinguish in presented spectra two groups of signals in the range of chemical shifts 15–50 ppm (aliphatic carbon atoms) and 115–160 ppm (aromatic and ester carbon atoms). Individual signals were assigned to respective fragments of stabilizers molecules or oligomers presented schematically in Figs. 1 and S1. In case of polypropylene we confirmed the presence of propylene oligomers and antioxidants from the group of hydroxyphenylpropionates and phosphites in the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of non-polymeric substances: in material/in amorphous phase (wt.%)</th>
<th>Semi-qualitative composition of extracted substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.97/1.83</td>
<td>Oligomers, Hydroxyphenylpropionate, Phosphate</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.37/1.34</td>
<td>Oligomers, Phosphate</td>
</tr>
<tr>
<td>HDPE_B</td>
<td>1.19/3.36</td>
<td>Oligomers, Phosphate</td>
</tr>
<tr>
<td>LDPE</td>
<td>1.60/2.86</td>
<td>Oligomers</td>
</tr>
</tbody>
</table>

Table 1
Quantitative/semi-qualitative analysis of non-polymeric substances localized in the amorphous phase of analyzed semicrystalline polymers.
Table 1 contains information on the chemical composition of mixtures of the substances extracted from the analyzed materials. Taking into account the differences in the intensity of the signals coming from stabilizers and oligomers we, may assume that the content of the latter in the mixture of non-polymeric substances, in case of the analyzed materials, is dominant. It is particularly seen on the $^{13}$C NMR spectra collected for the following materials: HDPE$_B$ and LDPE (Fig. 1S).

The extraction process was conducted at elevated temperature. Additionally, a too rapid reduction in pressure of the extraction chamber may induce a foaming process of the material and change its lamellar and/or spherulitic structure [28]. The factors mentioned above may therefore affect the crystalline structure of analyzed materials. Consequently, with
the use of X-ray techniques, differential scanning calorimetry and transmission electron microscopy, selected parameters of
the crystalline phase of the studied materials before and after extraction were determined. Fig. 2 presents WAXS profiles for
polypropylene (PP) and high density polyethylene (HDPE) (Fig. S2 presents WAXS profiles for the rest of analyzed materials).

As one can notice on Fig. 2, lack of significant differences between diffraction profiles of extracted and reference samples,
indicates no changes in the crystalline structure of the analyzed material caused by the supercritical CO$_2$ extraction.

Table 2 presents selected parameters of the crystalline phase determined for samples prior to and after the purification
process obtained with the use of DSC and SAXS techniques.

All parameters of the crystalline component of analyzed materials presented in Table 2 prior to and after extraction pro-
cess are almost identical.

Furthermore, with the use of transmission electron microscopy the influence of the extraction process on lamellar struc-
ture of the analyzed materials was determined. Fig. 3 contains TEM micrographs collected for polypropylene (PP) and high
density polyethylene (HDPE) before and after the extraction process.

We did not observe any influence of the extraction process of non-polymeric substances on the lamellar structures of ana-
lyzed materials. Both the thickness of lamellae and their length were not changed. Based on the results presented above we
may state that the process of supercritical CO$_2$ extraction enables effective separation of physically/chemically
not-connected non-polymeric substances localized in amorphous regions without affecting the structure of lamellar crystals.

In order to assess the influence of the extraction process on the structure of the amorphous phase of the analyzed mate-
rials (the content of the free volume of the amorphous phase), positron lifetime spectra were collected. The choice of the
model for spectra analysis is extremely important. Results presented further in the paper correspond to the model of the
spectra analysis, which assumes (1) the intensity ratio of annihilating para- and ortho-positronium of 1:3, (2) lifetime of

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**Fig. 2.** WAXS diffraction profiles of polypropylene (a) and high density polyethylene (b) prior to and after supercritical CO$_2$ extraction. Curves for samples after supercritical CO$_2$ extraction have been shifted along the vertical axis for better visualization.
annihilating para-positronium, $\tau_1$, of 125 ps, (3) the presence of the log-normal distribution of mean lifetimes corresponding to free annihilation of positrons and annihilation of ortho-positrons by "pick off". In the analyzed spectrum this corresponds to components with the mean value $\langle \tau_2 \rangle$ and dispersion value $\sigma_2$ as well as mean value $\langle \tau_3 \rangle$ and dispersion value $\sigma_3$, respectively. The spectrum model consists of the two components with dispersions because one could expect that the materials under investigation are not homogeneous ones as well as the atomic-scale empty spaces existing in them are of different sizes. The results of the obtained spectra are presented in Table 3 and Table 1S.

On the basis of the Tao-Eldrup model [29,30], the relationship between the lifetime $\tau_3$ of an ortho-positronium atom and the radius $R$ of the spherical empty space trapping the atom before its decay, could be described by the following formula:

$$\tau_3[\text{ns}] = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}$$

(1)

where $R_0 = R + \Delta R$, and $\Delta R = 0.1656$ nm. The formula (1) was used to calculate the normalized distributions $y(V)$ of volume of the empty spaces “seen” by positronium atoms in the studied materials. It was done on the basis of the obtained log-normal distribution of $\tau_3$ values, described by the $\langle \tau_3 \rangle$ and $\sigma_3$ parameters. The calculation results are presented in Figs. 4 and 3S.

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
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<tbody>
<tr>
<td>Results of positron lifetime spectra analysis.</td>
</tr>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>$\tau_1$ (ps)</td>
</tr>
<tr>
<td>PP</td>
</tr>
<tr>
<td>PP_E</td>
</tr>
<tr>
<td>HDPE</td>
</tr>
<tr>
<td>HDPE_E</td>
</tr>
</tbody>
</table>

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The distributions $y(V)$ obtained directly from PALS measurements (PP, PP_E, HDPE, HDPE_E) were normalized to the same area. To obtain a relative content of free volume of the amorphous phase in materials prior to and after the extraction process, the following corrections were applied: the extracted mass amounted to 0.97 wt.% for PP. All extracted substances were mainly localized in the amorphous regions. The volume of purified sample was not decreased due to the extraction process as it is concluded from the SAXS measurements—the values of long period for samples before and after the extraction process are almost identical (Table 2). Therefore, the compaction, that occurred during extraction was very low if any. It is very evident, if we take into consideration lamellar/spherulitic structure of the analyzed materials. It leads to the conclusion that the free volume in the amorphous phase was increased by a significant amount. In order to estimate, the extraction induced, the increase in free volume we assumed the number of free volume holes at $5.2 \times 10^{20}$ g$^{-1}$ for the amorphous phase of polypropylene in the rubbery state based on the work of Baer et al. [31]. The mean size of free volume pores in reference polypropylene obtained from PALS profiles is 0.104 nm$^3$. Therefore, the fraction of free volume of amorphous regions of PP at room temperature is then $NqD \approx 0.05$, where $N$ is the number of free volume pores in 1 g of amorphous phase, $q$ is the density of the amorphous phase and $D$ is the mean size of free volume pores. As a result of the extraction, additional free volume was generated due to the lack of the proper contraction of PP lamellar structure. The additional free volume generated by extraction is 0.97 wt.%/0.9 g/cm$^3 = 0.01$ vol of a sample. Considering that the additional free volume was generated only in the amorphous regions (degree of crystallinity of polypropylene, 48%) the additional free volume in the amorphous phase is $\approx 0.02$ vol. Therefore, total free volume in PP sample after extraction process is $\approx 0.07$ (0.05 + 0.02). Considering that the total free volume for the reference sample is 0.05, while for the sample after extraction is 0.07, the corrected profile of free volume pores size distribution for PP_E sample was presented in Fig. 4a. The PALS profile for HDPE_E was corrected in a

![Fig. 4. Normalized and relative (corrected curve) size distributions of free volume pores of the amorphous phase of polypropylene (PP) (a) and high density polyethylene (HDPE) (b) before to and after extraction process.](image-url)
similar way with the use of the following data: the number of free volume holes \((N)\): \(0.8 \times 10^{27} \text{ m}^{-1}\) \[32\], the mean free volume pore size \((D)\): \(0.116 \text{ nm}\), the extracted mass: 0.37 wt.%. Fig. 4b presents the properly corrected profile for HDPE_E material. We also performed a similar assessment for the rest of the analyzed materials and profiles after corrections were presented on Fig. 3S.

The analysis of presented data clearly shows that as a result of the extraction of non-polymeric substances filling non-crystalline regions, we observed a substantial increase of content and average size of free volume pores. Moreover, we can also observe a substantial increase of content of the largest pores which may be particularly important in view of the properties and phenomena analyzed further in this paper.

Fig. 5 presents DSC thermograms for PP, HDPE and extracted non-polymeric substances. Fig. 4S presents DSC thermograms for the rest of analyzed materials. The DSC thermograms for non-polymeric substances include only the range of temperatures in which they were thermally stable. In the case of non-polymeric substances extracted from a polypropylene matrix, we may observe two phase transitions: glass transition in temp. \(-28.2 \degree\text{C}\) (shifted by approx. 30 \degree\text{C} towards lower temperatures in relation to \(T_g\) of reference polypropylene) and a relatively weak peak of melting (4.9 J/g) in temperature 52.5 \degree\text{C} (shifted by approx. 110 \degree\text{C} towards lower temperatures in relation to the melting peak of reference polypropylene).

Additionally, we observed an interesting effect related to the glass transition temperature of polypropylene matrix. Fig. 6 presents DSC thermograms for non-polymeric substances and polypropylene before and after the extraction process.

Removing non-polymeric substances leads to the shift of glass transition temperature of polypropylene by 4.2 \degree\text{C} towards lower values. This effect seems to be surprising due to observed value of \(T_g\) for extracted substances \(-28.2 \degree\text{C}\). According to the Flory-Fox equation \[33\], the presence of a miscible component of a lower glass transition temperature should lead to a

![Fig. 5.](image_url)  
Fig. 5. DSC thermograms for PP, HDPE and extracted non-polymeric substances. The thermograms for non-polymeric substances were shifted vertically for better visualization.
shift of $T_g$, temperature of polypropylene after the extraction process towards higher values. In the analyzed case we observed an opposite effect. Therefore, it seems that the observed shift of value of $T_g$ after the extraction process is caused mainly by an increase of content of free volume of the amorphous phase according to the previously presented data obtained from PALS measurements.

On DSC thermogram recorded for non-polymeric substances extracted from HDPE matrix (Fig. 5b) we may observe a very broadened peak of melting ($\approx 110$ J/g) with a maximum in the range of temperatures: 20–60 °C. The extracted non-polymeric substances display a certain tendency to create strongly defected, irregular crystalline structures that may indicate a certain analogy to paraffin substances having similar properties. Furthermore, in the temperature of $-98$ °C we may observe a weak signal corresponding to a glass–rubber transition. A glass transition temperature is not observed on thermograms (in temp. from $-150$ to $-40$, not presented in this paper) recorded for polymer matrix both before and after the extraction process. Obviously it is caused by a high degree of crystallinity of the analyzed material.

In the case of polyethylene containing an increased amount of oligomers (HDPE_B, Fig. 4Sa) the extracted substances display a tendency to create more regular, ordered structures, what is confirmed by a melting peak (157 J/g) with a maximum temperature at 45 °C. The DSC thermogram collected for the substances extracted from LDPE is complex and contains several signals within almost the entire range of the analyzed temperatures. In temperature of $-77$ °C we may observe a glass–rubber transition and then highly broadened peak of melting in temperatures range: $-60$ to $110$ °C coming from irregular pseudo-crystalline structures. Only in temperature of $100$ °C the observed peak is relatively regular what indicates the presence of numerous objects with ordered structure.

The thermal properties of non-polymeric substances extracted from non-crystalline regions presented above are evidently different from the thermal properties of individual polymer matrix. On DSC thermograms for reference materials (especially for polyethylene (HDPE_B)) there are no signals coming from the corresponding phase transitions characteristic for the extracted substances. It indicates that non-polymeric substances lost their ability to create regular structures within the amorphous phase regions of individual matrices, from which they had been removed.

Despite the lack of ability to create ordered structures within the amorphous phase regions by non-polymeric substances, the presence of these molecules should affect the thermo-mechanical properties of the entire polymer matrix. Figs. 7 and 5S present DMTA curves collected for the analyzed semicrystalline polymers before and after the extraction process.

In case of polypropylene (Fig. 7a), the presence of non-polymeric substances, leads to the “stiffening” of polypropylene matrix (the effect is rather weak), in the low temperature range, below glass transition temperature. This fact is manifested by a higher modulus of the reference polypropylene recorded in this region of temperature. At temperatures, above glass transition of polymer matrix, the material containing molecules of non-polymeric substances is characterized by a lower modulus than the reference polypropylene.

In case of HDPE the influence of non-polymeric substances on thermo-mechanical properties of the polymer matrix is barely noticeable. It is probably caused by very a small amount of these substances (0.37 wt.%) localized in non-crystalline regions of the analyzed material. However, a strong effect is seen in case of HDPE_B containing a larger amount (1.19 wt.%) of removable non-polymeric substances fractions (Fig. 5Sa). The storage modulus of the reference material within temperatures from 10 to 100 °C is clearly lower than in case of the material after extraction process—the presence of plasticizing effect of non-polymeric substances is observed.

In order to determine the influence of non-polymeric substances presence on the course and intensity of the cavitation phenomenon the SAXS (Small Angle X-ray Scattering) patterns were collected (Fig. 8).
In case of reference HDPE (Fig. 8a) signals indicating a formation of cavitation pores in the material, on SAXS patterns, are already observed at the local strain equal to 0.13. The cavities at this stage of deformation are of ellipsoidal shape and are oriented by their long axis perpendicularly to tensile direction (signal in the meridional region on a scattering pattern). Specific arrangement and shape of cavities is forced by the lamellar structure of the material. On further deformation stages, an increase in intensity of the registered signal is observed, up to the strain of 0.8. At this local strain, a signal in the equatorial region of a scattering pattern is also registered. This fact indicates the presence of the population of cavities oriented parallel to the tensile direction. Signal appearing in this region of scattering pattern, at the cost of intensity in the meridional zone demonstrates that subsequent mechanisms of plastic deformation of the material (lamellar fragmentation) activated at this stage also forced reorganization of shape and orientation of cavities.

Further stages of deformation (>0.8) are accompanied by a substantial decrease in size of cavitation pores perpendicularly to the direction of deformation and their strong orientation towards the tensile direction.

The lack of non-polymeric substances is visible clearly during the deformation of HDPE_E sample (Fig. 8b). Deformation of such sample is also accompanied by cavitation phenomenon. It proceeds almost identically as in case of reference HDPE. However, a significant difference concerns the intensity of scattering signals coming from cavities at subsequent stages of deformation. Analysis of the presented scattering patterns indicates that the intensity of the cavitation process has increased in the extracted material.

Conclusions supported by X-ray examinations were also confirmed by the results of the volume strain measurements (Fig. 9b). Deformation of reference sample of polyethylene (HDPE) is accompanied by a significant volume increase (by ~50%) an effect of formation of cavities. After the removal of non-polymeric substances, the intensity of cavitation phenomenon was evidently higher what was indicated by the observed increase of the volume amounting to ~70%. A similar effect was also observed in the case of polypropylene (PP, Fig. 9a) and polyethylene containing increased amount of
oligomers (HDPE_B, Fig. 6S). Removing non-polymeric substances leads to an increase of the intensity of cavitation phenomenon. Simultaneously we can see that, the range of the observed changes of the intensity of the cavitation phenomenon is correlated with the amount of extracted non-polymeric substances. In case of HDPE_B, the intensity of the cavitation phenomenon after the extraction process was doubled.

It seems that the increase of intensity of cavitation phenomenon after removing non-polymeric substances is caused by increase of content of fraction of the largest free volume pores (Figs. 4 and 3S). Such pores can enable generating cavitation pores during the uniaxial stretching of materials after the extraction process. Therefore, in order to generate and stabilize the cavitation pores, we will need to lower the negative pressure according to the well-known relation:

\[ p = \frac{-2\gamma}{r} \]

where \( r \) means the radius of the free volume pore participating in the nucleation of cavitation pore.

Fig. 8. Small-angle X-ray scattering patterns obtained, in situ, during deformation of high density polyethylene (HDPE) samples prior to (a) and after (b) extraction process. Numbers correspond to local strain of samples. Direction of deformation: vertical.

Only in the case of LDPE, the removal of non-polymer substances does not affect the intensity of the cavitation phenomenon (Fig. 6Sb). The uniaxial stretching of LDPE, both before and after the extraction process, proceeds in a non-cavitation manner. To initiate the cavitation phenomenon, we still require higher tensile stress than to activate the mechanisms of the plastic deformation of crystalline component. In such case the cavitation phenomenon is not observed according to the well-known relation that the phenomenon to initiate which the lower stress is required proceeds first [15].

Moreover, we observed an interesting effect accompanying the deformation of the analyzed materials in the range of high values of local strain. In case of polypropylene above the local strain amounting to 5, we may observe a gradual decrease of the value of volume strain. This effect is observed both for the material before and after the extraction process. The course of deformation for HDPE in similar range of local strains occurs without any substantial change of values of volume strain.

To find the explanation of the observed effect, the SAXS patterns in the interesting range of values of local strain were collected (Fig. 10). In case of polypropylene (Fig. 10a) an increase of scattering intensity from cavities in an equatorial part of scattering patterns with increasing local strain is observed. This seems to be in contrary with the data obtained from volume strain measurements. However, we can explain the observed effect in a following way: there is a fraction of cavities at the local strain of 4.5, which are outside of SAXS detection limit. Due to the changes in the packing of material at higher local strains, a gradual decrease of the lateral size (along their short axis) of highly elongated cavities is induced. As a result, the decrease of volume strain is observed and additional fraction of cavities is detectable during the SAXS measurements (increase of scattering at SAXS patterns). In case of HDPE, (Figs. 9b and 10b) a new structure generated after the deformation of material to the local strain amounting to 5, is not subject to any additional reorganization (affecting the total content of volume generated by cavities) on further stages of its deformation (up to local strain amounting to 10).

As presented in this paper, the removal of non-polymeric substances from non-crystalline regions leads to the change of content of free volume of the amorphous phase. One of the parameters strongly correlated with the content of free volume of
Fig. 9. Volume strain as a function of local strain for polypropylene (PP) and high density polyethylene (HDPE). Deformation rate $3.3 \times 10^{-3} \text{s}^{-1}$.

Fig. 10. Small-angle X-ray scattering patterns of polypropylene (a) and high density polyethylene (b). Numbers correspond to local strain of samples. Direction of deformation: vertical.
the amorphous phase are the barrier properties. It is known that the gas permeation through the amorphous phase depends on dynamic (gas diffusivity) and static (gas solubility) free volume [34]. Fig. 11 presents the result of oxygen permeability measurements collected for selected materials (PP, HDPE_B) before and after the extraction process.

It is clearly seen that the presence of non-polymeric substances within the amorphous phase regions affects the barrier properties of the analyzed materials. A lack of those substances in non-crystalline regions results in an increase of content of free volume (Figs. 4 and 3S) and oxygen transmission rate through the polymer matrix.

The analysis of the influence of non-polymeric substances presence on the analyzed semicrystalline polymers crystallization process, amount of generated heat and mechanical behavior (yield stress, strain and stress at break) during its deformation was also performed. We did not observe any influence of non-polymeric substances on the above mentioned properties and phenomena.

4. Conclusions

In this paper we proved that the supercritical CO\textsubscript{2} extraction process allows to effectively remove physically/chemically not-connected non-polymeric substances such as oligomers and antioxidants from the amorphous regions of the analyzed semicrystalline polymers. Simultaneously, this process does not lead to any measurable change of the crystalline structure of the analyzed semicrystalline polymers. We proved that the thermal properties of such substances are visibly different than corresponding polymer matrices, from which they had been removed. The presence of oligomers may additionally affect thermo-mechanical properties of the polymer matrix particularly in case of the materials containing an increased amount of such substances. As a result of the extraction of non-polymeric substances, we also observed the increase of content of free volume of the amorphous phase and a fraction of the largest pores. This in turn resulted in deterioration of barrier properties of analyzed materials and increasing the intensity of cavitation phenomenon during the uniaxial stretching.

Acknowledgements

The project was financed from the funds of the National Science Centre on the basis of the decisions number DEC-2011/03/D/ST8/04156. We also express thanks to the Hamburg Synchrotron Laboratory (HASYLAB) for the beam time granted within the Project I-20130111 EC.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eur-polymj.2015.06.005.

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Please cite this article in press as: A. Rozanski, R. Idczak, Influence of non-polymeric substances localized in the amorphous phase on selected properties of semicrystalline polymers, Eur. Polym. J. (2015), http://dx.doi.org/10.1016/j.eur-polymj.2015.06.005