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Influence of the modification with polymer microspheres on the structural, mechanical and post-processing properties of extruded thin-walled LDPE films

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This work describes the production in blown film extrusion process and characterization of the thin-walled LDPE films modified with polymer microspheres as the blowing agent. Mechanical properties of the films are investigated with the emphasis on the post-processing (welding process) as the most common for films and crucial for the applications in packaging industry. Moreover, barrier properties and wettability of the obtained films are considered and all of the properties are explained based on the microstructure of the materials. Research shown the influence of changed blowing agent content on selected physical and structural properties of thin-walled LDPE films, specially deterioration of static and dynamic mechanical properties, reduction of air and oxygen permeability and weal adhesion of microspheres to the LDPE matrix. Studies of welding shown the need to increase the welding temperature of porous films.

Keywords Low density polyethylene, Films, Microspheres, Welding, Closed cells

Polymer films are essential materials in both consumer and industry sector. They have various applications among which the most common are in the packaging industry, where they can be classified as the consumer, commercial and industrial packaging foils. They are made primarily from polyolefins (HDPE, LDPE) or poly(ethylene terephtalate) (PET)[1].

Currently, both stable and degradable polymeric materials are subjected to various modifications during processing in order to improve their processability, give them appropriate properties and structure, increase functionality or degradability[2,3].

Porous materials are widely used as insulating or soundproofing materials, packagings, footwear, sport and even medical products. It is due to the unique properties of these materials: very low density, high thermo- and sound-insulation, high elasticity, and good compression resistance[4]. Porous polymer materials are obtained during typical processing methods—extrusion and injection moulding, with the use of physical or chemical blowing agents as modifiers. Depending on the blowing agent (endo- or exothermal), it is necessary to adjust the production line and processing parameters. Therefore, the selection of the modifier should complement the process.

Moreover, the type of the blowing agent and the processing method influence the pores formation, *e.g.* closed, open, of the specified size, shape, and distribution. For porous materials processing, the dimensions of the product are crucial, particularly wall thickness, to avoid discontinuities. That is the reason for the rare modification of the films with blowing agents, as it can cause a decrease in their barrier and mechanical properties. The best effects can be obtained for the thick-walled products (> 4 mm) which provides better distribution of the blowing agent. Addition of blowing agents to the thin-walled products, like films or membranes, remains a challenge but may open the door to new, promising materials. Porous films are used as the membranes[5], filters[6], and more sophisticated devices like light diffusers[7], but these are mostly films with open cells. Closed-cells films are used for electromagneting shielding or scattering[8,9], piezoelectric devices formation[10–13] and as a common industrial packaging material. Moreover, multilayer films with incorporated porous layers can be obtained via co-extrusion[1]. Such films can be characterized by good oxygen barrier properties and good mechanical

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properties and can be used in the packaging industry, *e.g.* for the extension of the shelf life of food products[4]. In such case, the use of the blowing agent safe for health is required, as the packaging is in contact with food.

The post-processing of such materials *e.g.* welding or thermoforming, where re-plasticization takes place, is still unexplored. Welding process is quite a popular method of films' post-processing. It allows for attaching film layers or other polymer components due to the temperature and pressing. There are a lot of welding methods which are dedicated to particular polymer materials. They differ in the welding temperature and the method of heat supply (Fig. 1). Classification includes also electrodes type and source of the energy.

Despite the variety of the welding methods, some of them cannot be used to the welding of thin-walled products. The most popular methods for films welding are high-frequency welding (HF)[15], ultrasonic welding[16] and hot-bar welding[17].

The product can lose its consistency and dimensions stability during welding which causes the drop in the mechanical properties, especially in the weld area. Selection of the process parameters, *e.g.* welding temperature, welding time, cooling time, is of high importance. These parameters affect the quality and durability of the weld. In terms of porous films welding, the temperature is also very significant because it can lead to the decomposition or expansion of the remaining blowing agent and the emergence of discontinuities or release of the modifier residues.

In this work, the examination of porous LDPE films is described. The film was obtained via blown film extrusion process with controlled parameters and the influence of the blowing agent content on its properties was investigated. Moreover, the influence of the blowing agent on the hot-bar welding process and mechanical properties of the welds, as well as their morphology, was explored.

Experimental

Materials

The low-density polyethylene LDPE Malen E FABS23D022 (Basell Orlen Polyolefins Sp. z o.o.) in granulated form was used for the film preparation. This material characterizes with the following properties (according to the manufacturer's data): density 0.926 g/cm^3, MFR (190 °C/2.16 kg) 1.95 g/10 min, melting point 112℃ and extrusion temperature in the range of 170–220 °C.

The blowing agent in the form of polymer microspheres—Expancel 920 MB 120 (Akzo Nobel) characterized by the mean size of the microspheres of 120 µm and 65% concentration of the microspheres in carrier copolymer of ethylene vinyl acetate EVA, was used as a modifier. Expancel microspheres are made from acrylates copolymer with volatile liquid encapsulated inside (mostly n-pentane or its isomers). Expancel was dosed in the amount of 0%, 1%, 3%, and 5% wt. and samples with these contents were named 0Ex, 1Ex, 3Ex, and 5Ex, respectively.

Blown film processing and methods

Blown film extrusion process was conducted with the use of single screw extruder W25/25 with the screw diameter 25 mm and L/D 25. Films was extruded with the use of cross extruder annular die (ring diameter 90 mm, gap width 0.8 mm). The process was carried out in a vertically upward extrusion system using a constant screw rotation speed 168 rpm (2.8 s^{-1}) and constant processing temperatures in individual plasticizing unit zones: 150 °C, 165 °C, 170 °C; and extruder die zones: 170 °C, 175 °C. The blown-extrusion process was carried out using previously prepared LDPE/Expancel micropheres granulate mixtures. Films were obtained in the form of a sleeve with a width after flattening of 240 mm. All processing parameters were constant factors in the experiment unless stated otherwise.

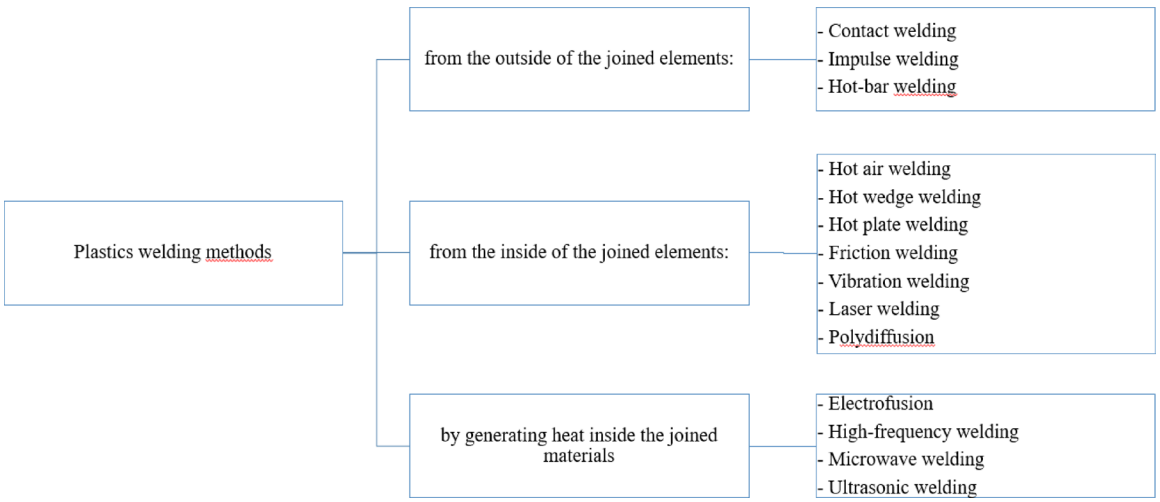

Fig. 1. The classification of the welding methods in terms of the method of heat supply[14].

Differential scanning calorimetry
Thermogravimetric (TGA) and differential scanning calorimetry (DSC) tests were performed using a simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter. DSC and TGA curves were recorded during heating of samples at a rate of 10 °C/min in the temperature range of 25 ÷ 900 °C. The tests were performed in a nitrogen atmosphere. The samples were cut and weighed using RADWAG AS 82/220.R2 scale.

Oxygen and air permeability (OTR)
Oxygen and air permeability at 25 °C and at an overpressure of 0.04 bar was measured with the use of dedicated APG-80 device (ReMi-Plast s.c., Poland) with accordance to PN-EN ISO 2556:2002 standard. The samples for permeability measurements were cut into the shape of circles with a diameter of 80 mm. The manufacturer's dedicated software Control Center Series 30 was used to record measurement results.

Scanning electron microscopy
Morphology of obtained films was recorded with the use of scanning electron microscopes—Tescan VEGA3 (Tescan) at the acceleration voltage of 30 kV and Phenom ProX (Thermo Fisher Scientific) at acceleration voltage of 5 or 10 kV. Samples for the analysis were not coated with metallic layer to avoid data misinterpretation. The analysis included the Expancel agent in the form of dry unexpanded microspheres powder (DU) and the masterbatch with unexpanded microspheres (MB) along with the surfaces of the film samples and the welds, and the cross-sections of the films before and after welding process in the middle of the weld. Moreover, images of the samples after the tensile tests are included.

Wettability
Wettability was measured in air at 20 °C using KRÜSS DSA25S Digital Droplet Shape Analyzer (KRÜSS GmbH). Surface free energy (SFE) was estimated using Owens–Wendt-Rabel-Kaelble method with two standard liquids: water (0.5 µl) and diiodo-methane (0.75 µl). Results of the static contact angle CA measurements and surface free energy SFE calculations were analyzed with the software KRÜSS ADVANCE 1.14.1.16701.

Mechanical properties
Mechanical properties measurements, *i.e.* tensile strength, elongation at break, modulus of elasticity, puncture resistance, weld strength and tear strength were performed on a Zwick Z010 testing machine. Mechanical properties tests in static tension were carried out in accordance with the PN-EN ISO 527 standard at a tensile speed of 100 mm/min. Puncture resistance tests were carried out in accordance with the ISO EN 14477, using a tensometric compression device, a penetration probe and a THS511 holder (Fig. S1a). Weld strength tests were performed in accordance with the ASTM F88 standard, method A—unsupported (Fig. S1b) at a test speed of 300 mm/min. Tear strength tests were performed in accordance with the PN-ISO 34-1 standard, method A (Fig. S1c) at a test speed of 100 mm/min. Dynamic impact tensile tests were performed using the Cometech Testing Machine Co. Ltd. stand in accordance with the PN-ISO 8256 standard, method A (Fig. S1d) with the used potential energy of 2 J and sample type 4 without notch (for materials characteristics before welding—in two directions: along and across extrusion) and sample type 1 (for welded samples).

Samples for testing static and dynamic mechanical properties were prepared using the dedicated die and a hand press, or the samples were cut using the scalpel in a shape according to the mentioned standards.

Films welding
The films in the form of an extruded sleeve were cut into sections of 100 mm length for the hot-bar welding process. The process was carried out on the FR-900 Multifunctional Automatic Film Sealing Machine (Fig. S2) in a horizontal system with 12 mm wide electrodes. A constant sealing speed of 2.9 m/min was used, which was measured with a tachometer (DT-6236B). The sealing time of one sample was 6.5 s. The welding time was established during preliminary research which showed failure of the microporous samples to bond at shorter times and burn-through and defects at longer welding times. The films with 0%, 1%, 3% and 5% of Expancel content were sealed at five different temperatures: 150 °C, 160 °C, 170 °C, 180 °C, 190 °C. For each temperature 5 samples were prepared for the mechanical properties' measurements according to the standards. The welded samples were cut for testing the weld strength in static test and in dynamic impact tensile test.

Samples received this way were marked with: Expancel content [%]/welding temperature [°C] *e.g.* 0/150, 1/160, 3/170 etc.

Results and discussion
The blown film extrusion process led to the production of the films with different content of the blowing agent—Expancel microspheres. With the increment of the microspheres amount the opacity of the films is stronger, and the tactile texture of the surface is rougher. Obtained films are presented in the Fig. 2. The films are similar to those obtained by Hamdi et al.[13]. However, due to the different blowing agents used, the opacity differs for the films with the same blowing agent content.

Thermal properties of the films
Differential Scanning Calorimetry (DSC) (Fig. S3) enabled determination of used modifier on the thermal properties of the material, especially differences in the melting temperature, enthalpy and characteristics. All samples have melting temperatures in the range ~ 111–113 °C and the degradation of the samples can be observed in the range of ~ 450–510 °C, with maximum at about 470–479 °C. It is typical of the LDPE[18–21] and visible as the endothermic peaks in Fig. S3. Samples with microspheres exhibit different features like exothermic peaks at around 200 °C and 275 °C, as well as the endothermic peak at 400 °C and wide peak around ~ 600–850 °C, which

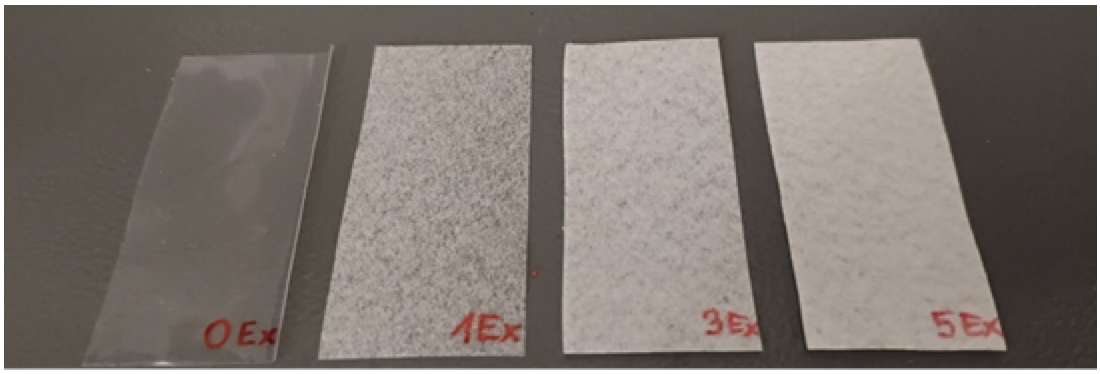

Fig. 2. Digital image of the prepared films with different Expancel content.

Sample	Expancel content [%]	Film Thickness [mm]	Tensile strength [MPa]	Young Modulus [MPa]	Elongation at break [%]	Impact tensile strength [kJ/m^2]		Puncture Strength [N]
						Along extrusion direction	Across extrusion direction	
0Ex	0	0.082	12.82	225.68	148.32	849.98	847.97	1.80
1Ex	1	0.150	5.95	119.29	122.94	406.68	312.07	1.33
3Ex	3	0.191	3.91	90.61	65.45	354.94	321.88	1.42
5Ex	5	0.234	2.31	63.72	19.81	238.37	212.69	1.04

Table 1. Mechanical characteristics of prepared films before welding.

are not present in bare LDPE. These peaks rise with the content of the microspheres and can be attributed to the thermal decomposition of Expancel additive. It is in agreement with the thermogravimetric analysis (TGA) curves (Fig. S3).

Mechanical properties of the films

Prepared films were tested for their mechanical properties before the welding process as well as after the welding process to test the strength of the weld and determine the impact of the post-processing of the extrudate.

Blown film extrusion process was conducted in stable conditions. Mechanical characteristics of prepared films are presented in Table 1.

Examination of the extruded films with different amounts of added Expancel, revealed that with the increase in the modifier dosage, the thickness of the films increases. The Expancel microspheres expand in the processing temperatures, increasing their diameters as the solvent inside evaporates, and form the closed cells in the film. Therefore, films with different content of Expancel have different thicknesses. Expansion of the microspheres lead to the increment of this parameter from 82% (1Ex), up to 185% (5Ex), compared to the pure LDPE film (sample 0Ex). Simultaneously, the mechanical properties of the film worsen. Tensile strength of the samples dropped from 12.82 MPa (sample 0Ex) to 2.31 MPa (sample 5Ex) (by about 43% between consecutive samples). At the same time, elongation at break decreased from 148.32% (0Ex) to 19.81% (5Ex) (*i.e.* for 17%, 46% and 70% between consecutive samples). Also, the elasticity of the samples decreases. The Young modulus changed from 225.68 MPa for pure LDPE film (0Ex) to 63.72 MPa for the film with 5% of Expancel (sample 5Ex).

The puncture tests showed that the addition of microspheres results in decrease of the puncture strength values, and the difference is most pronounced for the samples with 1% and 5% of Expancel. Sample with 3% is similar to the sample with 1% (only 7% difference in the strength value). The Levene test revealed that the standard deviations between test groups are not statistically significantly different (p-value: 0.61).

Tensile impact strength tests shown significant changes related to the Expancel content and changes of minor importance related to the direction of the sample alignment. Results for the samples aligned along the extrusion direction were slightly higher than these for the samples aligned in transverse direction. The direction did not influence the results obtained for the pure LDPE samples. In the case of microporous samples, the drop of the tensile impact strength in the direction across the extrusion direction was 23% (sample 1Ex), 9% (sample 3Ex) and 10% (sample 5Ex), compared to the values obtained for the samples aligned in the extrusion direction. Concerning the difference in the tensile impact strength between pure LDPE and samples with Expancel, it turned out that in the extrusion direction the drop of tensile impact strength between consecutive samples is 52%, 13% and 32%, respectively, whereas in the transverse direction the tensile impact strength is for 63%, 3% and 34% lower.

Addition of Expancel leads also to the significant decrease in tear strength of the polyethylene films (Fig. 3). It can be explained by formed cells behaviour as the defects which weaken the continuous structure of the film. Increase of the porosity diminishes then the durability of the films. This effect is observed both in the extrusion direction and in the transverse direction. The most notable effect is observed after addition of the 1% of the

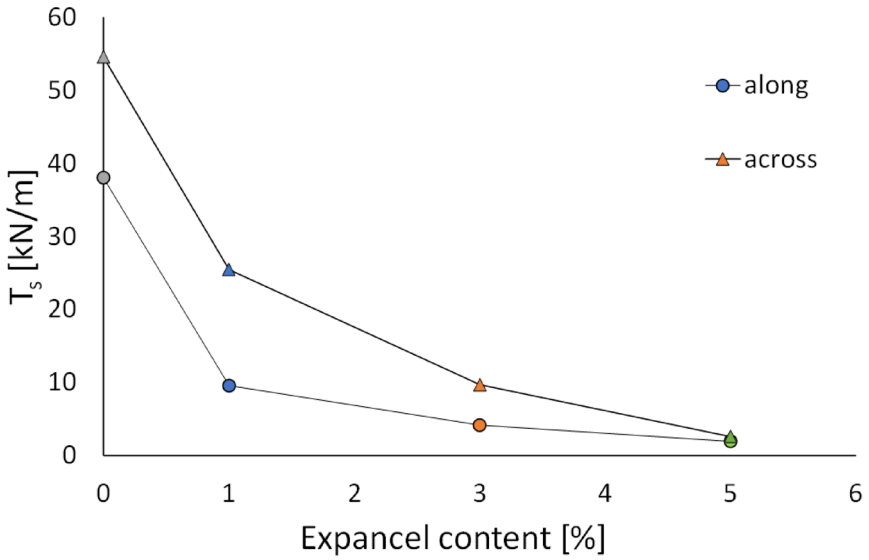

Fig. 3. Tear strength of LDPE film with different Expancel content measured across and along the extrusion direction.

additive. Further increase of the Expancel content does not lead to such pronounced decrease in tear strength, although, constant decrease is visible. Presence of the microspheres disrupts the structure of the polymer by changing the orientation of the chains. Moreover, weak adhesion of the microspheres' walls to the polymer matrix and formation of the thin walls between cells can lead to the easier decohesion of the material in the area of shear strains. Plot in the Fig. 3. depicts the dependence of the tear strength on the Expancel content and compares the values obtained for the samples prepared along the extrusion direction and in transverse direction. Values obtained for the tear along the extrusion direction are lower than in the transverse direction. The anisotrophy of the properties may be explained with the linear alignment of the polymer chains along the extrusion direction enhanced by the presence of expanding microspheres, which facilitates tear propagation. The statistic ANOVA test and Tukey post-hoc test revealed that all group comparisons showed statistically significant differences ($p < 0.001$) (Table S1 and Fig. S4). This means that each increase in microsphere content leads to a significant decrease in tear strength, both across and along the samples.

The tests of the static and dynamic mechanical properties shown significant decrease in the resulting values due to the Expancel presence. It is most pronounced for the 3Ex sample where microspheres are arranged in the agglomerations which may induce the ruptures propagation during dynamic loading. Material loses then its ability to the energy absorption. It corroborates with the data based on the micromechanical models[22,23]. Observed lower parameters (elongation at break and impact tensile strength) may be the effect of too high microspheres loading with their high local density and, therefore, existing of anisotrophy and additional strain concentration in the films[22,24].

Weld strength

Examination of the mechanical properties of the welds obtained at different temperatures revealed the microspheres amount (Fig. 4a–d) and temperature's (Fig. 4e and f) influence on the weld strength during tensile (T-peel) test.

In terms of the addition of the blowing agent, it causes the loss of the weld strength (both F_{max} and F_{av}) despite the temperature and the drop deepens with the increasing amount of the microspheres' (Fig. 4a and c). Similar trends can be observed during analysis of weld strength taking into account weld width (Fig. 4b and d). The highest values were obtained for the 0Ex sample (*e.g.* 990.6 N/m at 150 °C) and the lowest for the sample 5Ex (*e.g.* 454 N/m at 180 °C). The strongest drop of F_{max} and F_{av} (Fig. 4a and c) can be observed between samples with 1% and 3% of microspheres (samples 1Ex and 3Ex) for weld temperature 180 °C and it is 22% for F_{max} and 36% for F_{av}, respectively.

For the 0Ex sample, F_{max} values are the highest for the temperature 190 °C (25.48 N), and lowest for 180 °C (21.84 N). Similarly, 5Ex sample exhibit decrease of the weld strength F_{max} from 12.82 N (150 °C) to 11.34 N (180 °C), and then slight increase to 13.22 N in 190 °C. The same tendency is observed for average weld strength F_{av} for these samples. For samples 1Ex and 3Ex, weld strength decline with the increase of the temperature despite the small peak at the 170 °C. These data suggest that higher temperatures are more appropriate for porous films welding, and differences are related to their microstructure.

Described changes can be explained *e.g.* by better interactions and connections between polymer chains at higher temperatures, which causes better homogeneity of the welds and, therefore, the increment of the weld strength (visible at 190 °C). However, the presence of microstructures disrupts the uniform structure and

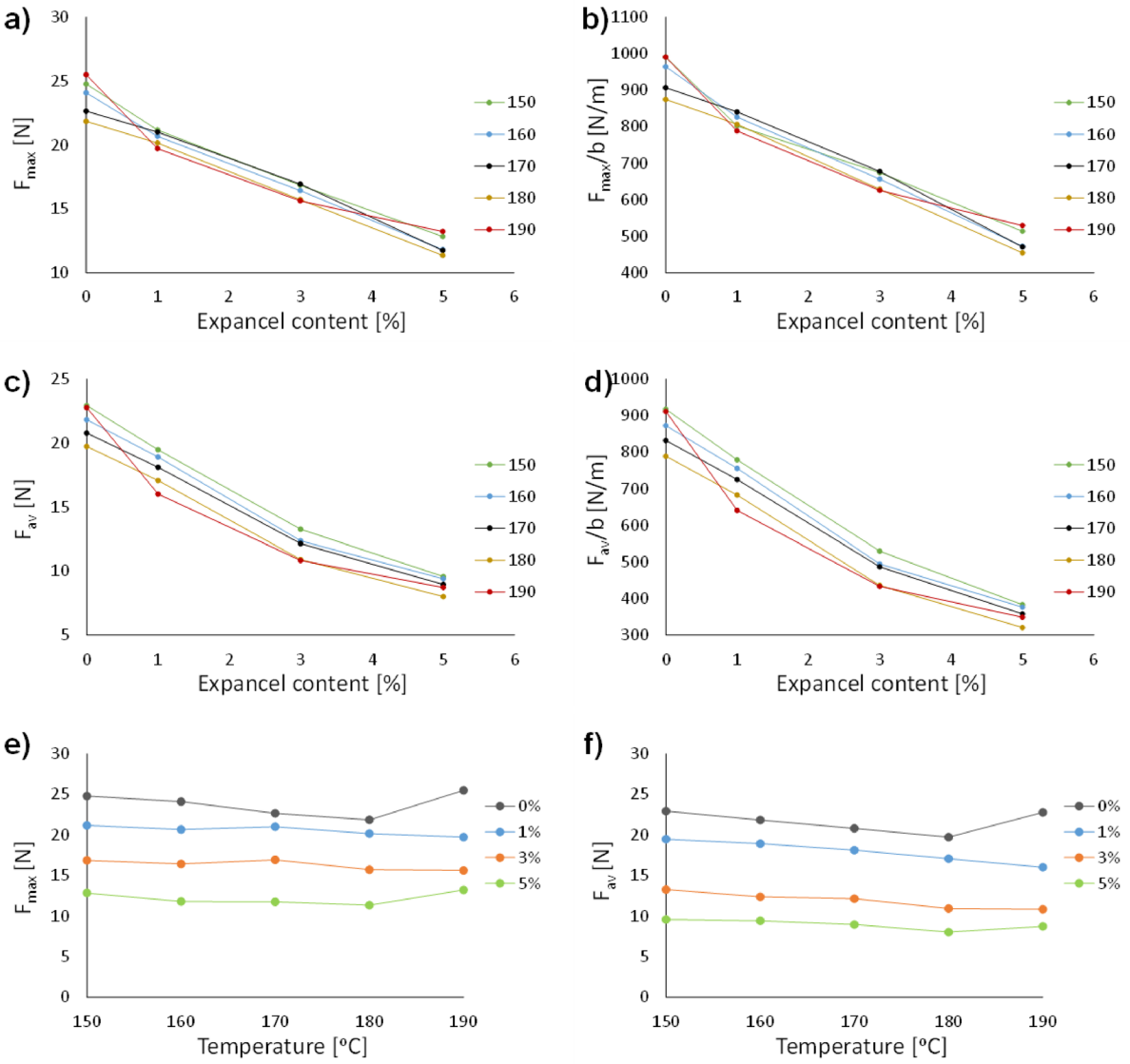

Fig. 4. The dependence of the maximal weld strength (F_{max}) and average weld strength (F_{av}) on the Expancel content (**a**–**d**) and on the temperature (**e**–**f**) during T-peel tests.

hinders the polymer chains movement, especially at lower temperatures. This leads to the observed drop in the mechanical properties of the welds at every examined temperature. This hypothesis can be beared with the literature. For example, in the work of Ge et al.[25] the results of the molecular dynamics simulation were described, showing the dependence of the weld strength on the entanglement of the polymer chains at the interface. In another work,[26] analysis of the welding of PDMS film with PMMA microspheres brought to the conclusion that the microspheres affect the structure and strength of the weld (changing this parameter for ~ 35 kPa). Moreover, films with higher content of microspheres required longer welding time, due to the films roughness induced by the microspheres, which was unfavorable and caused the weld damage. In other works, the influence of thermomechanical parameters on the weld strength was described[27–29].

In all cases, temperature was the crucial factor influencing the strength. During ultrasonic welding of polymers[28] it was demonstrated that temperature rise and contact time elongation result in weld strength increase. However, exceeding the melting temperature of polymer matrix can lead to its degradation[27] which can destruct the weld.

It is worth noting that in this work a constant welding time was set (6.5 s). During the experiment the negative influence of the time elongation on the weld quality was noted, especially at higher temperatures (180–190 °C). It appeared as the discontinuities and holes along the weld line and material adherence to the electrodes. Therefore, despite that, the 190 °C temperature seems the best for the welds resistance in the static tensile test, the welding time has to be adjusted.

To simulate the real conditions of the welds utilization, the impact tensile tests were also performed. In this case the weld strength declines both with the blowing agent content and with the welding temperature increment

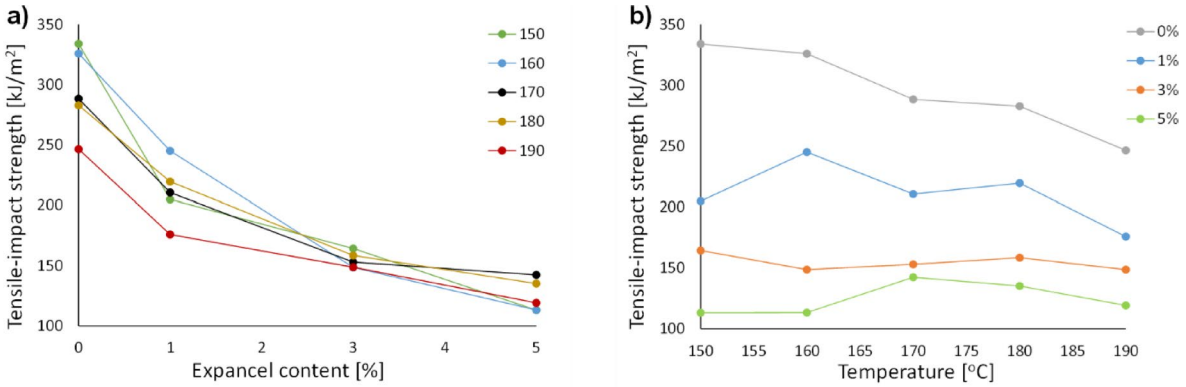

Fig. 5. The dependence of the weld strength on the Expancel content (**a**) and welding temperature (**b**) during impact tensile tests.

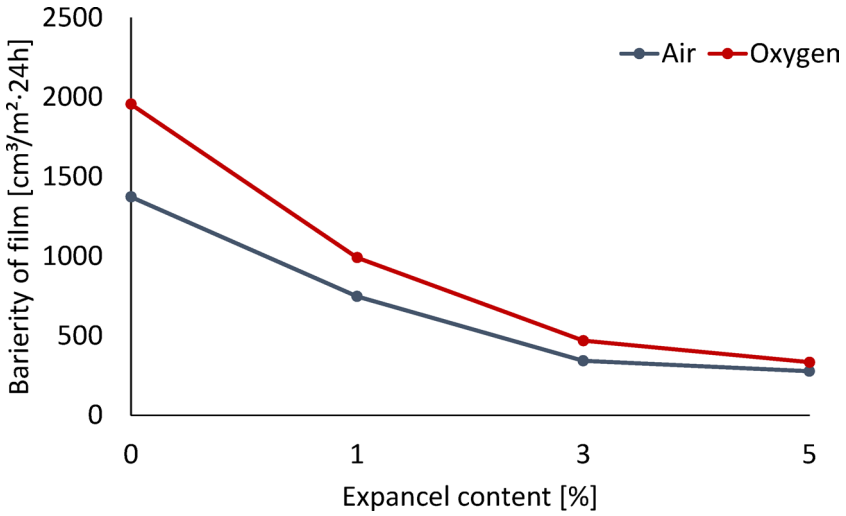

Fig. 6. Barrier properties of the films with different Expancel content.

(Fig. 5). It is most pronounced for the samples 0Ex and 1Ex, whereas for samples 3Ex and 5Ex a slight rise of the weld strength is observed above 170 °C. However, the value for the 190 °C is still similar or lower than the value obtained at the 150 °C. The discrepancies between the T-peel and impact tensile tests come from the different behaviour of the films during these tests. During T-peel tests the damage appeared mostly within the weld, and during impact tensile tests the rupture most often occured in front of the weld.

Barrier properties and wettability of the films

Another important issue was the influence of the microspheres' amount on the barrier properties of the LDPE films against oxygen and air (Fig. 6). For the reference sample 0Ex (pure LDPE), OTR values were 1372.73 cm^3/m^2·24 h for air and 1956 cm^3/m^2·24 h for oxygen, respectively. The addition of 1% microspheres resulted in 45.6% air permeability reduction (747.55 cm^3/m^2·24 h) and 49.3% oxygen permeability reduction (991 cm^3/m^2·24 h). Higher content of the microspheres (samples 3Ex and 5Ex) led to the further decrease in the OTR values up to 276.39 cm^3/m^2·24 h (for air) and 333 cm^3/m^2·24 h (for oxygen), which corresponds to the reduction for 79.9% and 83.0%, respectively in relation to the reference material. Obtained results confirm functionality of the Expancel microspheres as the barrier properties modifiers. Decrease in the permeability can be explained, *e.g.* by the diffusion path elongation and tortuosity, where the microspheres can act as the physical obstacles confining the gas pathways through the polymer matrix. This effect is consistent for both gases used, which confirms versatility of this modification. Similar effects considering material microstructure were described in the literature[4,30–32]. An important and necessary aspect of the analysis of the obtained barrier results may be the numerical simulation of this property based on the Nielsen Maxwell–Garnett and Bruggeman models[33,34].

To assess the influence of the microspheres' addition on the wettability of the extruded films, contact angle and SFE measurements were conducted using two standard liquids—water and diiodomethane. Results of the measurements and calculations are presented in Table 2 and Figure S5.

Analysis of the data reveals that the increase of Expancel content leads to the increment in the contact angle value. This is partially due to the arising surface microstructure of the foamed films, which causes their stronger

Sample	Water [°]	Diiodomethane [°]	SFE Total [mN/m]	Disperse component [mN/m]	Polar component [mN/m]
0Ex	90.03	47.97	36.85	35.40	1.45
1Ex	98.30	48.62	35.28	35.04	0.24
3Ex	104.06	61.91	27.66	27.48	0.19
5Ex	122.72	65.38	26.40	25.48	0.92

Table 2. Contact angle of water and diiodomethane with obtained films with different amount of Expancel, and results of the SFE calculations along with disperse and polar components.

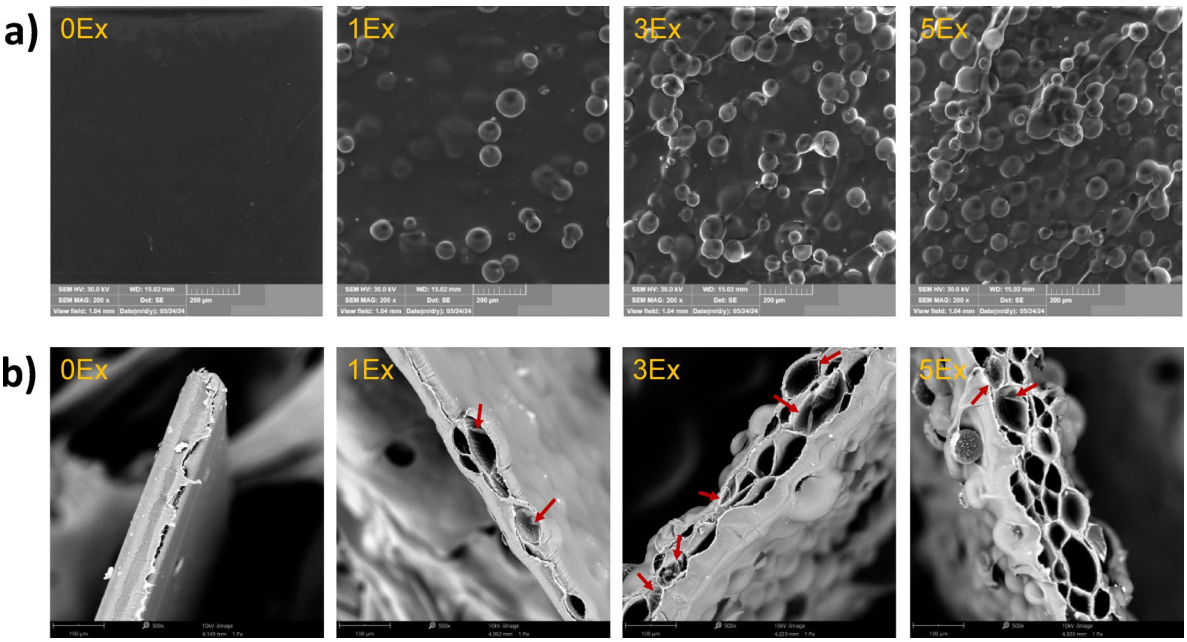

Fig. 7. Morphology of the obtained films surfaces Magnification 200x (**a**) and their cross-sections. Magnification 500x (**b**).

hydrophobicity. A similar tendency is observed for diiodomethane, which, along with the decrease of total SFE, and particularly the polar component, indicates the limited ability of strong interactions formation between the surface and liquids. Closed cells in the structure of the films with Expancel may reduce actual surface being in contact with liquid and, therefore, limit the availability of the polar groups to interact with the liquid molecules.

SEM of the films

SEM analysis revealed the morphology of the extruded LDPE films. It turned out that Expancel, even in thin-walled extrudates, forms closed cells which forms a microstructure on the surface and result in greater thickness and higher specific surface area of the films containing the blowing agent (Fig. 7a).

Cross-sections of these films present the interior of the cells with the shells of Expancel blowing agent remaining inside but flatten after the cut (marked with arrows) (Fig. 7b). It is clear that in contrast to the mentioned films obtained with the use of azodicarbonamide[13], the cells morphology is different (they are more round) and there are less cells in the films containing Expancel with the same amount of blowing agent added. Moreover, the surface of the films with Expancel are definitely rougher. Roughness of such modified films was examined and described in our previous study[35].

To confirm that these are definitely Expancel shells, SEM images of the bare Expancel microspheres in the form of powder and in the form of the used masterbatch were acquired showing the same morphology (Fig. S6). Corresponding morphology of the blowing agent itself and in the matrix after cross-section was observed by Yousaf et al.[36].

These results indicate that the shells are not adhering strongly to the LDPE matrix. Shells of the Expancel are made of the acrylate copolymer, which is far more polar than the polyolefins, therefore, interactions between these two phases may not be very strong.

The size of the cells differs between the films with different Expancel content and is largest in the film with 1% of the additive (sample 1Ex) and smallest in the one with the 3% of blowing agent (sample 3Ex). The size depends on the amount of Expancel as with the highest dosage of the blowing agent, the microspheres do not

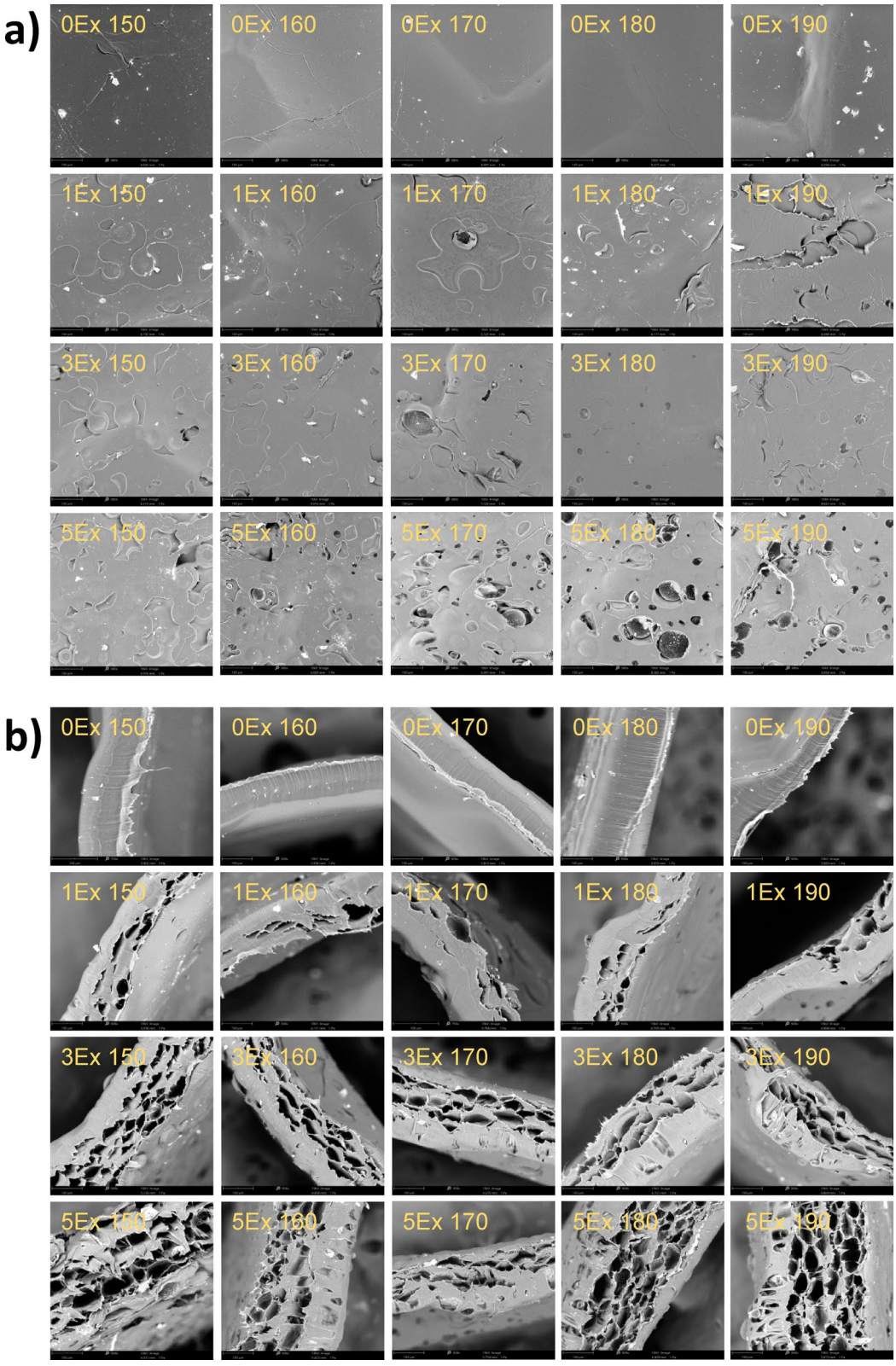

Fig. 8. Morphology of the surfaces of the welds obtained at different temperatures (**a**) and cross-sections of the welds obtained at different temperatures (**b**).

have the space to expand, and they are confined by the presence of adjacent microspheres and higher pressure during the extrusion process (Fig. 7).

Welding process led to the perforation of the microspheres in the surface layer of the film and collapse of the cells as evidenced by the images in Fig. 8a. Inside the weld, however, the cells are only slightly flattened (the most in the film with 1% of blowing agent—sample 1Ex) and form a uniform structure of the weld (Fig. 8b). Macroscopically, the welds seem to be more-sponge-like than the films themselves. Moreover, despite the pattern of the electrodes, they are smooth in the contrary to the films' surfaces.

Tensile and T-peel tests of the welds showed that the weld was most often not damaged. The samples were damaged just at the weld edge, as shown in Fig. S7. The SEM images of the samples recorded after the tensile tests of the welds, reveal the flow of the material before rupture and release of the untouched expanded Expancel microspheres from the material (Fig. S6). It confirms the hypothesis, that the microspheres are not strongly bonded to the LDPE and can facilitate the polymer matrix decohesion. Similar observations were made by Yousaf et al.[24] who investigated syntactic foams with thermoplastic microspheres. In their case the interfacial debonding of microspheres from the matrix led to the worse tensile properties of the samples.

It should be also taken into account, that the release of the microspheres may be a potential hazard. Therefore, use of the blowing agent should be matched with the final product application.

Conclusions

This work demonstrates that the introduction of blowing agent (Expancel polymer microspheres) to the LDPE matrix in blown film extrusion process enables obtaining thin-walled microporous films with closed-cell structure. Performed tests confirm fundamental influence of the microspheres content on the structural, mechanical and thermal properties and post-processing (welding) of obtained films.

Microspheres formed closed cells in the film structure resulting in the film thickness and surface roughness increase. SEM images revealed the expansion of the microspheres and their weak adhesion to the LDPE matrix in the film structure. For this reason, additional surface treatment of the microspheres or the addition of an adhesion compatibilizer during processing should be considered. The poor adhesion of microspheres and their release from the polymer matrix should be taken into account when selecting microsphere film applications, especially as food packaging.

Moreover, after welding, collapse and perforation of microspheres at the welds surfaces was observed with simultaneous formation of uniform porous structure inside the weld. The increment of microspheres content led to the gradual deterioration of the mechanical properties *i.e.* tensile strength, impact tensile strength, Young modulus, elongation at break, puncture resistance and tear strength. Microspheres act as the structural defects and generate local strain concentration and facilitate initiation of the ruptures. However, the addition of the microspheres enhanced barrier properties of the films. Air and oxygen permeability was reduced even by ~ 80%, which can be ascribed to the diffusion path elongation for the gas molecules with microspheres acting as the obstacles in the polymer structure. Moreover, increment of the Expancel content result also in the lowering of the surface free energy of the obtained films due to the microstructure of their surfaces.

Hot-bar welding was performed successfully for all obtained films. In this case, microspheres also led to the drop in the mechanical properties i.e. weld strength. Film with 5% of microspheres had the weld strength lower by about 50% compared to the pure LDPE film. Also, the welding temperature and time were found to be important in terms of the weld strength.

Despite the fact that Expancel microspheres causes deterioration of the mechanical properties of the films and welds, in some cases the new functionalities like barrier properties or lower adhesion may be more important. Decrease of the mechanical integrity of the polymer matrix lead also to the microspheres' release from the films structure. Therefore, it should be taken into account when designing materials for the food or medical industry, or the better adhesion of the microspheres to the matrix has to be achieved.

Performed research confirms the possibility of closed-cell films production and their post-processing which is an important issue in terms of future applications in the industry.

Data availability

The data will be made available upon reasonable request from the corresponding author Aneta Tor-Świątek (a.tor@pollub.pl).

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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