Study of the biodegradability of polylactide fibers in wastewater treatment processes*)

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Abstract: The aim of this research was to study what happens to polylactide (PLA) fibers when they are released to wastewater systems. Samples of PLA fibers were immersed in activated sludge and subjected to typical activated sludge treatment in mesophilic (36 °C) and thermophilic (56 °C) conditions for up to 4 weeks. The characteristics of the surface and cross-sections of PLA fibers were analyzed by scanning electron microscopy (SEM), showing the settlement of the microorganisms on the surface of PLA fibers immersed in sludge and also the erosion of the material with time. Differential scanning calorimetry (DSC) analysis provided information on small changes in the crystalline structure of PLA fibers, and the results of tensile tests proved only partial degradation of PLA material treated in the activated sludge system during the processing time. The study confirmed that the standard processing of wastewater in the activated sludge system, in both mesophilic and thermophilic variants, is insufficient for the biodegradation of PLA. Therefore, PLA microplastics can be released from wastewater treatment plants.

Keywords: polylactide, wastewater treatment, microplastics, fibers.

Badanie możliwości biodegradacji włókien polilaktydowych w procesach oczyszczania ścieków

Streszczenie: Zbadano oddziaływanie osadu czynnego w procesach przebiegających w oczyszczalni ścieków na włókna polilaktydowe (PLA) uwolnione z wyrobów włókienniczych. Próbki włókien PLA umieszczano w osadzie ściekowym i poddawano klasycznemu procesowi oczyszczania ścieków metodą osadu czynnego, w procesie mezofilowym (36 °C) oraz termofilowym (56 °C), w ciągu 4 tygodni. Powierzchnię i przekrój poprzeczny włókien charakteryzowano z zastosowaniem skaningowej mikroskopii elektronowej (SEM). Wykazano zasiedlenie mikroorganizmami powierzchni włókien inkubowanych w osadzie czynnym oraz stopniową erozję badanego materiału. Na podstawie wyników badań metodą różnicowej kalorymetrii skaningowej (DSC) stwierdzono nieznaczne zmiany w strukturze krystalicznej włókien PLA, natomiast badania wytrzymałościowe potwierdziły częściową degradację włókien poddanych działaniu osadu ściekowego. Dowiedziono, że standardowe procesy oczyszczania ścieków metodą osadu czynnego, zarówno w wersji mezofilowej, jak i termofilowej, nie powodują biodegradacji PLA, dlatego też polilaktydowe mikrocząstki mogą być uwalniane z osadu ściekowego.

Słowa kluczowe: polilaktyd, oczyszczanie ścieków, mikrocząstki polilaktydu, włókna.

Global plastic production has increased dramatically in recent years and waste plastics are one of the most dangerous environmental problems facing the world today. Even though some plastics are potentially biodegradable they truly decompose only under specific conditions. According to different authors, microplastics have been defined as particles smaller than 5 mm. However, some set the upper size limit even smaller at 1 mm [1–3]. Microplastics cause the most pronounced problem in the marine environment as they can absorb different poisonous chemical compounds [4, 5]. Moreover, they are taken up by plankton eating organisms [6, 7]. Particles of microplastics, including microfibers, move from the gastrointestinal system of a host fish into its cells, accumulate over time and grow in concentration up the food chain [1]. There are different sources of microplastics in the marine environment, one of them is the textile sector with short

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fibers released from garments during laundering or hygienic products and others, rayon and polyester microfibers are commonly observed in the marine environment [8] due to this process.

One of the interesting polymers in this context is polylactide (PLA) as it is a pretty new raw material for textile applications [9–13]. It has relatively good mechanical and thermal properties [14–16]. This thermoplastic, aliphatic polyester derived from renewable resources is fully biodegradable in compost conditions but its biodegradability in other conditions is still being investigated [17, 18]. The biodegradability in other conditions, such as sewage treatment plants, is particularly important.

The aim of this research was the investigation of the biodegradability of PLA fibers deposited in activated sludge.

Biological treatment is an important and integral part of any wastewater treatment plant that treats wastewater coming from two major sources: as human sewage and as process waste from manufacturing industries, or a mix of the two types of wastewater sources.

Biological treatment using the aerobic activated sludge process has been in practice for well over a century. Increasing pressure to meet more stringent discharge standards has led to the implementation of a variety of advanced biological treatment processes in recent years [19].

Numerous attempts have been made to recognize and solve the problem of pollutants removed by the activated sludge process where wastewater containing organic matter is aerated with microorganisms to metabolize the suspended and soluble organic matter.

The activated sludge process is a biological method of wastewater treatment technique in which a mixture of wastewater and biological sludge (microorganisms) is agitated and aerated. The biological solids are subsequently separated from the treated wastewater and returned to the aeration process as needed [20]. The activated sludge of the aeration basin of a wastewater treatment works is a complex ecosystem of competing organisms. Three basic types of organisms important to the operation of an activated sludge system are bacteria, plants and animals. Plants include algae and fungi. Bacteria are the most important and constitute the majority of microorganisms present in activated sludge. Bacteria that require organic compounds for the supply of carbon and energy (heterotrophic bacteria) predominate, whereas bacteria that use inorganic compounds for cell growth (autotrophic bacteria) occur in proportion to concentrations of carbon and nitrogen [21].

In our study, samples of PLA fibers were immersed in the activated sludge for 1–4 weeks upon constant aeration. As the thermal characteristics of polymers very well capture changes of the supramolecular and molecular structure, DSC analyses were done in order to track the biodegradation of PLA in the activated sludge environment. Moreover, scanning electron microscopy (SEM) observations were performed to provide information on the morphology of the fibers, as well as tensile tests to analyze the mechanical properties of single fibers.

EXPERIMENTAL PART

Materials and the biodegradation test

Commercial PLA multifilament yarn (1100 dtex, 210 f x 3 Z60) from Huck (Germany) was used in the experiment (Fig. 1). The biodegradation tests were conducted in activated sludge from a local sewage treatment plant in Bielsko-Biala. The samples of PLA fibers (10 samples for each batch for statistics) were immersed for the period of 1–4 weeks in the reactors with activated sludge and aerated during the whole period of testing. Samples of PLA fibers immersed in activated sludge were subjected to typical activated sludge treatment in mesophilic (36 °C) and thermophilic (56 °C) conditions. In parallel, fibers were also immersed in distilled water at the temperatures of 36 °C and 56 °C for comparison, so that the tracking of hydrolysis in water was also possible. After a specified period, samples were removed from the sludge, rinsed carefully with distilled water and dried.

Fig. 1. PLA multifilament used for analysis

Methods of testing

– Weight loss of the PLA fibers treated in activated sludge and in water was evaluated by determining the dry weight of the samples before and after biodegradation, according to the formula:

$$\text{Weightloss} = -\frac{(W_1 - W_2)}{W_1} \cdot 100\ \% \qquad (1)$$

where: W_1, W_2 – dry weights of the samples before and after treatment, respectively.

– Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Thermal Analysis System 5100 equipped with TA Instruments 2920 Calorimeter and RCS cooling system. The temperature was calibrated with the melting point of indium (156.6 °C) and the enthalpy was calibrated with indium (28.4 J/g). The measurements were registered in the temperature range -20–240 °C, using TA standard aluminum

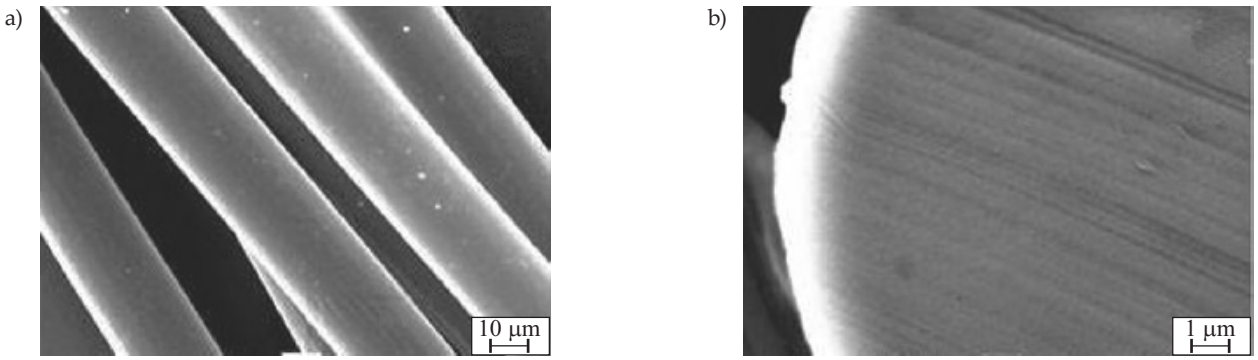

Fig. 2. SEM microphotographs of PLA fibers before biodegradation: a) surface, b) cross-section

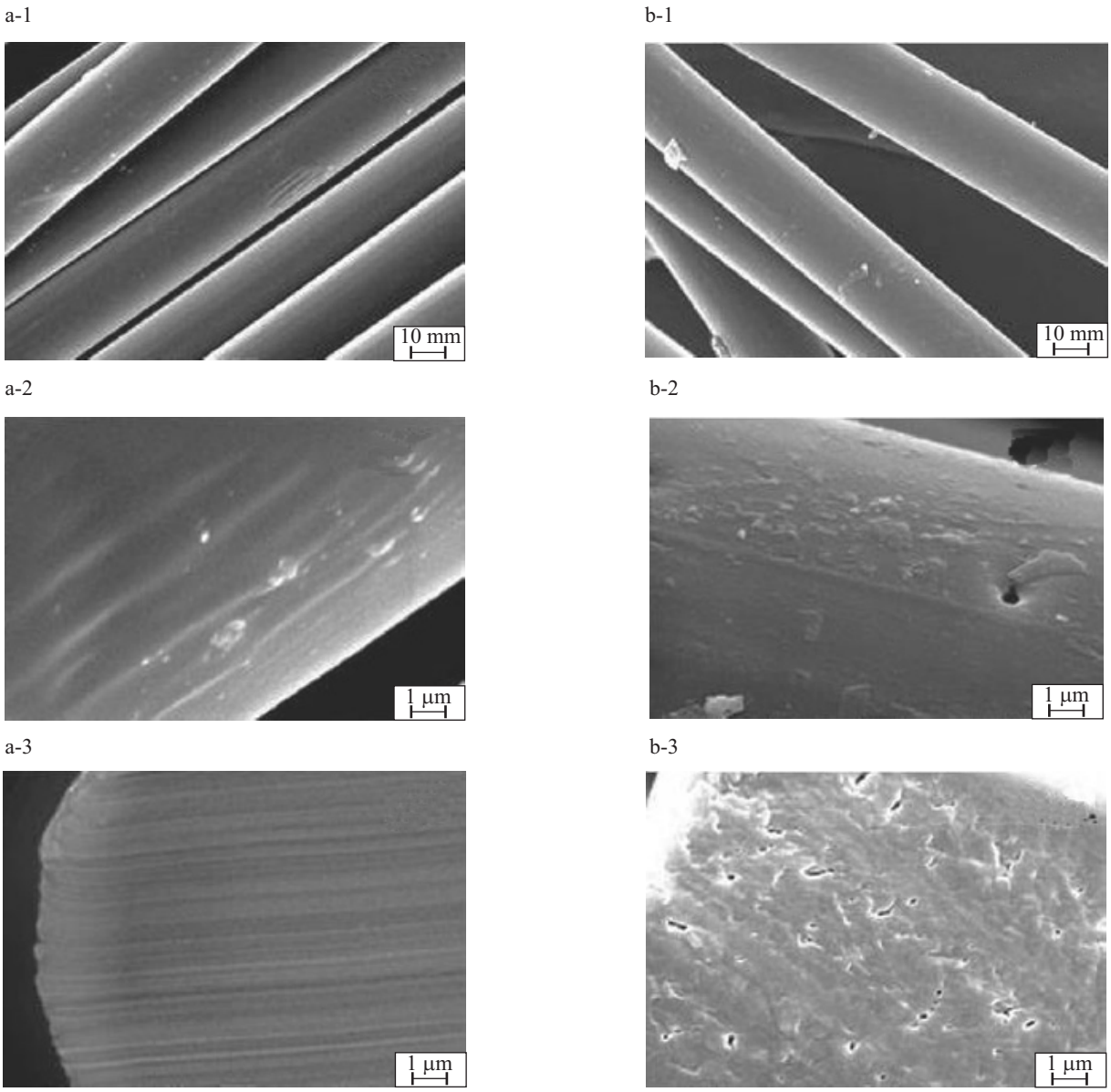

Fig. 3. SEM microphotographs of PLA fibers after processing at 36 °C in: a) water, b) activated sludge for 4 weeks (1 – general view, 2 – surface, 3 – cross-section)

pans, under a nitrogen atmosphere (flow 40 cm^3/min) with a heating and cooling rate of $\beta+ = \beta- = 10$ °/min. The data were evaluated by means of the Universal V2.6D (TA Instruments) software. Glass transition temperatures T_g and melting temperatures T_m were evaluated. For a quantitative consideration, the crystallinity index as a main parameter of the nanostructure of investigated PLA fibers, corrected for the cold crystallization process (perfection of existing crystallites), was calculated as follows:

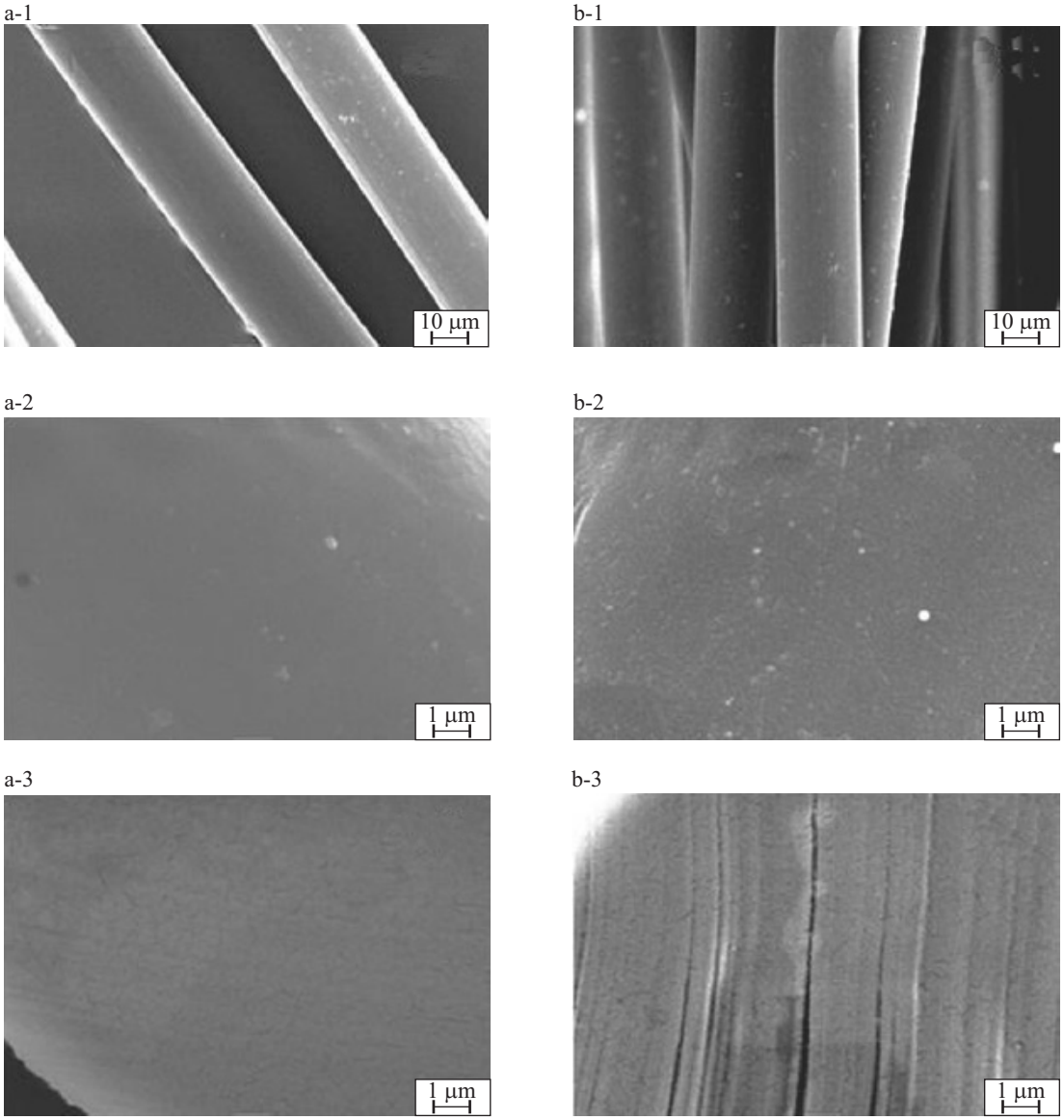

Fig. 4. SEM microphotographs of PLA fibers after processing at 56 °C in: a) water, b) activated sludge for 4 weeks (1 – general view, 2 – surface, 3 – cross-section)

$$\kappa = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^0} \cdot 100\ \% \qquad (2)$$

where: ΔH_m – enthalpy of sample melting (measured value, J/g), ΔH_{cc} – enthalpy of cold crystallization which appears in the sample during the DSC measurement (in our study we have assumed 0 J/g, as cold crystallization did not occur), ΔH^0 – enthalpy of melting of a fully crystalline pure PLA standard sample (calculated value, in our study we have assumed 106.0 J/g [22]).

– Scanning electron microscopy (SEM) analyses were performed in a conventional SEM mode using a Jeol JSM 5500LV instrument operating at 10 kV, after coating the samples with a thin layer of gold by sputter deposition. Surfaces of samples were observed at up to 10 000x magnification.

– The fibre strength properties were determined using an Instron 5544 single column tensile tester, according to the PN-EN ISO 5079:1999 standard. All tests have been made at standard atmosphere (temperature 20 ± 2 °C; relative humidity 65 ± 5 %). Breaking force and elongation at break were measured, tenacity was calculated according to standard.

RESULTS AND DISCUSSION

SEM analysis shows that the surface of untreated fibers is smooth and even, and the cross-section is regular and compact (Fig. 2).

As the effect of inoculation of fibers in activated sludge, a biofilm of microorganisms is formed on the surface of fibers. Biofilm deposition is not observed in the case of fibers immersed in distilled water, their surface remains smooth for the whole testing period (Fig. 3a-2, Fig. 4a-2).

The cross-section of fibers inoculated in activated sludge remains compact within the biodegradation process until week 4, when it becomes more porous (Fig. 3b-3, Fig. 4b-3), for this reason there are presented only micro-

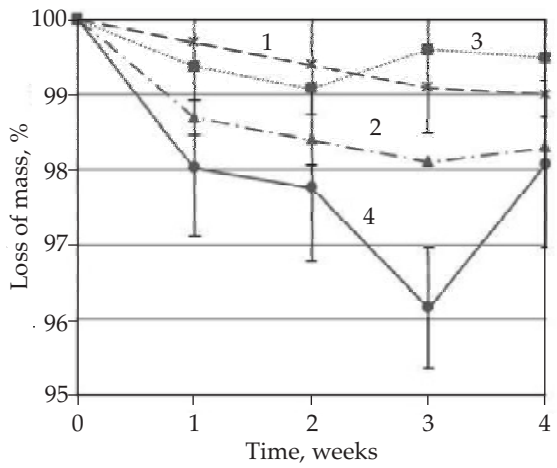

Fig. 5. Weight loss of PLA fibers after incubation in water and activated sludge for the period of 1–4 weeks at 36 °C and 56 °C: 1 – 36 °C water, 2 – 36 °C sewage, 3 – 56 °C water, 4 – 56 °C sewage

photographs of fibers after 4 weeks of incubation. The porosity is observed at both processing temperatures, 36 °C and 56 °C, and it was not observed for samples immersed in distilled water. The porosity observed in the cross-sections of fibers after 4 weeks of biodegradation can be explained by the loss of mass occurring during biodegradation in the activated sludge system (Fig. 5) as the effect of erosion of polymer by hydrolytic degradation.

According to our results, the maximum loss of weight was approx. 4 %, and it was observed after 3 weeks of incubation of PLA fibers in sludge at 56 °C. In the 4th week, an increase of weight was observed, which may be attributed to the formation of the thicker layer of biofilm on the surface of fibers, which masks the actual loss of weight. In the case of fibers incubated in sludge at 36 °C, the loss of weight was less pronounced, up to 2 %. The weight loss in the case of samples immersed in distilled water was lower at both temperatures, and did not exceed 1 %.

According to literature data, the biodegradation process is faster and more intensive when it is conducted above the T_g [22]. All of the samples analyzed in this study were subjected to biodegradation below the glass transition temperature. From DSC curves, one can deduce that, during the production of fibers, hot drawing was applied as there is no effect of so-called cold crystallization on the DSC curves and the T_g is relatively high (approx. 70 °C) (Figs. 6, 7).

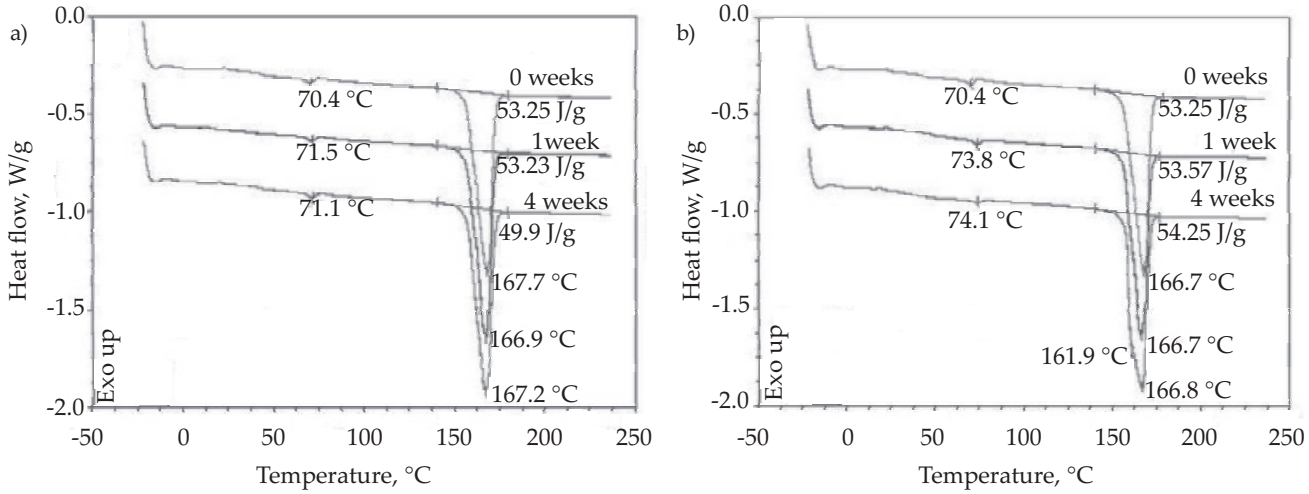

Fig. 6. DSC curves of samples incubated at 36 °C in: a) water, b) activated sludge

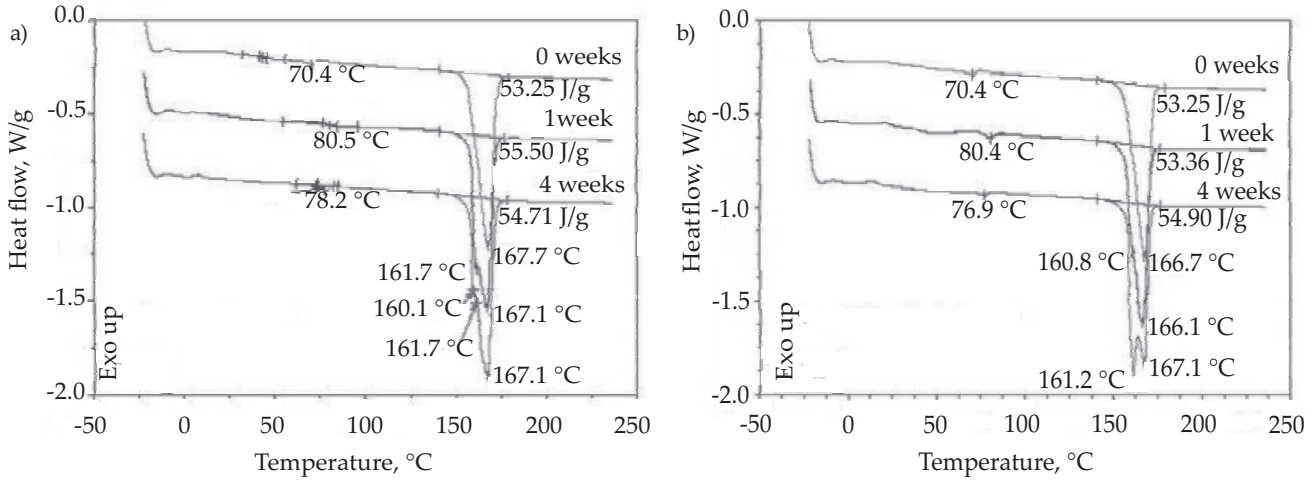

Fig. 7. DSC curves of samples incubated at 56 °C in: a) water, b) activated sludge

T a b l e 1. Values of thermal parameters from DSC analysis

Process temp. °C	Time weeks	Water				Sewage			
		Temperature of glass transition T_g, °C	Temperature of melting T_m °C	Enthalpy of melting ΔH_m, J/g	Degree of crystallinity κ, %	Temperature of glass transition T_g, °C	Temperature of melting T_m °C	Enthalpy of melting ΔH_m, J/g	Degree of crystallinity κ, %
–	0	70.4	167.7	53.25	50.2	70.4	167.7	53.24	50.2
36	1	71.5	166.9	53.23	50.2	73.8	166.7	53.57	50.5
36	4	71.1	167.2	52.96	49.9	74.1	161.9/166.8	54.25	50.5
56	1	80.5	161.7/167.1	55.50	52.4	80.4	160.8/166.1	53.36	50.3
56	4	78.2	160.1/161.7/167.1	54.71	51.6	76.9	161.2/167.1	54.90	51.8

T a b l e 2. Values of mechanical parameters of PLA fibers subjected to activated sludge and water

Time weeks	Process temp. °C	Water						Sewage					
		Breaking force cN		Elongation at break, %		Tenacity cN/tex	Tensile strength MPa	Breaking force cN		Elongation at break, %		Tenacity cN/tex	Tensile strength MPa
		Average	*SD*	Average	*SD*			Average	*SD*	Average	*SD*		
0	–	22.05	6.14	23.70	6.66	56.35	699.89	22.05	6.14	23.70	6.66	56.35	699.98
1	36	15.07	3.14	22.67	6.77	53.23	661.17	15.07	2.95	10.57	3.48	38.51	478.34
2		15.47	3.52	18.81	5.51	49.55	615.50	15.47	3.50	10.44	4.18	39.53	491.04
3		13.18	3.09	17.33	6.07	47.76	593.20	13.18	3.50	9.60	5.61	33.68	418.35
4		10.69	2.93	15.17	6.08	44.88	557.38	10.69	3.77	8.51	4.85	27.32	339.31
1	56	17.64	2.99	21.47	8.88	45.08	559.92	19.72	2.43	22.63	4.21	50.40	625.94
2		18.02	3.67	16.75	5.94	46.05	571.98	17.80	2.62	21.20	6.01	45.49	564.99
3		18.13	2.36	16.53	4.27	46.33	575.47	18.93	3.11	20.98	7.39	48.38	600.86
4		19.97	2.49	23.74	8.05	51.03	633.87	12.57	1.46	15.10	4.40	32.12	389.99

The glass transition temperature is related to the macromolecular movements in the amorphous phase of the polymer, the higher the T_g is, the higher the energy necessary to move chains in the amorphous state. The increase of T_g can be attributed to the decrease of the content of the amorphous phase. Processing of fibers in sewage sludge conditions results in only slight changes of supramolecular structure as seen from DSC scans (Fig. 6, Fig. 7). Parameters calculated from DSC are presented in Table 1.

The thermal effects of water and sludge at treatment at 36 °C are negligible. The only change that is worth commenting on is the splitting of the melting endotherm after 4 weeks of processing at 36 °C in sludge (Fig. 6b). Multiple melting peaks can be attributed to (1) the presence of more than one crystallographic form, (2) the presence of melting, recrystallization and remelting, (3) changes in the morphology, for example lamellar thickening or changes of crystal perfection. However, in order to conclude which mechanism takes place in the case of analyzed samples, further structural XRD analysis should be performed. Multiple melting peaks were observed for samples treated at 56 °C in both water and sludge conditions (Fig. 7). As the effect of sewage sludge treatment, a very slight increase of crystallinity was detected in the case of samples after 4 weeks of treatment at 56 °C (~ +1.5 %) (Table 1).

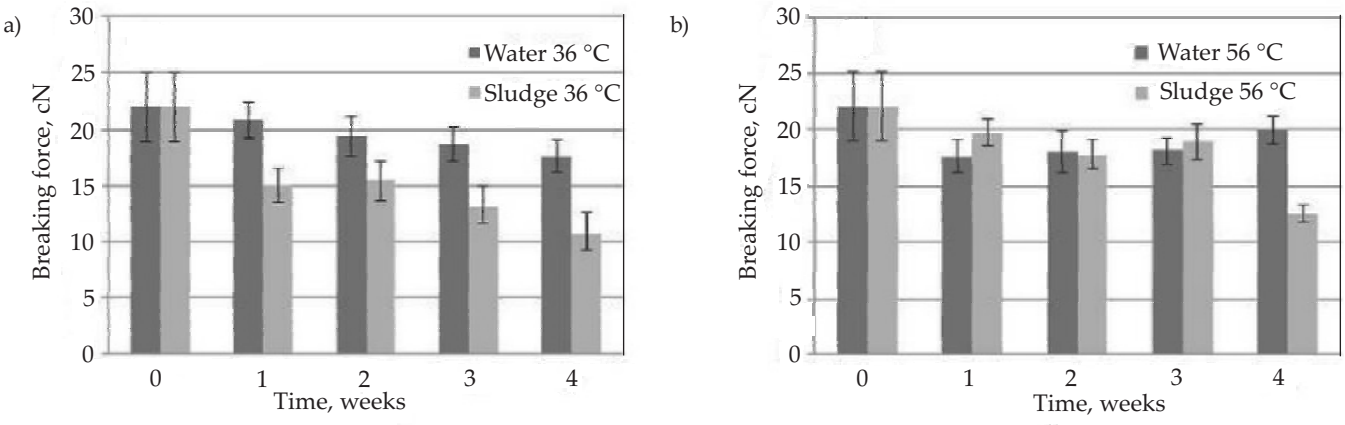

Fig. 8. Breaking force measured for fibers incubated at: a) 36 °C, b) 56 °C

As the result of treatment of PLA fibers in sewage sludge system, the mechanical properties of fibers change (Table 2).

The breaking force measured for fibers treated at 36 °C and 56 °C is presented in Fig. 8.

The specific strength of fibers treated in sewage sludge drops almost by half after 4 weeks at both temperatures (from 56 to 27 cN/tex at 36 °C, and from 56 to 32 cN/tex at 56 °C). The drop of tenacity is related to changes in fiber morphology – after 4 weeks of fiber processing in sewage sludge the fibers become porous and less compact as confirmed by SEM (Fig. 3 and Fig. 4). In the case of incubation in water, the effect is less pronounced. Along with the specific strength, other parameters also change dramatically. Elongation at break resulting with increased brittleness of fibers drops as the effect of biodegradation.

CONCLUSIONS

The study confirmed that the standard processing of wastewater in the activated sludge system in both mesophilic and thermophilic variants is insufficient for the biodegradation of PLA during the standard processing time. Within the 4 weeks of activated sludge treatment, the hydrolytic degradation slowly begins, the effect is only slightly more pronounced than in the case of hydrolysis in water until week 4, when the difference between samples incubated in water and activated sludge is more visible. After wastewater treatment, the microplastics of PLA can be liberated from wastewater treatment plants with the remaining sludge. The biodegradation process of PLA microplastics will not continue as long as the thermodynamic conditions regarding the humidity and temperature are fulfilled, so that in order to enable effective biodegradation of PLA in wastewater plants a process temperature above the T_g should be provided.

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