

# Influence of poly(3-hydroxybutyrate) addition on the properties of poly(lactic acid) nonwoven obtained by the melt-blown technique<sup>\*)</sup>

Marta Łatwińska<sup>1), \*\*)</sup>, Jadwiga Sójka-Ledakowicz<sup>1)</sup>, Marcin Kudzin<sup>1)</sup>

DOI: [dx.doi.org/10.14314/polimery.2015.486](https://doi.org/10.14314/polimery.2015.486)

**Abstract:** Poly(lactic acid) (PLA) nonwoven and PLA (85 wt %)/P(3HB) (15 wt %) [P(3HB) — poly(3-hydroxybutyrate)] composite nonwoven were obtained using the melt-blown technique. The thermal properties, physical-mechanical parameters, specific surface area and susceptibility to hydrolytic degradation were studied for the obtained nonwovens. DSC analysis indicated noticeable changes in the polymers structure during melt-blowing. The addition of P(3HB) to PLA nonwoven generally downgraded the physical-mechanical properties and caused specific surface area decrease. Both analyzed nonwovens were more susceptible to hydrolysis in alkaline than neutral medium.

**Keywords:** biodegradable polymers, composites, nonwovens, melt-blown technique.

## Wpływ dodatku poli(3-hydroksybutanianu) na właściwości włókniny z poli(kwasu mlekowego) otrzymanej techniką *melt-blown*

**Streszczenie:** Techniką *melt-blown* otrzymano włókninę z poli(kwasu mlekowego) (PLA) oraz włókninę kompozytową PLA (85 % mas.)/P(3HB) (15 % mas.). [P(3HB) — poli(3-hydroksybutanian)]. Zbadano właściwości termiczne, parametry fizykochemiczne, powierzchnię właściwą i podatność na degradację hydrolytyczną uzyskanych włókien. Termogramy DSC wykazały zmiany w strukturze polimerów na skutek przetwórstwa techniką *melt-blown*. Dodanie P(3HB) generalnie pogorszyło parametry fizykochemiczne włókniny z PLA i spowodowało zmniejszenie powierzchni właściwej. Badane włókniny hydrolyzowały szybciej w środowisku zasadowym niż w obojętnym.

**Słowa kluczowe:** polimery biodegradowalne, kompozyty, włókniny, technika *melt-blown*.

Biodegradable polymers (of natural, synthetic and microbial origin) include, among others, polysaccharides, poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly( $\epsilon$ -caprolactone) (PCL) and polyhydroxyalkanoates (PHA) [1]. Among them, PLA is of great importance as it is an easily accessible and relatively cheap synthetic polymer with good processing properties [2]. For commercial purposes, lactic acid is obtained by the fermentation of starch using the bacteria *Lactobacillus* or through the submission of ethylene to a range of chemical processes [3]. Poly(lactic acid) is obtained by polymerization of lactic acid molecules or polymerization of lactides (cyclic dimers of lactic acid) [4]. The first method is relatively simple and inexpensive, the second allows PLA of larger molecular masses to be obtained. PLA is already used in the industrial production of packages, cups for drinks, bottles, fibers for different applications, etc. [5].

Polyhydroxyalkanoates are a family of aliphatic polyesters made of hydroxyacids (mainly 3-hydroxyacids) [6, 7]. Nowadays, more than 150 different PHA monomers are known but poly(3-hydroxybutyrate) [P(3HB)] was the first to be discovered and the most commonly used PHA [8]. PHA are biodegradable and biocompatible, and are obtained by biosynthesis (also transgenic) using bacteria or plants [9, 10]. Unfortunately, although they have desired properties, PHA processing is difficult due to the low thermal resistance and narrow processing window. Currently, PHA are used, among others, in medical applications [11, 12].

In order to provide the relevant properties of the most desired biodegradable materials, composites are produced from biodegradable polymers (among others, PLA and PHA). Renard *et al.* obtained composite films from PLA and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)] or poly(3-hydroxyoctanoate) [P(3HO)]. The authors examined the influence of PLA addition on the hydrolytic degradation of both PHA [13]. Cheng *et al.* described electrospun fibers received from a composite consisting of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] and PLA (the PLA content

<sup>1)</sup> Textile Research Institute, Brzezińska 5/15, 92-103 Łódź, Poland.

<sup>\*)</sup> Materials contained in this article were presented at POLYMAT60, June 30—July 1, 2014, Zabrze, Poland.

<sup>\*\*)</sup> Author for correspondence; e-mail: [mlatwinska@iw.lodz.pl](mailto:mlatwinska@iw.lodz.pl)

was 25 %, 50 % and 75 %) [14]. Depending on the composition, the fibers revealed different properties — those with higher PLA content were more elastic and more susceptible to hydrolytic degradation, while those with higher P(3HB-co-3HHx) content showed higher tensile strength.

The first aim of this work was to obtain PLA and PLA/P(3HB) composite nonwoven using the melt-blown technique. One of the important advantages of this technique is the possibility to obtain nonwovens with fine fibers (fiber diameter of a few micrometers) [15]. The melt-blown nonwovens, thanks to fine fibers, are mainly used as barrier materials (filters, absorbents) and hygiene materials (wipes, pads) [15]. The second aim of this work was to examine the influence of P(3HB) addition on the thermal properties, physical-mechanical properties and susceptibility to hydrolytic degradation of PLA nonwoven.

## EXPERIMENTAL PART

### Materials

— Poly(lactic acid) (PLA) granulate was purchased from NatureWorks LLC (type Ingeo™ Biopolymer 3251D,  $MFR = 30–40$  g/10 min (190 °C/2.16 kg),  $T_{mp} = 160–170$  °C).

— Poly(3-hydroxybutyrate) [P(3HB)] granulate was purchased from Biomer (type Biomer(r) P209F,  $MFR = 10$  g/10 min (180 °C/2.16 kg),  $T_{mp} = 165$  °C).

— Phosphate buffer (pH = 7,  $KH_2PO_4$  0.071 mol/dm<sup>3</sup> +  $K_2HPO_4$  0.117 mol/dm<sup>3</sup>) and tetraborate buffer (pH = 10,  $Na_2B_4O_7$  0.130 mol/dm<sup>3</sup> + NaOH 0.060 mol/dm<sup>3</sup>) were applied as chemical reagents.

### Melt-blowing

Nonwovens were obtained using the melt-blown technique, which is an integrated nonwoven technology linking the fiber-forming and web-forming processes [16]. The strings of molten polymer come out from the ex-

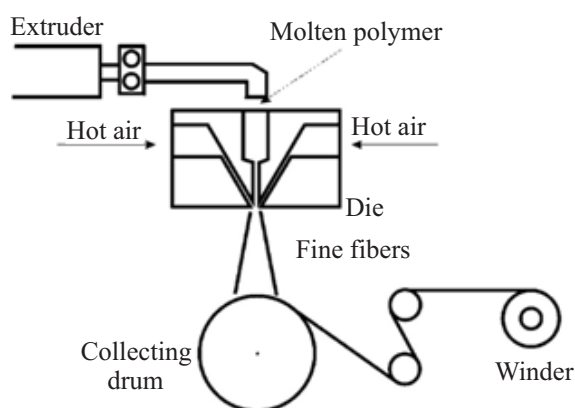


Fig. 1. Fiber formation according to melt-blown technique

truder head through the multi-hole nozzle where they are blown by a stream of hot compressed air and set as fine fibers on a collecting drum (Fig. 1). Laboratory, one-screw extruder (Axon product) with head (with 30 holes of 0.35 mm diameter each), compressed air heater and collecting drum were used.

Two kinds of nonwovens were obtained: PLA nonwoven and composite PLA (85 wt %)/P(3HB) (15 wt %) nonwoven. In both cases, the temperature in the extruder zones 195–260 °C and of compressed air 275 °C were applied, compressed air consumption was 7 m<sup>3</sup>/h and polymer consumption was 4 g/min. PLA and P(3HB) were dried before processing for 3 h at 100 °C and for 2 h at 80 °C, respectively.

### Methods of testing

— DSC analyses were carried out for granulates and nonwovens using a DSC 6200 Exstar SII Nano Technology apparatus (Haas product); samples (*ca.* 5 mg) were heated in a nitrogen atmosphere to 200 °C and then cooled to 25 °C, the scanning speed was 5 °C/min.

— The following physical-mechanical parameters of nonwovens were analyzed: elementary fiber diameter (according to PN-ISO 137:2000, with the exception of the number of measurements and preparation of samples), air permeability (according to PN-EN ISO 9237:1998), maximum breaking force and elongation at maximum force (according to PN-EN 29073-3:1994), mass per unit area (according to PN-EN 29073-1:1994) and thickness (according to PN-EN ISO 9073-2:2002).

— Specific surface area ( $S_{BET}$ ), total pore volume ( $V$ ) and average pore diameter ( $D$ ) were analyzed for nonwovens using the liquid nitrogen sorption method on an Autosorb-1 apparatus (Quantochrome Instruments product). In the case of specific surface area, the 5 point BET method was applied, in the case of total pore volume and average pore diameter, one point at  $P/P_0 \approx 1.00$  on an adsorption-desorption isotherm was analyzed by the apparatus.

— Hydrolytic degradation of nonwovens (according to PN-EN ISO 10993-13:2002) was carried out using *ca.* 1 g samples, in neutral (phosphate buffer) and alkaline (tetraborate buffer) media, at 65 °C, for 21, 42, 63 and 84 days.

## RESULTS AND DISCUSSION

DSC analysis indicated that processing caused noticeable changes in the polymers structure. Comparing the PLA granulate and nonwoven thermograms, a shift in the melting peak from 171.7 °C to 168.0 °C was observed (Fig. 2a, b). Moreover, new peaks appeared on the PLA nonwoven thermogram — at 62.2 °C (an endothermic process, probably glass transition), at 98.9 °C (peak assigned to recrystallization [17]), and at 100.4 °C (broad crystallization peak). Changes in the DSC thermograms of PLA

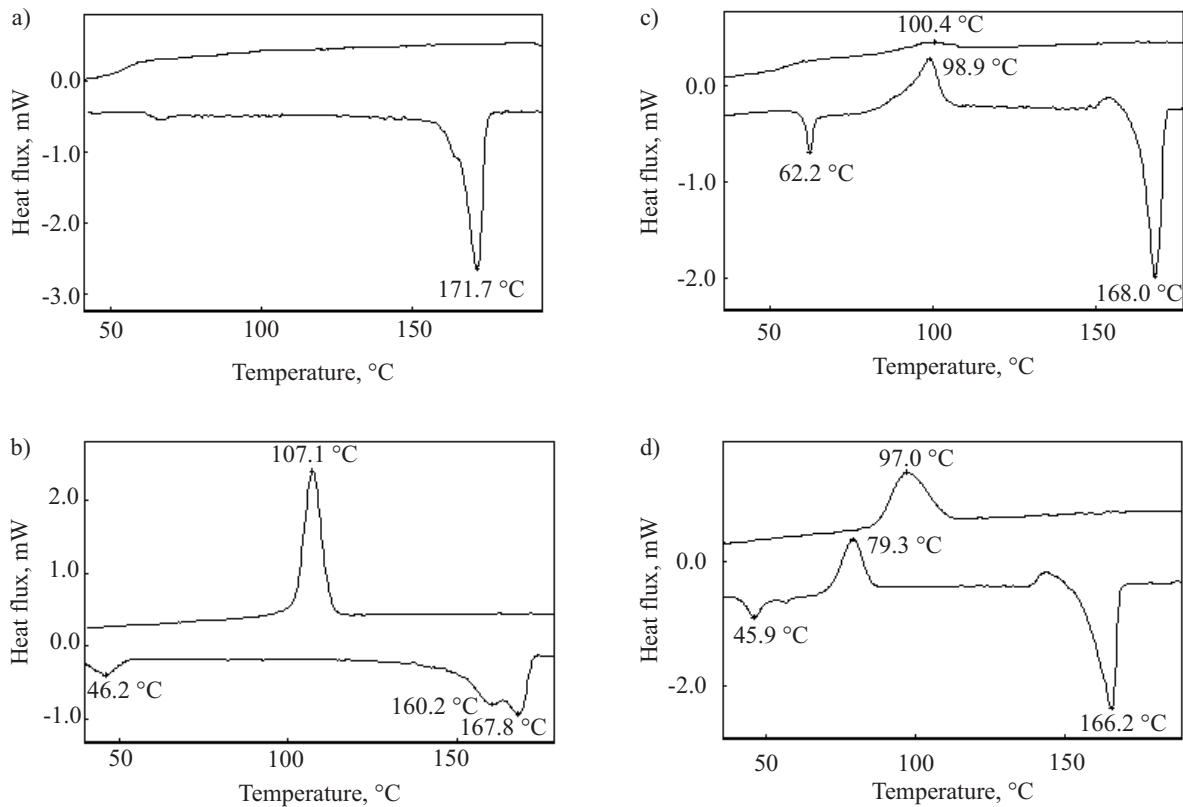


Fig. 2. DSC heating and cooling thermograms of: a) PLA granulate, b) P(3HB) granulate, c) PLA nonwoven, d) PLA/P(3HB) composite nonwoven

before and after processing could be partially ascribed to thermal decomposition of the polymer. P(3HB) addition caused a shift of all the peaks to lower temperatures, and a new peak, assigned to an endothermic process of P(3HB), appeared at 45.9 °C in the PLA/P(3HB) composite nonwoven thermogram (Fig. 2d). It can be stated that the melting peak at 166.2 °C and crystallization peak at 97.0 °C on the discussed thermogram consisted of melting and crystallization peaks of both polymers. The significant decrease (about 20 °C) of the temperature of

recrystallization of PLA in the case of PLA/P(3HB) composite nonwoven and low value of this temperature (79.3 °C) is worth mentioning (Fig. 2b, c). It may be evidence of the low molecular weight of P(3HB) in composite nonwoven, which is made more probable by the high [for P(3HB)] temperatures of the melt-blown process. Ohkoshi *et al.* proved that PLA and low molecular weight P(3HB) are miscible in the melt [18], so miscibility of PLA and P(3HB) is very probable in the case of the analyzed PLA/P(3HB) composite nonwoven.

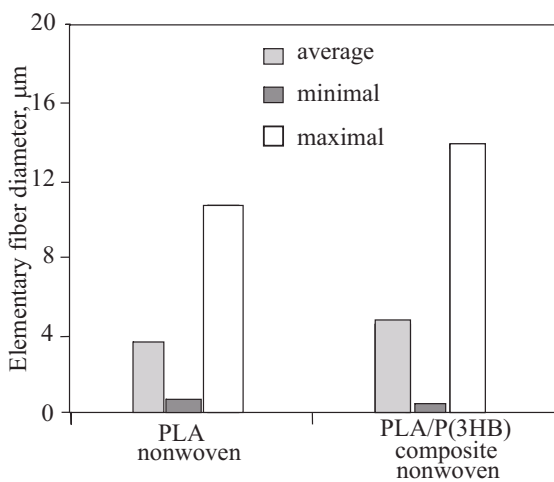


Fig. 3. Elementary fiber diameter of PLA nonwoven and PLA/P(3HB) composite nonwoven

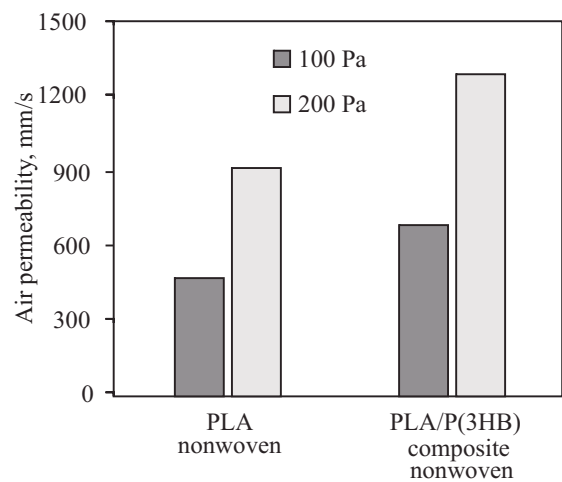


Fig. 4. Air permeability of PLA nonwoven and PLA/P(3HB) composite nonwoven

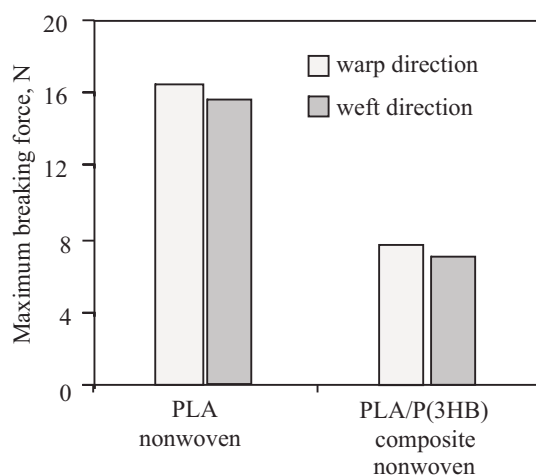


Fig. 5. Maximum breaking force of PLA nonwoven and PLA/P(3HB) composite nonwoven

The average elementary fiber diameter of PLA nonwoven ( $3.56 \mu\text{m}$ ) was low and comparable to PP nonwoven obtained under similar conditions [19]. P(3HB) addition resulted in a 30 % increase in the elementary fiber diameter to  $4.62 \mu\text{m}$  (Fig. 3). Growth of elementary fiber diameters caused a 43 % increase in the air permeability of PLA/P(3HB) composite nonwoven (Fig. 4).

Maximum breaking force and elongation at maximum force of PLA nonwoven were also similar to PP nonwoven [19]. Only 15 % addition of P(3HB) to PLA nonwoven radically impaired these parameters — for PLA/P(3HB) composite nonwoven, the maximum breaking force was two times smaller and elongation at maximum force was as much as sixteen times smaller compared to PLA nonwoven (Figs. 5, 6). These results are the consequence of the hardness, stiffness and brittleness of P(3HB) [20].

P(3HB) addition caused an about 17 % decrease of mass per unit area of PLA nonwoven, which can be a result of some degradation of P(3HB) during processing

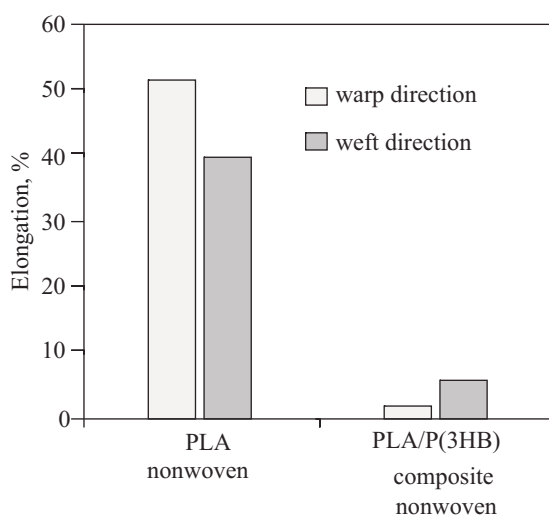


Fig. 6. Elongation at maximum force of PLA nonwoven and PLA/P(3HB) composite nonwoven

Table 1. Mass per unit area and thickness of PLA nonwoven and PLA/P(3HB) composite nonwoven

	Mass per unit area, $\text{g}/\text{m}^2$	Thickness mm
PLA nonwoven	$159 \pm 15$	$2.49 \pm 0.16$
PLA/P(3HB) composite nonwoven	$132 \pm 9$	$1.65 \pm 0.16$

(Table 1). An about 34 % decrease of thickness in the case of PLA/P(3HB) composite nonwoven (compared to PLA nonwoven) is probably connected with high viscosity in the melt of P(3HB) (Table 1). Differences in viscosity manifest in a significantly lower MFR of P(3HB) in relation to PLA.

The specific surface area of PLA nonwoven ( $0.64 \text{ m}^2/\text{g}$ ) (Table 2) was compared to the specific surface area of polyacrylonitrile (PAN) electrospun nanofiber nonwoven [21]. In the case of PAN nonwoven, the elementary fiber diameter was  $1.3 \mu\text{m}$  and the specific surface area was  $2 \text{ m}^2/\text{g}$ . As the elementary fiber diameter of PLA nonwoven was about three times greater, an about three times smaller specific surface area seems to be the correct result. It is worth mentioning that, according to basic knowledge, the specific surface area correlates with the elementary fiber diameter — the finer the fibers are, the greater the surface area is. The specific surface area of PLA/P(3HB) composite nonwoven was about 42 % smaller when compared to PLA nonwoven, which was a natural result of a greater diameter of the elementary fiber (Table 2). For each nonwoven type sample, an one adsorption-desorption isotherm was prepared. Isotherms of both nonwovens were of type II and had hysteresis loops that indicated that the analyzed nonwovens were macro- and mesoporous materials [22]. An explicitly larger hysteresis loop for the adsorption-desorption isotherm of PLA nonwoven indicated that this nonwoven was more mesoporous than PLA/P(3HB) composite nonwoven. The same conclusion was made after analysis of the total pore volume and average pore diameter — for PLA nonwoven the first parameter was higher and the second smaller compared to PLA/P(3HB) composite nonwoven (Table 2). Thanks to the greater specific surface area of PLA nonwoven (which also indicated that PLA nonwoven was a more mesoporous material), the conclu-

Table 2. Specific surface area ( $S_{\text{BET}}$ ), total pore volume ( $V$ ) and average pore diameter ( $D$ ) of PLA nonwoven and PLA/P(3HB) composite nonwoven

	Specific surface area (average of 3 samples) $\text{m}^2/\text{g}$	Total pore volume $\text{cm}^3/\text{g}$	Average pore diameter, nm
PLA nonwoven	$0.64 \pm 0.07$	$2.99 \cdot 10^{-3}$	18.4
PLA/P(3HB) composite nonwoven	$0.37 \pm 0.05$	$2.05 \cdot 10^{-3}$	24.4

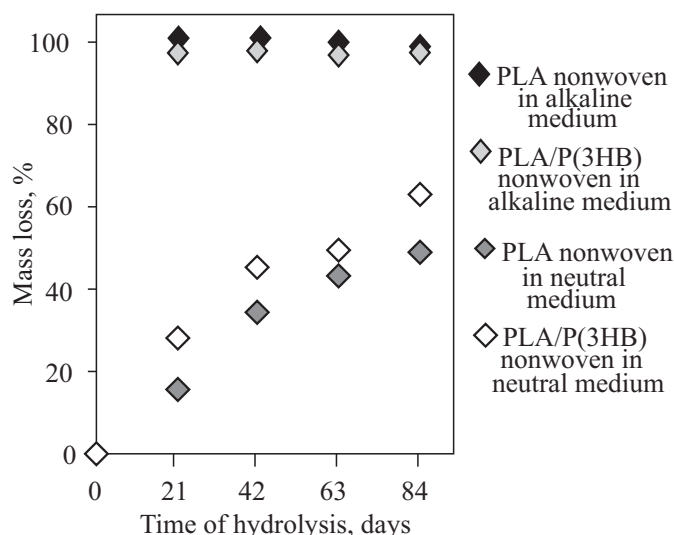


Fig. 7. Hydrolytic degradation of nonwovens in different media

sions made for one adsorption-desorption isotherm could be accepted.

Neutral and alkaline media for the analysis of hydrolytic degradation of PLA and PLA/P(3HB) composite nonwovens were chosen based on literature data [23]. The obtained results indicated that PLA and PLA/P(3HB) composite nonwovens were more susceptible to hydrolysis in alkaline medium — after 21 days of hydrolysis in tetraborate buffer, decomposition of both nonwovens was practically complete (Fig. 7). This resulted from the reaction mechanism — in contrast to neutral medium, hydrolysis of organic esters in alkaline medium is not reversible and hence more efficient. Comparing the analyzed nonwovens, PLA nonwoven hydrolyzed slightly faster in alkaline medium, which was expected due to the degradability of PLA. Unexpectedly, PLA/P(3HB) composite nonwoven hydrolyzed faster in neutral medium — after 84 days of hydrolysis 62 % mass loss of PLA/P(3HB) composite nonwoven and 49 % mass loss of PLA nonwoven were observed (Fig. 7). The reason for such behavior of PLA/P(3HB) composite nonwoven may be the partial thermal degradation, with molecular weight decrease, of P(3HB) during processing. This explanation fits well the DSC data received for PLA/P(3HB) composite nonwoven. Krasowska *et al.*, who analyzed PLA degradation in sea water, also found an accelerating influence of P(3HB) addition on the degradation rate of PLA [24].

## CONCLUSIONS

Research led to obtain PLA nonwoven and PLA (85 wt %)/P(3HB) (15 wt %) composite nonwoven using the melt-blown technique. For P(3HB) very high temperatures were successfully applied during PLA/P(3HB) composite nonwoven obtaining, which indicates that processing of P(3HB) is significantly easier when this polymer is a part of composite than it is processed alone

[25]. DSC analysis indicated that thermal decomposition accompanying processing changed the thermograms of both polymers. The shifting of peaks to lower temperatures and the appearing of new peaks were observed. Despite that elementary fiber diameter was comparable to PLA nonwoven, PLA/P(3HB) composite nonwoven had greater air permeability. PLA/P(3HB) composite nonwoven was less resistant to breaking and significantly less elastic, when compared to PLA nonwoven. PLA nonwoven and PLA/P(3HB) composite nonwoven were macro- and mesoporous materials. Based on specific surface area and adsorption-desorption isotherm parameters, PLA nonwoven was classified as more mesoporous than PLA/P(3HB) composite nonwoven. After 21 days of hydrolysis in alkaline medium, the mass loss of both nonwovens was similar and almost reached 100 % but PLA/P(3HB) composite nonwoven unexpectedly hydrolyzed faster in neutral medium. Summarizing the conclusions, the addition of P(3HB) resulted in a generally negative impact on PLA nonwoven physical-mechanical properties but accelerated its hydrolytic degradation in neutral medium, thus making PLA/P(3HB) composite nonwoven utilization easier on typical landfills.

*The study was financed by Polish Ministry of Science and Higher Education within statutory research work carried out in 2012–2013 at Textile Research Institute, Łódź, Poland.*

## REFERENCES

- [1] Doppalapudi S., Jain A., Khan W., Domb A.J.: *Polymers for Advanced Technologies* **2014**, 25, 427. <http://dx.doi.org/10.1002/pat.3305>
- [2] Auras R., Lim L.T., Selke S.E.M., Tsuji H.: "Poly(lactic acid): synthesis, structures, properties, processing and applications", John Wiley & Sons, Inc., Hoboken, New Jersey 2010, p. 3.
- [3] Gupta B., Revagade N., Hilborn J.: *Progres in Polymer Science* **2007**, 32, 455. <http://dx.doi.org/10.1016/j.progpolymsci.2007.01.005>
- [4] Luckachan G.E., Pillai C.K.S.: *Journal of Polymers and the Environment* **2011**, 19, 637. <http://dx.doi.org/10.1007/s10924-011-0317-1>
- [5] Garlotta D.: *Journal of Polymers and the Environment* **2001**, 9, 63. <http://dx.doi.org/10.1023/A:1020200822435>
- [6] Sudesh K., Abe H., Doi Y.: *Progres in Polymer Science* **2000**, 25, 1503. [http://dx.doi.org/10.1016/S0079-6700\(00\)00035-6](http://dx.doi.org/10.1016/S0079-6700(00)00035-6)
- [7] Reddy C.S.K., Ghai R., Rashmi, Kalia V.C.: *Bioresource Technology* **2003**, 87, 137. [http://dx.doi.org/10.1016/S0960-8524\(02\)00212-2](http://dx.doi.org/10.1016/S0960-8524(02)00212-2)
- [8] Keshavarz T., Roy I.: *Current Opinion in Microbiology* **2010**, 13, 321. <http://dx.doi.org/10.1016/j.mib.2010.02.006>
- [9] Schubert P., Steinbüchel A., Schlegel H.G.: *Journal of Bacteriology* **1988**, 170, 4431.
- [10] Bohmert K., Balbo I., Steinbüchel A. *et al.*: *Plant Physiology* **2002**, 128, 1282. <http://dx.doi.org/10.1104/pp.010615>
- [11] *EU Pat.* 2231913 (2008).

- [12] Cheng M.L., Lin C.C., Su H.L. *et al.*: *Polymer* **2008**, *49*, 546. <http://dx.doi.org/10.1016/j.polymer.2007.11.049>
- [13] Renard E., Walls M., Guerin P., Langlois V.: *Polymer Degradation and Stability* **2004**, *85*, 779. <http://dx.doi.org/10.1016/j.polymdegradstab.2003.11.019>
- [14] Cheng M.L., Chen P.Y., Lan C.H., Sun Y.M.: *Polymer* **2011**, *52*, 1391. <http://dx.doi.org/10.1016/j.polymer.2011.01.039>
- [15] Batra S.K., Pourdeyhiki B.: "Introductions to nonwovens technology", DEStech Publications, Inc., Lancaster, Pennsylvania 2012, p. 238.
- [16] Smorada R.: *Nonwovens Industry* **1996**, *10*, 48.
- [17] Cui L., Zhu C.L., Zhu P. *et al.*: *Journal of Applied Polymer Science* **2012**, *125*, 158. <http://dx.doi.org/10.1002/app.36429>
- [18] Ohkoshi I., Abe H., Doi Y.: *Polymer* **2000**, *41*, 5985. [http://dx.doi.org/10.1016/S0032-3861\(99\)00781-8](http://dx.doi.org/10.1016/S0032-3861(99)00781-8)
- [19] Sójka-Ledakowicz J., Łatwińska M., Kałużka J. *et al.*: *Polimery* **2013**, *58*, 557.
- [20] Orts W.J., Nobes G.A.R., Kawada J. *et al.*: *Canadian Journal of Chemistry* **2008**, *86*, 628. <http://dx.doi.org/10.1139/v08-050>
- [21] Hussain D., Loyal F., Greiner A., Wendorff J.H.: *Polymer* **2010**, *51*, 3989. <http://dx.doi.org/10.1016/j.polymer.2010.06.036>
- [22] Sing K.S.W., Everett D.H., Haul R. *et al.*: *Pure and Applied Chemistry* **1985**, *57*, 603. <http://dx.doi.org/10.1351/pac198557040603>
- [23] *US Pat.* 6 864 090 (2005).
- [24] Krasowska K., Brzeska J., Rutkowska M. *et al.*: *Polimery* **2008**, *53*, 730.
- [25] Sójka-Ledakowicz J., Łatwińska M., Kudzin M.: *e-Polymers* **2014**, *14*, 373. <http://dx.doi.org/10.1515/epoly-2014-0089>

Received 4 VII 2014.