LogForum

> Scientific Journal of Logistics <

2020, 16 (2), 279-286

http://doi.org/10.17270/J.LOG.2020.391

http://www.logforum.net p-ISSN 1895-2038 e-ISSN 1734-459X

ORIGINAL PAPER

BIODEGRADABLE PACKAGING BASED ON PLA WITH ANTIMICROBIAL PROPERTIES

Natalia Czaja-Jagielska, Anna Praiss, Michał Walenciak, Dajana Zmyślona, Natalia Sankowska

Poznan School of Logistics, Poznań, **Poland**

ABSTRACT. **Background:** Packaging is an inseparable element of most consumer products. In addition to its primary passive protective and logistic function, it is also an excellent tool for the innovation development. One of the types of packaging innovations in the food and cosmetic industry are antimicrobial packaging. They are an example of packaging that actively protects packed products and eliminates harmful preservatives. Protection of goods against microbial spoilage extends shelf life and at the same time facilitates storage processes.

Methods: This paper aims to obtain biodegradable films based on PLA with antimicrobial properties. Four different natural antimicrobial agents were used: clove essential oil, peppermint essential oil, and two commercial powders containing nisin (Nisaplin and Novagard). The mechanical, barrier and optical properties were tested.

Results: The implementation of antimicrobial agents changed the properties of the tested bio-packaging in different rate depending on the agent. The new blends showed antimicrobial activity, however the addition of antimicrobials weakened the mechanical properties and changed the colour.

Conclusions: The biodegradable packaging materials can be used as a polymer matrix of different antimicrobial agents. They can inhibit the growth of bacteria in food or cosmetics and regarding their future use the influence on mechanical properties should be considered. Moreover, the biodegradability of biopolymers containing antimicrobial agents has barely been investigated.

Key words: antimicrobial packaging, biodegradable packaging, mechanical properties, barrier properties, innovation.

A part of this study was presented as oral presentation at the „8th International Logistics Scientific Conference WSL FORUM 2019" in Poznan (Poland), 18th-19th of November 2019.

INTRODUCTION

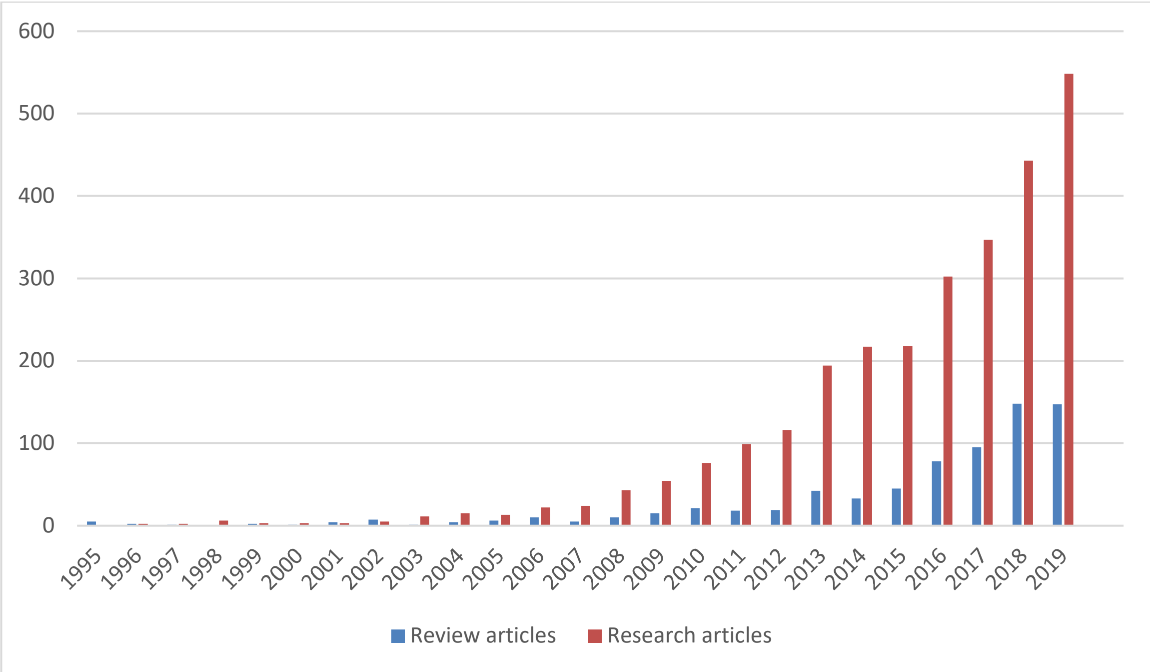
Packaging is a very important factor in the food industry. The mail goal of packaging is to preserve the quality and safety of products during transport and storage. Protection of the packaged product should include protection against the damaging effects of mechanical and climatic exposures, quantitative losses, changes or loss of product performance as a result of reactions taking place in the product. The reason for the short shelf life of many products is their microbial infection during entire logistics system. Therefore active packaging has been very common in the last years as a new approach to food security. According to Fig. 1 there has been visible growth of interest in research into combining bio- and functional packaging in the recent 10 years. They are very important for supply chain professionals in the food, pharmaceutical and other industries due to limited longevity and specific environmental requirements, waste reduction and increased efficiency.

The most often used biopolymers are starch [ZhaO et al. 2019; Fonseca et al. 2019; Ali et

Citation: *Czaja-Jagielska N., Praiss A., Walenciak M., Zmyślona D., Sankowska N., 2020. Biodegradable packaging based on PLA with antimicrobial properties. LogForum 16 (2), 278-286,* *http://doi.org/10.17270/J.LOG.2020.391*

Received: 26.09.2019, Accepted: 06.02.2020, on-line: 30.03.2020.

al. 2019], PLA [Qin et al 2019; Heydari-Majd 2019], PVAL [Lan et al. 2019; Liu et al. 2017], chitosan [Zheng et al. 2019; Wang, et al. 2019] and zein-proteins [Boyacı et al 2019, Kashiri et al. 2019].



Source: Science Direct

Fig. 1. Number of publications concerning antimicrobial biodegradable packaging

Antimicrobial agents can be either incorporated into packaging material or covered as active coating. There are numerous types of active substances which can be used in the active packaging system: synthetic (e.g. organic acids, metals, antibiotics) or natural (e.g. natural extracts, essential oils, enzymes, bacteriocins) [Korzeniowski et al 2011; Malhotra et el. 2015].

Plant-derived essential oils (EOs) are generally accepted as great potential to be used for extending the shelf life of different foods [Talebi et all 2018]. The most cited are: rosemary, eucalyptus, oregano, thyme, cinnamon, clove and citrus fruit [Lee et al 2015, Agrimonti et al. 2019]

The effectiveness of these composites depends on product and goods combination of bio-matrix and the antimicrobial agent. Yahyaoui et al [2016] proved that the incorporation of essential oils from rosemary, myrtle and thyme in the PLA matrix can improve the mechanical properties and does not affect the colour change of the films significantly.

Therefore the aim of the study was to obtain PLA films with natural antimicrobial agents (nisin and essential oils) and investigate the effects on the optical, mechanical and antimicrobial properties of these blends. The studies are an attempt to confirm that the use of biomaterials with antimicrobial agents has a positive effect on extending the shelf life of food products by limiting contamination.

MATERIALS AND METHODS

Materials

The PLA (plylactic acid) was an Ingeo™ Biopolymer 4043D obtained from Natureworks LLC. The polymer was in the form of pellets that can be converted into film.

Antimicrobial agents used in the study were: clove essential from Etja Company, peppermint essential from PPHU KEJ

Company, Nisaplin and NovaGARD CB1-35 from Danisco Company.

The following strains of bacteria were used in this study: *Clostridium perfringens, Staphylococcus Aureus, Pseudomonas aeruginosa, Yersinia enterocolitica, Salmonella enteritidis, Bacillus subtilis, Listeria innocua, Eschericha coli, Staphylococcus paratyphi* and *Enteroccocus fecalis.*

Descriptions of the samples are presented in Table 1.

Table 1. Description of samples tested

Code	Description
PLA	Pure PLA film
PLA_N	PLA with 2% Nisaplin
PLA_NG	PLA with 2% NovaGard
PLA_C	PLA with 2% clove essential
PLA_PM	PLA with 2% peppermint essential

Film formation

Films of PLA (20-40 mm) were prepared by solvent cast technique. Pure PLA films were obtained by solving 16g PLA pellets in 400 ml chloroform under magnetic stirring for 6h in the temperature of 23°C. After the films were casted, they were dried overnight (24h) at room conditions. The antimicrobial films were prepared by solving 16g of PLA pellets in chloroform under magnetic stirring for 6h with addition of 2% of antimicrobial agent.

Mechanical properties

Thickness

The thickness of the films was measured at several locations randomly around the film using a micrometre SYLVAC with 0.001mm accuracy.

Tensile strength

The mechanical resistance of films was performed on a Zwick Roell Z020 strength testing machine according to the PN-EN ISO 527-3 standard. Tensile strength [MPa] and elongation at break [%] were evaluated. At least five samples were tested for each film and the average value was reported.

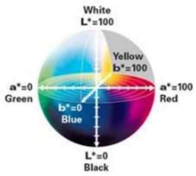
Puncture testing

The test consists in determining the puncture force [N] and elongation at puncture [mm] on the

Zwick Roell Z020 instrument in accordance with PN-EN 14477.

Optical properties

The colour measurement was made with the Focus on Color envisense NH 310. The L*a*b model was used to describe the colour of the samples tested. The L* parameter specifies the brightness (L * value = 100 means perfectly white, while 0 value – perfectly black), while a * and b * are trichromatic coordinates that specify the tone and colour saturation (Fig 2.).



Source: www.perten.com

Fig. 2. CIE Lab colour space

Antimicrobial activity

The antimicrobial effectiveness of the composite films was tested against 10 bacteria mentioned above. Suspensions of microbes were prepared, then seeded onto Petri dishes by the flooding method, consisting in applying 1ml of inoculum to the dish and pouring Agar medium.

On the solid agar the test films (dimensions of 10x10mm) were applied and incubated at 37^{0}C. After incubation, antimicrobial activity was measured by observation of zones inhibiting the growth of microorganisms around the film samples.

RESULTS

Mechanical properties of the samples tested are shown in Table 2, 3 and 4. They are, especially tensile strength and elongation at break, very crucial parameters in exploiting different bio-based films for packaging purposes. The addition of antimicrobial agents enlarges the thickness of the PLA films (Table 2).

Table 2. Thickness

	Thickness [mm]
PLA	0.211±0.021
PLA_N	0.420±0.076
PLA_NG	0.490±0.072
PLA_C	0.290±0.033
PLA_PM	0.405±0.032

Source: own work

Table 3 represents tensile strength and elongation at break for pure PLA films and modified with antimicrobial agents. According to these data the incorporation of essential oil into PLA matrix resulted in a significant decrease in the tensile strength and elongation at break.

he same was observed by other authors [Qin et all 2017].

Table 3. Tensile strength and elongation at break

	Tensile strength [MPa]	Elongation at break [%]
PLA	16.00±1.23 16.94±2.57	267±24 162±42
PLA_N	8.07±1.65 19.6±0.89	18±5,0 20±8.0
PLA_NG	6.19±0.92 6.63±1.12	3.8±0.4 3.6±0.5
PLA_C	10.09±0.37 7.69±1.36	156±24 140±26
PLA_PM	4.86±0.34 5.64±0.35	2.6±0.3 2.1±0.4

Source: own work

The resistance for puncture was determined for the films tested. Pure PLA film did not break through, which means that it had high strength and flexibility. The addition of antimicrobials weakened the puncture strength. The film with Nisaplin and clove essential oil showed the highest strength, while the lowest was observed for PLA with peppermint essential oil.

Table 4. Puncture test

	Force [N]	Elongation at puncture [mm]
PLA	*	*
PLA_N	38.3±3.25	13.2±1.12
PLA_NG	23.0±2.27	13.1±0.98
PLA_C	40.5±0.22	14.3±2.23
PLA_PM	7.25±0.44	2.85±0.35

*The sample was not damaged till elongation reached the maximum for the instrument (300 mm)

Source: own work

Table 5. Optical parameters of samples tested

	L*	a*	b*
PLA	31.6±0.01	0.18±0.02	-0.4±0.02
PLA_N	48.4±0.51	0.94±0.01	6.1±0.02
PLA_NG	45.9±0.05	0.09±0.02	7.24±0.01
PLA_C	42.6±0.03	-1.2±0,02	0.17±0.05
PLA_PM	58.0±0.01	-1.22±0.01	-1.3±0.02

Source: own work

The PLA sample had the lowest brightness. A positive value of the a* parameter indicates that the sample is in the yellow space, and a negative value of the b* parameter indicates that the sample is in the blue space. There is visible change in colour after the addition of antimicrobial additives. They are a little brighter and have different colours. PLA film with peppermint essential oil showed the highest brightness. t In the first quarter of the colour space diagram (Fig 2.) the colour of the sample with nisin (PLA_N) was between red and yellow. The addition of essential oils turned the colour into green-yellow space (PLA_C) and dark blue and blue (PLA_PM). NovaGARD powder located the sample in the first quarter between the red and yellow colour (PLA_NG).

The results of the antimicrobial study are presented in Table 6. It shows that pure PLA film has no antimicrobial activity. The strongest antimicrobial effect was observed for the film with Nisaplin powder. Its antimicrobial activity was against all the bacteria tested - the largest against *Pseudomonas aeruginosa, Bacillus subtilis* (Fig. 4) and *Clostridium perfringers* (Fig. 3) and the smallest against Listeria innocua. Clove oil incorporated in PLA film was effective in three cases: against *Bacillus subtilis* (Fig 4), E coli (Fig. 5) and Pseudomonas aureginosa. For the other bacteria, clove oil showed the bacteriostatic effect, except *Clostridium perfringens* that was resistant to this film.

Table 6. Clear zones (in mm) after antimicrobial testing

	PLA	PLA_N	PLA_C	PLA_NG	PLA_PM
Clostridium perfringens	0	20	0	12	10.5
Staphylococcus aureus	0	18	11	10.5	0
Pseudomonas aeruginosa	0	22	12	0	0
Yersinia enterocolitica	0	12	10.5	10.5	0
Salmonella enteritidis	0	13	10.5	10.5	0
Bacillus subtilis	0	21	17	10.5	10.5
Listeria innocua	0	12	10.1	0	0
Eschericha coli	0	16	14	11	0
Staphylococcus paratyphi	0	16	10.5	14	10.5
Enteroccocus faecalis	0	16	10	12	10.5

Source: own work

The addition of Novagard powder showed no significant antibacterial activity. Only growth of four bacteria (*Clostridium perfringens, Eschericha coli, Staphylococcus paratyphi, Enteroccocus faecalis*) was slightly inhibited and for the other 4 (*Staphylococcus aureus, Yersinia enterocolitica, Salmonella enteritidis, Bacillus subtilis*) there was the bacteriostatic effect. There was no effect for Pseudomonas aeruginosa and Listeria innocula. The film with peppermint oil had the worst results. The bacteriostatic effect was observed in the case of four bacteria: *Clostridium perfringens, Bacillus subtilis, Staphylococcus paratyphi* and *Enteroccocus faecalis*.

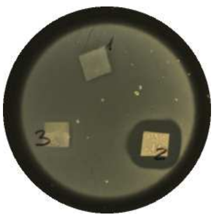


Fig. 3. Antimicrobial properties of PLA (1), PLA_N (2) and PLA_C (3) against Clostridium perfringers

Fig. 4. Antimicrobial properties of PLA (1), PLA_N (2) and PLA_C (3) against Bacillus subtilis

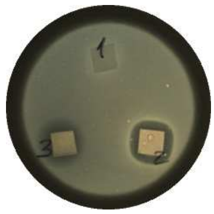


Fig. 5. Antimicrobial properties of PLA (1), PLA_N (2) and PLA_C (3) against E. Coli

CONCLUSIONS

This investigation showed the possibility of obtaining PLA films with natural antimicrobial substances such as bacteriocins and essential oils. Based on this research and the literature view, we can conclude that the incorporation of natural antimicrobial substances into PLA film positively influences its antimicrobial properties, however there are some differences in their activity. While pure PLA film does not show any antimicrobial activity, the highest limitation of the growth of microorganisms was for nisin. It can help maintain the high quality of products and ensure safety of consumers. The antimicrobial protection of films tested can extend food storage and protect against the adverse effects of microorganisms throughout the entire logistics chain.

Nevertheless in this study these additives weakened the mechanical properties (tensile strength, elongation at break and puncture strength) of PLA blends. It was also observed that the addition of active ingredients changed the colour of the films, which is not always preferable.

Summarizing, the use of antimicrobial additives applied is an excellent proposition for producers looking for new ecological solutions. Moreover, it is advisable to use biodegradable materials, including PLA pellets as matrix for new active packaging. It is an innovative and excellent offer for producers who are searching for innovative ideas and who care about ecology.

For future investigations it is very important to check the biodegradability and compostability of these novel packaging systems..

ACKNOWLEDGMENTS AND FUNDING SOURCE DECLARATION

Statutory fund of Poznan School of Logistics.

REFERENCES

Agrimonti C., White J.C., Tonetti S., Marmiroli N., 2019. Antimicrobial activity of cellulosic pads amended with emulsions of essential oils of oregano, thyme and cinnamon against microorganisms in minced beef meat, International Journal of Food Microbiology, 305, 108246, http://doi.org/10.1016/j.ijfoodmicro.2019.108246.

Ali A., Chen Y., Liu H., Yu L., Baloch Z., Khalid S., Zhu J., Chen L. 2019. Starch-based antimicrobial films functionalized by pomegranate peel, International Journal of Biological Macromolecules, 129, 1120-1126, http://doi.org/10.1016/j.ijbiomac.2018.09.068.

Aswathy J., Heera K.V., Sumi T.S., Meritta J., Shiji M., Praveen G., Indu C. Nair, Radhakrishnan E.K., 2019. Starch-PVA composite films with zinc-oxide nanoparticles and phytochemicals as intelligent pH sensing wraps for food packaging application, International Journal of Biological Macromolecules, 136, 395-403, http://doi.org/10.1016/j.ijbiomac.2019.06.018.

Boyacı D., Iorio G., Sozbilen G. S., Alkan D., Trabattoni S., Pucillo F., Farris S., Yemenicioğlu A., 2019. Development of flexible antimicrobial zein coatings with essential oils for the inhibition of critical pathogens on the surface of whole fruits: Test of coatings on inoculated melons, Food Packaging and Shelf Life, 20, 100316, http://doi.org/10.1016/j.fpsl.2019.100316.

Heydari-Majd M., Ghanbarzadeh B., Shahidi-Noghabi M., Najafi M.A., Hosseini M. 2019. A new active nanocomposite film based on PLA/ZnO nanoparticle/essential oils for the preservation of refrigerated Otolithes ruber fillets, Food Packaging and Shelf Life, 19, 94-103 http://doi.org/10.1016/j.fpsl.2018.12.002.

Fonseca L., dos Santos Cruxen C.E., Bruni G.P., Fiorentini A.M., da Rosa Zavareze E., Lim L., Dias A. 2019. Development of antimicrobial and antioxidant electrospun soluble potato starch nanofibers loaded with carvacrol, International Journal of Biological Macromolecules, 139, 1182-1190, http://doi.org/10.1016/j.ijbiomac.2019.08.096.

Kashiri M., López-Carballo G., Hernández-Muñoz P., Gavara R., 2019. Antimicrobial packaging based on a LAE containing zein coating to control foodborne pathogens in chicken soup, International Journal of Food Microbiology, 306, 108272, http://doi.org/10.1016/j.ijfoodmicro.2019.108272.

Lee, H., Kim, K., Choi, K.-H., Yoon, Y., 2015. Quantitative microbial risk assessment for Staphylococcus aureus in natural and processed cheese in Korea. J. Dairy Sci. 98, 5931–5945. http://doi.org/10.3168/jds.2015-9611.

Lan W., Zhang R., Ahmed S., Qin W., Liu Y., 2019. Effects of various antimicrobial polyvinyl alcohol/tea polyphenol composite films on the shelf life of packaged strawberries, LWT, 113, 2019, 108297, http://doi.org/10.1016/j.lwt.2019.108297.

Liu B., Xu H., Zhao H., Liu W., Zhao L., Li Y. 2017. Preparation and characterization of intelligent starch/PVA films for simultaneous colorimetric indication and antimicrobial activity for food packaging applications, Carbohydrate Polymers, 157, 842-849, http://doi.org/10.1016/j.carbpol.2016.10.067.

Malhotra B, Keshwani A and Kharkwal H., 2015. Antimicrobial food packaging: potential and pitfalls. Front. Microbiol. 6:611. http://doi.org/10.3389/fmicb.2015.00611

Qin Y., Li W., Liu D., Yuan M., Li L. 2017. Development of active packaging film made from poly (lactic acid) incorporated essential oil, Progress in Organic Coatings 103, 76–82, http://doi.org/10.1016/j.porgcoat.2016.10.017

Talebi F., Misaghi A., Khanjari A., Kamkar A., Gandomi H., Rezaeigolestani M. 2018. Incorporation of spice essential oils into poly-lactic acid film matrix with the aim of extending microbiological and sensorial shelf life of ground beef, LWT, 96, 482-490, http://doi.org/10.1016/j.lwt.2018.05.067.

Wang K., Lim P.N., Tong S.Y., Thian E.S. 2019. Development of grapefruit seed extract-loaded poly(ε-caprolactone)/chitosan films for antimicrobial food packaging, Food Packaging and Shelf Life, 22, 2019,100396, http://doi.org/10.1016/j.fpsl.2019.100396.

Yahyaoui M., Gordobil O., Díaz R. H., Abderrabba M., Labidi J., 2016. Development of novel antimicrobial films based on poly(lactic acid) and essential oils, Reactive and Functional Polymers, 109, 1-8, http://doi.org/10.1016/j.reactfunctpolym.2016.09.001.

Zhao Y., Teixeira J.S., Saldaña M. D.A., Gänzle M. G., 2019. Antimicrobial activity of bioactive starch packaging films against Listeria monocytogenes and reconstituted meat microbiota on ham, International Journal of Food Microbiology, 305, 108253, http://doi.org/10.1016/j.ijfoodmicro.2019.108253.

Zheng K., Xiao S., Li W., Wang W., Chen H., Yang F., Qin C. 2019. Chitosan-acorn starch-eugenol edible film: Physico-chemical, barrier, antimicrobial, antioxidant and structural properties, International Journal of Biological Macromolecules, 135, 344-352, http://doi.org/10.1016/j.ijbiomac.2019.05.151.

BIODEGRADOWALNE OPAKOWANIA NA BAZIE PLA O WŁAŚCIWOŚCIACH PRZECIWDROBNOUSTROJOWYCH

STRESZCZENIE. **Wstęp:** Opakowanie jest nieodłącznym elementem większości produktów dostępnych na rynku. Oprócz pierwotnej, pasywnej funkcji ochronnej i logistycznej jest także doskonałym narzędziem do rozwoju innowacji. W poszczególnych ogniwach łańcucha dostaw rola opakowań w sprawnym przemieszczaniu towarów od producenta do odbioru odgrywa duże znaczenie. Odpowiednio zaprojektowane i wykonane opakowania nie tylko w istotny sposób mogą wpłynąć na obniżenie kosztów, ale także zapewnić jakość i bezpieczeństwo całego łańcucha. Z punktu widzenia ekologicznego coraz częściej wykorzystuje się opakowania na bazie surowców odnawialnych, np. na bazie PLA. Podstawowym zadaniem opakowań jest zabezpieczenie produktu przed niekorzystnymi zmianami jakie są następstwem oddziaływań czynników zarówno egzo – jak i endogennych na zapakowany w nie produkt podczas transportu i przechowywania. Jednym z rodzajów innowacji opakowaniowych są opakowania przeciwdrobnoustrojowe - jako sposób aktywnej ochrony zapakowanych produktów. Ochrona towarów przed psuciem mikrobiologicznym wydłuża okres przydatności do spożycia, a jednocześnie ułatwia procesy przechowywania.

Metody: Celem badania jest uzyskanie biodegradowalnych folii na bazie PLA o właściwościach przeciwdrobnoustrojowych. Zastosowano cztery różne naturalne środki przeciwdrobnoustrojowe: olejek goździkowy, olejek miętowy i dwa proszki zawierające nizynę (Nisaplin i Novagard). Przetestowano właściwości mechaniczne, barierowe, antymikrobiologiczne i optyczne.

Wyniki: Dodatek środków przeciwdrobnoustrojowych zmienił właściwości badanych prób w różnym stopniu. Badane folie wykazały aktywność przeciwdrobnoustrojową, jednak dodanie środków przeciwdrobnoustrojowych osłabiło właściwości mechaniczne i zmieniło ich kolor.
Wnioski: Przytoczone badania potwierdziły, że PLA można stosować jako matrycę polimerową dla różnych środków przeciwdrobnoustrojowych. Mogą hamować rozwój bakterii w żywności lub kosmetykach, a przy ich przyszłym zastosowaniu należy wziąć pod uwagę wpływ na właściwości mechaniczne. Testowane folie mogą korzystnie oddziaływać na zapakowane produkty w całym systemie logistycznym, wydłużając ich termin przydatności do spożycia, a jednocześnie ich biodegradowalność sprawia, że są opakowaniami przyjaznymi środowisku.

Słowa kluczowe: opakowania przeciwdrobnoustrojowe, opakowanie aktywne, opakowanie biodegradowalne, właściwości mechaniczne, właściwości barierowe

Natalia Czaja-Jagielska ORCID ID: https://orcid.org/0000-0001-7472-1319
Poznan School of Logistics
Estkowskiego 6, 61-755 Poznań, **Poland**
e-mail: natalia.czaja-jagielska@wsl.com.pl

Anna Praiss ORCID ID: https://orcid.org/0000-0003-2642-5165
Poznan School of Logistics
Estkowskiego 6, 61-755 Poznań, **Poland**

Michał Walenciak ORCID ID: https://orcid.org/0000-0003-1016-3359
Poznan School of Logistics
Estkowskiego 6, 61-755 Poznań, **Poland**

Dajana Zmyślona
Poznan School of Logistics
Estkowskiego 6, 61-755 Poznań, **Poland**

Natalia Sankowska
Poznan School of Logistics
Estkowskiego 6, 61-755 Poznań, **Poland**