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Analysis of Thermogravimetric and Dynamic Mechanical Properties of PLA/PBS Blends Doped with Zinc Oxide Nanoparticles

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Abstract

In the present work, PLA-PBS blends of 80/20 weight ratio were doped with zinc oxide (2.5; 5; 7.5 and 10 phr) and the flow, thermogravimetric and thermomechanical behaviour of the resulting blends were investigated. Using capillary plasstometry, thermogravimetry (TGA) and dynamic mechanical analysis (DMA), it was found that the increase in zinc oxide content resulted in an increase in the flow indices (MFI, MVR), as well as in the storage and loss modulus values, and a decrease in the thermal stability and glass transition temperature.

Keywords*: PLA, blends, zinc-Oxide, thermogravimetry.*

1. Introduction

Polylactic acid (PLA) is one of the most widely used biodegradable polymers today. Its popularity is demonstrated by the fact that, according to the Web of Science database [1] 7301 new research articles containing the term PLA or polylactic acid in their title were published in 2021 and 6867 in 2020.

Much of this research is related to the use of PLA as a packaging material, as about 40 % of the polymers produced are used as packaging materials, which are generally single-use and have a very short life cycle due to their function [2]. In general, polylactic acid (PLA) has properties comparable to those of currently used bulk polymers, but it is a very brittle base material with poor gas barrier properties and is therefore poorly suited for food packaging applications (without plasticisers or other additives) [3]. The brittleness can be addressed by blending PLA with various tough materials, preferably also biodegradable polymers (e.g. polybutylene succinate (PBS), polybutylene adipate terephthalate (PBAT)). Furthermore, to improve the gas barrier properties, it is advisable to use various nanoadditives, such as zinc-oxide (ZnO). Zinc-oxide is a multifunctional, environmentally friendly nanoadditive, which is classified by the US Food and Drug Administration as a „Generally Recognised as Safe" (GRAS) additive, i.e. it can be used in food packaging [4]. In addition, a number of studies have confirmed that zinc-oxide improves the gas barrier properties of the material [5], and has antibacterial [6], and even to some extent antiviral [7, 8] properties.

In the present study, we investigated the extent to which the thermogravimetric and thermomechanical properties of tista PLA are modified by blending with PBS and by the addition of zinc-oxide to the blend.

2. Materials and methods

2.1. Preparation of test samples

The specimens required for the tests were prepared using Ingeo Biopolymer 2500HP polylactic acid (PLA) manufactured by Natureworks LLC, PBE 003 polybutylene succinate (PBS) manufactured by NaturePlast, and Zincweiss Reszsiegel ME-004 zinc-oxide (ZnO).

The compounds were prepared using a Labtech Engineering Co., Ltd. (Thailand) LTE 26-44 twin screw extruder. The temperatures of the 10 zones

of the extruder were as follows: 190/190/190/190/190/190/200/200/210/210.

The screw rotation speed was 25 rpm and the feed speed was 5 rpm. The zinc-oxide (2.5; 5; 7.5 and 10 phr), measured to the nearest two tenths of a gram, was mechanically mixed with a dry mixture containing 80 % PLA and 20 % PBS, respectively. This mixture was then fed into the extruder in order to obtain a more uniform distribution of the ZnO nanoparticles.

After exiting the extruder, the extrudate was passed through a fibre conveyor while being cooled by cooling fans mounted above the conveyor, and finally granulated using a Labtech Engineering (Thailand) LZ-120/VS. Thus, the test samples shown in **Table 1** were prepared. It is important to note that in the table phr (parts per hundred rubber) means the amount of zinc-oxide added to 100 mass units of polymer.

Table 1. *Prepared test samples and their ZnO content*

Sample name	PLA %	PBS %	ZnO	
			phr	%
PLA	100	100	0	0
PBS	0	0	0	0
PLA/PBS/0	80	20	0	0
PLA/PBS /2,5	78.0	19.5	2.5	2.4
PLA/PBS/5	76.2	19.0	5	4.8
PLA/PBS/7,5	74.4	18.6	7.5	7
PLA/PBS/10	72.7	18.2	10	9.1

For energy dispersive spectroscopy and dynamic mechanical tests we needed pressed plates, which were prepared on a Teach-Line Platen Press 200E hydraulic press from Dr. Collin GmbH (Germany). For pressing we use a press frame of 160x160x1 mm. The pressing temperature was 210 °C. The pressing process consisted of the following steps: preheating at 0 MPa for 3 minutes, followed by pressing at 0.98, 1.96 and 2.94 MPa for 1-1 minute (opening the die for glass evaporation and closing between steps), and finally pressing at 3.92 MPa for 3 minutes and cooling.

2.2. Test methods

The Melt Flow Index (MFI) and Melt Volume Rate (MVR) were measured using Instron CEAST 7027.000 machine, with 5 measurements per type of material. The measurements were performed at 210 °C (final temperature of the compounding) with a load of 2.16 kg in accordance with MSZ EN ISO 1133 **[9]**.

Energy-dispersive spectroscopy (EDS) was performed on cryogenic array surfaces coated with a thin gold layer using a JEOL JSM 6380LA scanning electron microscope (SEM) manufactured by Jeol Ltd.

The thermal stability and the evolution of thermal decomposition processes were analysed by thermogravimetric analysis (TGA) (according to MSZ EN ISO 11358-1 **[10]** The tests were carried out on 5-10 mg samples, using a TA Instruments Q500 machine in the temperature range 50 to 600 °C at a heating rate of 10 °C/min.

Dynamic mechanical tests were carried out using a TA Instruments Q800 machine with temperature sweeps ranging from subambient to 150 °C at a heating rate of 2 °C/min. For each measurement, an amplitude was chosen that was within the linear viscoelastic range. The tests were performed using a dual cantilever beam arrangement, with 10x60 mm samples cut from precut sheets. Temperature sweeps were carried out on both the neat polymers and the compounds, however, the blends containing 7.5 and 10 phr zinc-oxide were so brittle that they broke during capture.

3. Results

3.1. Energy dispersive spectroscopy

EDS was also used to investigate the zinc-oxide content and distribution in the blends, EDS images of the pure PLA/PBS blend and blends containing 2.5;5;7.5 and 10 phr zinc-oxide are shown in **Figures 1–5.** The red dots in the figures indicate the zinc particles. The PLA/PBS blend does not contain zinc-oxide, the red dots in the figure only indicate measurement noise. In the case of the 2.5

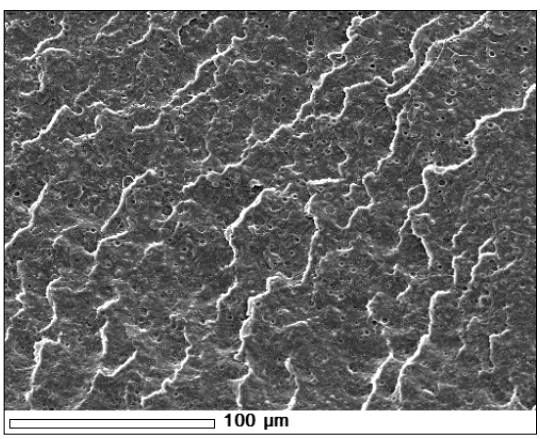

Figure 1. *SEM micrograph of PLA/PBS mixture.*

phr blend, zinc-oxide particles are already visible and evenly distributed in the blend. For the 5 and 7.5 phr blends, the amount of zinc-oxide increases, but the distribution of zinc-oxide is not as uniform, with zinc-oxide aggregates being observed in the polymer matrix. Finally, in the case of the 10 phr blend, zinc-oxide is present in larger aggregates. As the zinc-oxide content increases, the uniform distribution of particles deteriorates spectacularly. The resulting aggregates cause the polymer matrix to be discontinuous, creating potential defect sites.

As can be seen from **Figures 1–5** the careful preparation of the base material resulted in a particularly good dispersion at 2.5 and 5 phr ZnO content, but even so, the 5 phr aggregated ZnO particles with a high surface/volume ratio still failed to disperse properly.

Table 2 shows the content of zinc (Zn) and zinc-oxide (ZnO) for the different Kev products. Only the amount of Zn can be determined directly in the measurement, the equimolar amount of oxygen must be added to the amount of zinc to determine the ZnO content. The atomic mass of zinc is 65.38 g, the oxygen is 16 g. In this case, for every 65.38 g of zinc there is 16 g of oxygens, so that 65.38 g of zinc actually corresponds to 81.38 g of zinc-oxide. That is, 1 mass ratio zinc corresponds to 1.24 mass ratio zinc-oxide. Having made this correction, it can be seen from **Table 2** that the values obtained are almost identical to the amount added. For the 2.5; and 5 phr zinc-oxide,

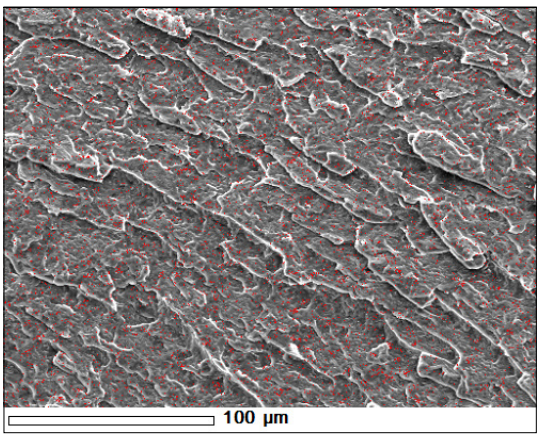

Figure 2. *SEM micrograph of a PLA/PBS blend containing 2.5 phr ZnO (red colour indicates Zn element).*

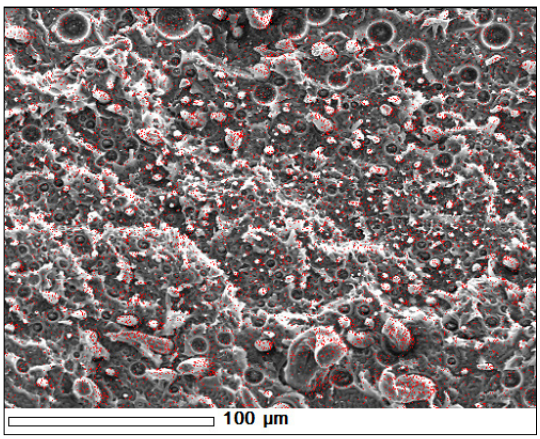

Figure 4. *SEM image of a PLA/PBS mixture containing 7.5 phr ZnO (red colour indicates Zn element).*

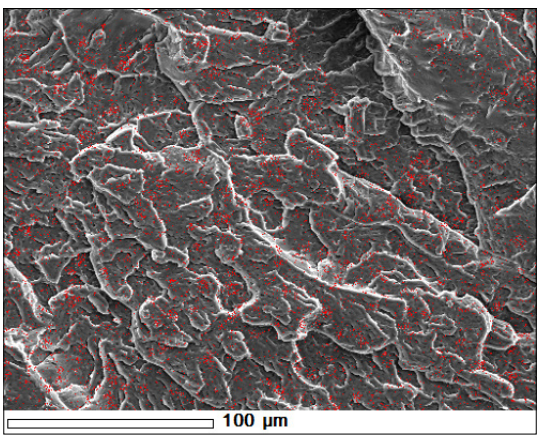

Figure 3. *SEM image of a PLA/PBS mixture containing 5 phr ZnO (red colour indicates Zn element).*

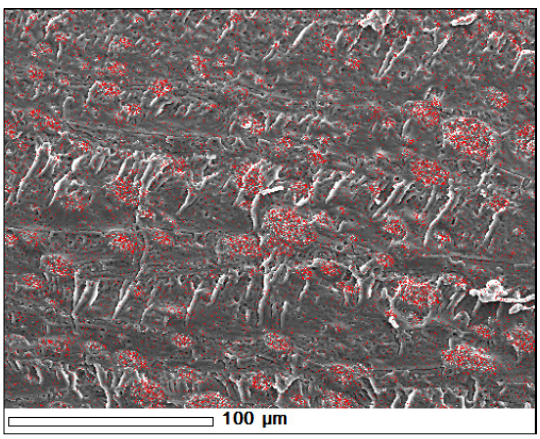

Figure 5. *SEM image of a PLA/PBS mixture containing 10 phr ZnO (red colour indicates Zn element).*

Table 2. *Zn and ZnO content of blend and compounds.*

Sample name	Zn	ZnO	Added ZnO
PLA/PBS/0	0.02±014	0.02±0.02	0
PLA/PBS/2.5	1.82±0.10	2.26±0.12	2.44
PLA/PBS/5	3.87±0.13	4.80±0.16	4.76
PLA/PBS/7.5	5.16±0.10	6.40±0.12	6.98
PLA/PBS/10	5.64±0.13	7.00±0.16	9.09

Table 3. *Melt Flow Index and Melt Volume Rate for the tested materials/*

Sample name	MFI (g/600 s)	MVR (cm^3/600 s)
PLA	8.06±0.13	7.31±0.10
PBS	3.42±0.95	3.26±0.91
PLA/PBS	8.55±0.12	7.81±0.16
PLA/PBS/2,5	58.85±4.33	73.91±14.13
PLA/PBS/5	60.38±2.85	70.74±13.82

the calculated results are almost identical to the amount added. However, at higher ZnO contents, the distribution of particles is not uniform, aggregates remain in the blend, which explains the discrepancy between the added and measured data. It can be seen that the higher the zinc-oxide content, the greater the discrepancy.

3.2. Thermogravimetric analysis

The results of the MFI measurements are presented in **Table 3** The average of the measured PLA values is the same as the 8 g/600 s reported in the data sheet **[11]** PBS produced lower values compared to those in the datasheet **[12],** but the MFI determination of 5 g/600 s in that datasheet was made at 190 °C. A small increase in the average MFI value of the PLA/PBS blend was observed, however, a jump-like increase in both MFI and MVR was observed with the addition of zinc-oxide. This jump-like increase indicates a significant degradation. The increase in the flow properties with increasing zinc-oxide content was so significant that the waiting and residence times for the 5 phr mixture had to be reduced. Although the 2.5 phr ZnO mixture was still measurable, such an increase in MFI could cause problems during processing. Measurement of the 7.5 and 10 phr mixtures was not possible even with parameter changes.

3.3. Thermogravimetric analysis

The thermal stability of the samples was investigated using TGA, the results of the test are shown in **Figures 6** and **7** and **Table 4** mutatja. The decomposition process was carried out in one step for PLA, PBS and blend, and in two steps for zinc-oxide doped compounds. The heights of the steps indicate the PLA and PBS content, respectively. The thermal decomposition of pure PBS started at a higher temperature (344 °C) than the decomposition of PLA (309 °C). These results indicate that PBS is more resistant to thermal degradation than PLA. The thermal stability of the PLA/PBS blend was higher than that of pure PLA, which means that PBS has an effect on thermal stability, as confirmed by Jompang et al **[13]**.

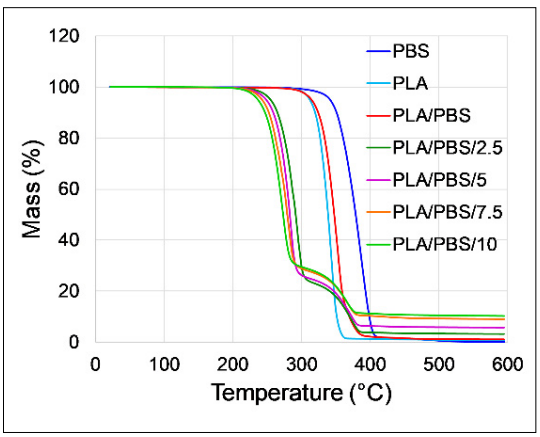

Figure 6. *Thermogravimetric curves of the tested materials.*

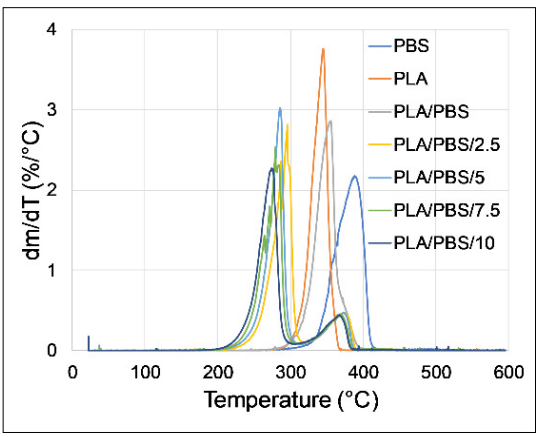

Figure 7. *Differential thermogravimetric curves of the tested materials.*

Table 4. *Quantified results of thermogravimetric analysis*

	PBS	PLA	PLA/PBS	PLA/ PBS/2,5	PLA/PBS/5	PLA/ PBS/7,5	PLA/ PBS/10
Number of stages	1	1	1	2	2	2	2
Start point of the 1st stage, A1 (°C)	344	309	310	256	251	241	236
End point of the 1st stage, B1 (°C)	402	352	365	301	291	288	286
End point of the 2nd stage, A2 (°C)	–	–	–	347	345	344	339
End point of the 2nd stage, B2 (°C)	–	–	–	384	381	378	376
1st loss in mass (%)	100	99.2	98.9	77.5	75.5	72.6	71.5
2nd loss in mass (%)	–	–	–	19.3	18.8	18.4	18.2
Residue (%)	0.03	0.82	1.06	3.19	5.71	9.00	10.28
Corrected residue (%)	–	–	0	2.13	4.65	7.94	9.22
1st peak on the DTG curve (°C)	387	343	352	294	284	280	273
2nd peak on the DTG curve (°C)	–	–	–	374	373	369	367

The thermal decomposition of ZnO-containing compounds started at increasingly lower temperatures with increasing zinc-oxide content. The large decrease in thermal stability indicates that ZnO has a strong degradation effect on PLA at high temperatures.

The corrected residual (corrected here means corrected by the mass remaining in the PLA/PBS blend) values show the ZnO content of the sample. It can be seen that these values are in good approximate agreement with the EDS determined and the coated ores (**Table 2**).

At the same time, it can be observed that the increasing zinc-oxide content only slightly reduced the thermal stability of the PBS phase.

3.4. Dynamic mechanical analysis

The results of the DMA tests are shown in **Figures 8–10.** A strange anomaly is observed in the PBS curve around 30 °C, however, it can be seen that around 105 °C there is a drastic decrease in the storage and loss modulus values, indicating the crystallization temperature of PBS. For the blend and the compounds, it can be seen that around 60 °C the storage modulus drops drastically (since this is where the glass transition temperature of PLA is located), and then around 80 °C the storage modulus starts to increase again. This increase can be explained by the cold crystallization of PLA. It can also be seen that around 110 °C there is a decrease in the curves, possibly due to the fact that at this temperature the PBS particles melt and enter the melt state, but after this the storage modulus values continue to increase until the cold crystallisation takes place. From the curves, it can also be seen that the storage and loss modulus values increase with the limit of blending compared to pure PLA, and further increase with increasing the amount of zinc-oxide content. The values of the glass transition temperatures (T_g) determined by MSZ EN ISO 6721 **[14]** based on the maximum loss factor are given in

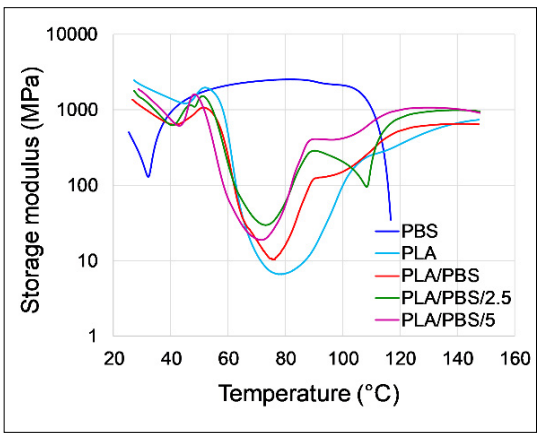

Figure 8. *Storage modulus curves of the tested materials.*

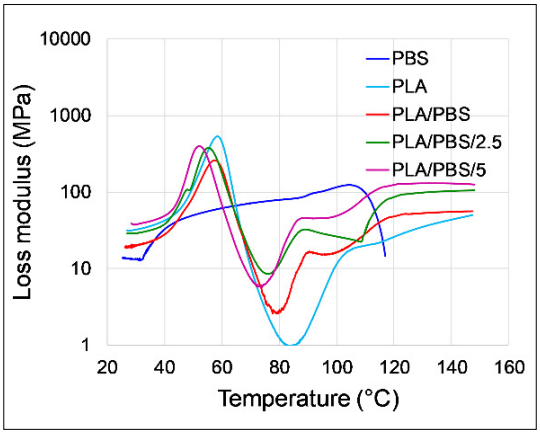

Figure 9. *Loss modulus curves of the tested materials.*

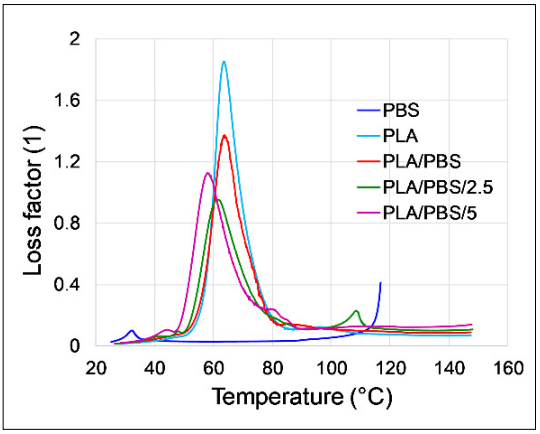

Figure 10. *Loss factor curves of the tested materials.*

Table 5. The table shows that the glass transition temperature of the blend did not change compared to pure PLA, but that the glass transition temperature of the blend decreased slightly with increasing zinc-oxide content.

Table 5. *Glass transition temperature of PLA and blends*

Sample name	T_g (°C)
PLA	63.4
PLA/PBS	63.9
PLA/PBS/2,5	61.2
PLA/PBS/5	58.1

4. Conclusions

In the present work, PLA-PBS blends (in 80-20 mass ratio) were doped with zinc-oxide (2.5; 5; 7.5 and 10 phr) and the flow, thermogravimetric and thermomechanical behaviour of the resulting blends were investigated. Using energy dispersive spectroscopy, it was found that there was no significant difference between the amount of zinc-oxide added and the actual ZnO present in the material up to 5 phr, but that this difference increased with increasing zinc-oxide content above 5 phr due to the ZnO aggregates. The MFI and MVR values of the tested blend increased drastically with increasing zinc-oxide content. It can be concluded that zinc-oxide caused a significant degradation of the material. This was also confirmed by the TGA results, which showed a decrease in the thermal stability of the blend with increasing zinc-oxide content, by 54 °C for 2.5 phr and by 74 °C for 10 phr. The dynamic mechanical tests showed that the storage and loss modulus values increased with blending compared to pure PLA, and further increased with increasing the zinc-oxide content. Overall, it can therefore be concluded that with increasing the amount of zinc-oxide added to the 80-20 % PLA/PBS blend, the flowability increases dramatically, the thermal decomposition temperature decreases significantly, the storage and loss modulus values increase and the glass transition temperature decreases slightly.

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References

[1] https://www.webofscience.com/wos/woscc/advanced-search (accessed on: 2022. 02. 28.)
[2] PlasticsEurope, Plastics: the Facts 2021, https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/ (letöltve: 2022. 02. 28.)
[3] Sonchaeng U., Iniguez-Franco F., Auras R., Selke S., Rubino M., Lim L.: *Poly(lactic acid) mass transfer properties.* Progress in Polymer Science, 86/11. (2018) 85–121. https://doi.org/10.1016/j.progpolymsci.2018.06.008
[4] Matai I., Sachdev A., Dubey P., Uday Kumar S., Bhushan B., Gopinath P.: Antibacterial activity and mechanism of Ag–ZnO nanocomposite on S. aureus and GFP-expressing antibiotic resistant E. coli. Colloids and Surfaces B: Biointerfaces, 115/3. (2014) 359–367.

https://doi.org/10.1016/j.colsurfb.2013.12.005
[5] Reddy K. M., Feris K., Bell J., Wingett D. G., Hanley C., Punnoose A.: Selective toxicity of zinc oxide nanoparticles to prokaryotic and eukaryotic systems. Applied Physics Letters, 90/5. (2007) 213902–213903.
https://doi.org/10.1063/1.2742324
[6] Sharma R., Jafari S. M., Sharma S.: *Antimicrobial bio-nanocomposites and their potential applications in food packaging*. Food Control, 112/6. (2020) 1–11.
https://doi.org/10.1016/j.foodcont.2020.107086
[7] Merkl P., Long S., McInerney G. M., Sotiriou G. A.: *Antiviral Activity of Silver, Copper Oxide and Zinc Oxide Nanoparticle Coatings against SARS-CoV-2*. Nanomaterials, 11/5. (2021) 1–9.
https://doi.org/10.3390/nano11051312
[8] Mizielinska M., Nawrotek P., Stachurska X., Ordon M.: *Packaging Covered with Antiviral and Antibacterial Coatings Based on ZnO Nanoparticles Supplemented with Geraniol and Carvacrol*. International Journal of Molecular Sciences, 22/4. (2021) 1–14.
https://doi.org/10.3390/ijms22041717
[9] ISO 1133: Plastics — Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics, 2011.
[10] ISO 11358: Plastics — Thermogravimetry (TG) of polymers, 2014.
[11] Ingeo™ Biopolymer 2500HP Technical Data Sheet, https://www.natureworksllc.com/~/media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet_2500HP_extrusion_pdf.pdf?la=en (accessed on: 2022. 03. 01.)
[12] Natureplast PBE-003 Technical Data Sheet, (letöltve: 2022. 03. 01.)
http://natureplast.eu/wp-content/uploads/2019/03/190319-Material-Portfolio-ENG.pdf
[13] Jompang L., Thumsorn S., On J. W., Surin P., Apawet C., Chaichalermwong T., Kaabbuathong N., O-Charoen N., Srisawat N.: *Poly(lactic acid) and poly(butylene succinate) blends fibers prepared by melt spinning technique*. Energy Procedia, 34/3. (2013) 493–499.
https://doi.org/10.1016/j.egypro.2013.06.777
[14] ISO 6721: Plastics — Determination of dynamic mechanical properties, 2019.